Pressure Dependence of Hydrogen-Induced Amorphization in C15 Laves Phase TbFe₂

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The pressure dependence of structural changes of C15 Laves phase TbFe₂ heated in a hydrogen atmosphere was investigated using a pressure differential scanning calorimeter (PDSC), a powder X-ray diffractometer (XRD), a differential scanning calorimeter (DSC) and a hydrogen analyzer. Hydrogen absorption in the crystalline state, hydrogen-induced amorphization (HIA), precipitation of TbH₂ and decomposition of the remaining amorphous alloy into α -Fe and TbH₂ occurred exothermally with increasing temperature above 0.5 MPa H₂, independent of the heating rate. HIA and precipitation of TbH₂ occurred simultaneously in 0.2 MPa H₂ (0.33 K/s) and in 0.1 MPa H₂ (0.17 K/s). On the contrary, hydrogen absorbed crystalline *c*-TbFe₂H_{3.5} decomposed directly into α -Fe and TbH₂ in 0.1 MPa H₂ (0.33 K/s). That is, no amorphous phase was formed at the lower hydrogen pressure and at a high heating rate. The reason why HIA occurs above the critical hydrogen pressure and below the critical heating rate was discussed on the basis of the hydrogen content absorbed in the crystalline state of TbFe₂.

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1. Introduction

Hydrogen-induced amorphization (HIA), *i.e.*, the transformation from the crystalline to the amorphous phase by hydrogenation, has been observed in intermetallic compounds having the C15, B8₂, C23, D0₁₉ and L1₂ structures and containing a large amount of a hydride-forming element.^{1–8)} Although the effect of hydrogenation on magnetic properties of C15 Laves phases RFe₂ has been extensively investigated by many groups,^{9–11)} the conditions and the mechanism of HIA in RFe₂ are still unclear. Recently, the present authors clarified origins of thermal peaks of C15 Laves phases RFe₂ during heating in 1.0 MPa H₂.^{12,13)} According to these papers, hydrogen absorption, HIA, precipitation of RH₂ and decomposition occur exothermally with increasing temperature in RFe₂ (R=Y, Sm, Gd, Tb, Dy and Ho), although HIA in YFe₂ occurs via two steps. In these alloys, a single-phase crystalline *c*-RFe₂H_x and amorphous *a*-RFe₂H_x are formed at low temperatures and at intermediate temperatures, respectively. On the other hand, hydrogen absorption and HIA occur simultaneously in CeFe₂, while HIA and precipitation of ErH₂ occur simultaneously in ErFe₂. The single-phase crystalline *c*-CeFe₂H_x and amorphous *a*-ErFe₂H_x alloys are not formed under the above-mentioned conditions. However, it is still unclear whether or not these reactions depend on the hydrogen pressure and the heating rate. In the present work, the pressure dependence of structural changes of C15 Laves phase TbFe₂ during heating in a hydrogen atmosphere and at different heating rates is investigated and discussed.

2. Experimental

TbFe₂ was prepared by arc melting using high-purity metals in an argon atmosphere. The ingot was homogenized at 973 K for 1 week in an evacuated quartz tube. Structures of the samples before and after hydrogenation were identified by powder X-ray diffraction (XRD). Thermal analysis was

carried out using a pressure differential scanning calorimeter (PDSC) at heating rates of 0.17 K/s and 0.33 K/s in a hydrogen atmosphere of 0.1–5.0 MPa. The origin of each thermal peak was determined by heating the samples to respective stages in the PDSC followed by rapid cooling, and by subjecting them to XRD measurement, conventional DSC (Ar-DSC) measurement in a flowing argon atmosphere and hydrogen analysis. The thermal desorption spectra (TDS) of hydrogenated samples were measured by the hydrogen analyzer.

3. Results and Discussion

Figure 1 shows PDSC curves of TbFe₂ heated at rates of 0.17 K/s (dotted line) and 0.33 K/s (solid line) at H₂ pressures from 0.1 to 5.0 MPa. Four exothermic peaks are seen in the PDSC curves above 0.2 MPa H₂ (0.17 K/s) and above 0.5 MPa H₂ (0.33 K/s). Three exothermic peaks are seen in the PDSC curves of 0.1 MPa H₂ (0.17 K/s) and 0.2 MPa H₂ (0.33 K/s). Two exothermic peaks are seen in the PDSC curve of 0.1 MPa H₂ (0.33 K/s). In order to elucidate the origin of these peaks, TbFe₂ was heated to respective stages in the PDSC, followed by rapid cooling and then XRD, Ar-DSC and hydrogen analyses.

Figure 2 shows the change in the hydrogen content (H/M) for the samples which show typical PDSC curves, *i.e.*, for those heated in 1.0 MPa H₂ (0.17 K/s) and in 0.1 MPa H₂ (0.17 K/s and 0.33 K/s). In this figure, the arrow denotes the temperature to which the samples were heated and then cooled.

