Protium Absorption and Desorption Properties of bcc Ti-Fe Solid Solution Alloys Stabilized by Mo Addition*¹

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The present study investigates the effect of Mo addition to the TiFe alloys on a stabilization of bcc phase and their protium absorption and desorption properties. $\text{Ti}_{0.5}\text{Fe}_{0.5}$ alloys with more than 10 mol% Mo had CsCl phase and bcc phase, which show single plateaus in the PCT curves and were easily hydrogenated without homogenization. The bcc phase has larger lattice parameter than that of the CsCl phase. TiFe–10 mol% Mo annealed alloys with the Ti/Fe ratio of more than 2 had a bcc phase as a main phase and CsCl as a minor one. The alloys had 3 mass% of the maximum protium capacity and desorbed protium only 1 mass%. The phases of the hydrogenated alloy were fcc and orthorhombic structure, which may be caused by di-hydrides of bcc solid solution and mono-hydrides of CsCl phase, respectively. It is found that the Mo addition to TiFe alloys could stabilize bcc phase and enhances the hydrogenation reaction of the disordered bcc Ti–Fe–Mo phase similar to Ti–Cr–X bcc alloys.

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1. Introduction

Ti based protium (hydrogen atom) storage alloys with a bcc structure, such as Ti–Cr–V alloys, have a large capacity and are unnecessary to undergo activation treatment.^{1–4)} Recently, it is reported that Mo addition to Ti–Cr alloy is effective on stabilizing bcc phase.^{5,6)} However, the heat treatment at high temperature up to 1600 K and following rapid-quenching are required in order to stabilize a bcc as high temperature phase. On the other hand, The TiFe intermetallic compound has a capacity of about 1.8 mass%⁷⁾ and consists of low cost element of Fe. But the initial activation of the TiFe alloys is known to be difficult and requires high temperature up to 700–800 K at above the hydrogen pressure of 1 MPa.²⁾ Partial substitution of the elements had been found to be effective to improve the activation characteristics.^{8,9)} Since, the TiFe alloy has a B2 ordered (CsCl) structure related to a bcc structure in the wide temperature range between under the melting point and ambient temperature,¹⁰⁾ it is expected that the bcc phase in the Ti based alloy could be achieved by including Mo and Fe elements and heat treatment temperature is possibly lowered.

Then the purpose of the present work is to investigate the stabilization of a bcc structure in Ti–Fe–Mo alloys on and their protium absorption and 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%; Fe > 99.95 at%; Cr > 99.99 at%; Mo > 99.99 at%; and La > 99.99 at%. Some samples were homogenized at 1273 K for 48 h and cooled in a furnace.

Some of other samples were annealed at 1523 K for 1 h, and quenched into iced water.

Crystal structures and lattice parameters were studied by X-ray diffractometer (XRD) using Cu-K α radiation (Philips, X'pert System). Hydrogenated sample for the XRD experiment was prepared by pressurizing the alloys at 0.1 MPa hydrogen gas and soaking protium absorbed alloys in ethanol to confine the protium in the sample. The microstructures were observed by scanning electron microscopy (SEM) with an energy dispersive X-ray spectrometer (EDS).

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. Then, hydrogen was introduced gradually into the vessel up to a pressure of 10 MPa at 313 K. An activation treatment was carried out, if the samples unreact with hydrogen at 313 K. The activation procedure was performed three times, that was evacuation at 673 K for 1 h and pressurization to 7 MPa at the same temperature for 1 h. The first cycle of the PCT curve is shown as the protium absorption and desorption property in this study.

3. Results and Discussion

At first, we investigated the effect of the Mo addition on the stabilization of a bcc structure in the TiFe based alloys. Figure 1 shows XRD patterns of $(\text{Ti}_{0.5}\text{Fe}_{0.5})$ - x mol% Mo as-cast alloys ($x = 0, 5, 10, 15, 20$). All samples have CsCl (B2) structured phases with superlattice lines existing at about 30 degrees 2 θ in XRD profiles. In the more than 10 mol% Mo alloys, the other reflection peaks corresponding to a bcc structure are observed without obvious superlattice-line, which has larger lattice parameter than that of the CsCl phase. Furthermore, $(\text{Ti}_{0.5}\text{Fe}_{0.5})$ -20 Mo alloy has TiFe_2 Laves phase. Figure 2(a) shows PCT curves of $(\text{Ti}_{0.5}\text{Fe}_{0.5})$ - x mol% Mo as-cast alloys without activation treatment ($x = 0, 2.5, 5, 10, 20$). The alloys with more than 10 mol% Mo react with hydrogen and show single plateau in the PCT curve, but the maximum capacity decreases with increasing

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Fig. 1 XRD patterns of $(\text{Ti}_{0.5}\text{Fe}_{0.5})$ - x mol% Mo as-cast alloys ($x = 0, 5, 10, 15, 20$).

Fig. 2 PCT curves of $(\text{Ti}_{0.5}\text{Fe}_{0.5})$ - x mol% Mo as-cast alloys (a) without activation, (b) after activation. ($x = 0, 2.5, 5, 10, 20$).

Mo content. In contrast, the alloys with less than 5 mol% Mo unreact with hydrogen. Then, in order for all samples to react with hydrogen, it is attempted to perform the activation treatment. Figure 2(b) shows the corresponding PCT curves of these alloys after activation treatment. All samples shows plateau region in the PCT curves, and there is no difference in

PCT curves for the alloys with more than 10 mol% Mo with or without the activation. The curves at plateau regions of the alloy without Mo are sloped. Two flattened plateau regions in the PCT curves of homogenized TiFe alloy are observed in Fig. 3. However as shown in Fig. 2(b), the 2.5 and 5 Mo alloys without homogenization have flattened plateau region. This result suggests that the small amount of Mo addition to the alloys with CsCl structure may enhance homogeneity of the alloys.

Figure 4 shows a SEM micrograph of $(\text{Ti}_{0.5}\text{Fe}_{0.5})$ -20 mol% Mo as-cast alloy, which consists of two-phases where the dark phase embedded in a bright matrix phase. Table 1 shows the compositions of the dark and bright phases determined by EDS analysis. TiFe_2 phase is not observed in a SEM analysis. The amount of Ti content in the bright phase is as much as that of Fe, thus the bright phase might be a TiFe compound with a CsCl structure. On the other hand, the Ti/Fe ratio of the dark phase is around 2.5. According to XRD studies, the bcc phase has larger lattice parameter than that of CsCl phase. The bcc phase contains a larger amount of Ti or Mo with larger atomic radius. The large amount of Mo in this

Fig. 3 PCT curves of TiFe as-cast and homogenized alloys.

Fig. 4 SEM micrograph of $(\text{Ti}_{0.5}\text{Fe}_{0.5})$ -20 mol% Mo as-cast alloy.

Table 1 EDS analysis of microstructure in (Ti_{0.5}Fe_{0.5})-20 mol% Mo as-cast state alloy.

Phase	Composition (at%)		
	Ti	Fe	Mo
Light	41.8	46.9	11.3
Dark	31.7	11.4	56.9

alloys lowers the mass-metric capacity, therefore, the bcc phase might has small protium capacity. Thus, in order to get a larger volume fraction of bcc phase in the alloys, it is attempted to prepare the alloys with the Ti/Fe ratio similar to dark phase and with Mo less than 10 mol%.

Figures 5 and 6 show XRD patterns and PCT curves of (TiFe)-10 mol% Mo alloys with 2.5 of Ti/Fe ratio, respectively. The reflection peaks of the bcc phase are mainly observed and there is no difference of XRD patterns for the Ti-rich alloys between as-cast state and after annealing at 1573 K. This could be the first observation that the bcc phase

Fig. 5 XRD patterns of (TiFe)-10 mol% Mo as-cast and annealed alloys with 2.5 of the Ti/Fe ratio.

Fig. 6 PCT curves of (TiFe)-10 mol% Mo as-cast and annealed alloys with 2.5 of the Ti/Fe ratio.

Fig. 7 XRD patterns of (TiFe)-10 mol% Mo annealed alloys at 1573 K (Ti/Fe = 2, 2.125, 2.25, 2.375, 2.5).

is main phase in Ti-Fe-Mo protium storage alloys. The as-cast alloy has sloped curves in the PCT curves, on the other hand, the annealed alloy has obvious plateau region. The heat-treatment might enhance the homogeneity of the alloy. The maximum capacity of the alloys achieves 3.0 mass%, but the amount of protium desorption is only 1.0 mass%. These phenomena are similar to the hydrogenation behavior of Ti-based bcc solid solution alloys.^{1-6,11,12)}

Figure 7 shows XRD patterns of (TiFe)-10 mol% Mo annealed alloys with varying Ti/Fe ratio from 2 to 2.5. Lattice parameters of the CsCl phase and bcc phase are also indicated in this figure. There are the bcc phase as main phase and the CsCl phase as minor one. The lattice parameter of the bcc phase increases with increasing the amount of Ti content in the alloys. It is known that increment of the lattice parameter of the Ti-Cr-X bcc alloys cause decrement of the plateau pressure in the PCT curves.^{3,6)} However, the lattice parameter of CsCl phase remains almost unchanged.

Figure 8 shows corresponding PCT curves of these alloys. The plateau pressure of the alloys decreases with increasing the amount of Ti/Fe ratio. According to the change in the lattice parameter of bcc phase, the behavior of the plateau region in the PCT curves might be caused by transformation known as hydrogenation of Ti-based bcc solid solution alloys. Another plateau regions in the curves are also observed slightly at about 0.02 MPa. It is expected that the smaller plateau regions are caused by hydrogenation of the TiFe intermetallic compound with a CsCl structure.

Figure 9 shows XRD pattern of the (TiFe)-10 mol% Mo annealed alloy (Ti/Fe = 2.25) before and after hydrogenation. The hydrogenated alloys prepared by applying 0.2 MPa hydrogen gas, and following by soaking protium absorbed alloys in ethanol to confine the protium in the sample, consist of two phases, which have a fcc and an orthorhombic structures. It is suggested that fcc and orthorhombic phases

Fig. 8 PCT curves of (TiFe)-10 mol% Mo annealed alloys at 1573 K (Ti/Fe = 2, 2.125, 2.25, 2.375, 2.5).

will be di-hydride of bcc and mono-hydride of CsCl phases, respectively. It is found that the hydrogenation of the bcc TiFe phase is similar to Ti-based bcc alloys (ex. Ti-Cr-V) that are reported previously. The heat-treatment temperature to obtain bcc phase in TiFe alloy is lower than that of Ti-Cr based alloy. However, it will be necessary to investigate a protium capacity enhancement and an achievement of single phase in the TiFe bcc alloys in future work.

4. Conclusions

The present study investigates protium absorption and desorption properties of Ti-Fe-Mo Alloys, and drew the following conclusions.

- (1) $\text{Ti}_{0.5}\text{Fe}_{0.5}$ alloys with less than 5 mol% Mo had only CsCl phase and activation treatment was required. To achieve flattened plateau region in the $\text{Ti}_{0.5}\text{Fe}_{0.5}$ alloy without Mo, the homogenization was required. However, the alloys with small amount of Mo had double flattened plateaus without homogenization.
- (2) $\text{Ti}_{0.5}\text{Fe}_{0.5}$ alloys with more than 10 mol% Mo had CsCl phase and bcc phase with larger lattice parameter than that of the CsCl phase, which showed single plateaus in the PCT curve and were easily hydrogenated without homogenization. The 20 mol% Mo alloy had two-phases microstructures where the composition of one phase is about 1 of the Ti/Fe ratio, and the other had about 2.5 of the Ti/Fe ratio.
- (3) TiFe-10 mol% Mo annealed alloys at 1523 K with the Ti/Fe ratio of more than 2, had a bcc phase as a main

Fig. 9 XRD patterns of the (TiFe)-10 mol% Mo annealed alloy before and after hydrogenation (Ti/Fe = 2.25).

phase and CsCl as a minor one. This could be the first observation that bcc phase becomes main phase in the Ti-Fe-Mo protium storage alloys. The alloys had 3 mass% of the maximum capacity and desorbed only 1 mass%. The phases of the hydrogenated alloy were fcc and orthorhombic structures.

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