Figures 3 and 4 show XRD patterns and Ar-DSC curves of TbFe₂, respectively, after heating to respective stages of PDSC shown by the arrows in Fig. 2 in 1.0 MPa H₂ (0.17 K/s).¹³⁾ The XRD pattern of the original sample indicates that this alloy has the C15 Laves phase structure. The XRD pattern of the sample heated to above the first exothermic peak (to 423 K) shows Bragg peaks of a rhombohedral structure. The hydrogen content of this sample is 1.60 (H/M). The Ar-DSC curve of this sample shows over-

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Fig. 1 PDSC curves of TbFe_2 heated at rates of 0.17 K/s (dotted line) and 0.33 K/s (solid line) at H_2 pressures from 0.1 to 5.0 MPa.

Fig. 2 Change in the hydrogen content of TbFe_2 heated at a rate of 0.17 K/s and H_2 pressure of 1.0 MPa and at 0.17 K/s and 0.33 K/s at H_2 pressure of 0.1 MPa.

lapping endothermic peaks resulting from hydrogen desorption at around 400–600 K, but does not show any exothermic peak of crystallization. Consequently, the first exothermic peak of PDSC results from hydrogen absorption in the crystalline state, *i.e.*, crystalline $c\text{-TbFe}_2$ changes to $c\text{-TbFe}_2\text{H}_{4.8}$. In the XRD pattern of the sample heated to above the second exothermic peak (to 563 K), the Bragg peaks disappear and are replaced by a broad peak. The Ar-DSC curve of this sample shows two exothermic peaks of crystallization along with endothermic peaks of hydrogen desorption. Consequently, the sample heated to above the second exothermic peak is in an amorphous state, *i.e.*, this peak results from HIA. The hydrogen content decreases from 1.49 (H/M) to 1.20 (H/M) upon HIA, so that this amorphous alloy is expressed as $a\text{-TbFe}_2\text{H}_{3.6}$. In the XRD pattern of the sample heated to above

Fig. 3 XRD patterns of TbFe_2 after heating to respective stages of PDSC at a rate of 0.17 K/s and H_2 pressure of 1.0 MPa.

Fig. 4 Ar-DSC curves of TbFe_2 after heating to distinct stages of PDSC at a rate of 0.17 K/s in 1.0 MPa H_2 .

the third exothermic peak (to 673 K), new broad, small Bragg peaks of TbH_2 appear overlapping with the broad peak of the amorphous phase. The Ar-DSC curve of this sample shows one exothermic peak of crystallization along with the endothermic peaks of hydrogen desorption. Consequently, the third exothermic peak results from precipitation of TbH_2 in

the amorphous phase. The XRD pattern of the sample heated to above the fourth exothermic peak (to 749 K) is indexed on the basis of α -Fe and TbH₂. The Ar-DSC curve of this sample shows no exothermic peak of crystallization. Consequently, the fourth exothermic peak results from decomposition of the remaining amorphous phase into α -Fe and TbH₂. Thus, the amorphous hydride a -TbFe₂H_x crystallizes via two steps, *i.e.*, precipitation of TbH₂ and decomposition into α -Fe + TbH₂. The hydrogen content decreases slightly upon precipitation of TbH₂ and decomposition of the amorphous phase. The reaction sequence of TbFe₂ during heating in a hydrogen atmosphere is expressed as follows.

(i) 0.17 K/s in 1.0 MPa H₂

Figure 5 shows TDS of c -TbFe₂H_{4.8}, a -TbFe₂H_{3.6}, a -Tb_{1-y}Fe₂H_x + TbH₂ and α -Fe + TbH₂, which were obtained using the hydrogen analyzer after heating TbFe₂ to respective stages of the PDSC in 1.0 MPa H₂ (0.17 K/s), at a rate of 2 K/s in an argon atmosphere. The spectrum represents the hydrogen signal upon hydrogen desorption, which corresponds to the desorption rate of hydrogen at the corresponding temperature. The amount of desorbed hydrogen is calculated by integrating the desorption rate. The peak temperature of the spectrum is related to the energy states of hydrogen occupation sites. A relatively sharp spectrum at around 400 K of c -TbFe₂H_{4.8} implies that hydrogen in the crystalline hydride is weakly trapped in tetrahedral sites with a narrow energy vari-

Fig. 5 TDS of TbFe₂ heated at a rate of 0.17 K/s and H₂ pressure of 1.0 MPa.

ation. Some hydrogen in a -TbFe₂H_{3.6} occupies sites similar to those of crystalline hydride, although the sites have various energy states and are deformed. A wide spectrum appears at around 650–800 K in a -TbFe₂H_{3.6}, which indicates that some hydrogen is strongly trapped in the amorphous hydride. The spectra of a -Tb_{1-y}Fe₂H_x + TbH₂ and α -Fe + TbH₂ are similar to the spectrum of a -TbFe₂H_{3.6}, which implies that the local environments of hydrogen atoms in a -TbFe₂H_{3.6} are similar to those in TbH₂. The present authors previously investigated the structures, *e.g.*, the interatomic distance r and the coordination number N of Gd–Gd pairs, in a -GdFe₂H_{3.0} prepared by hydrogenation and suggested that the short-range order in a -GdFe₂H_{3.0} is similar to that in c -GdH₂.¹⁴ The present TDS data strongly support this previous suggestion.

Figure 6 and Fig. 7(a) show XRD patterns and Ar-DSC curves, respectively, of TbFe₂ heated to corresponding stages of PDSC in 0.1 MPa H₂ (0.17 K/s). The XRD pattern of the sample heated to above the first exothermic peak (to 490 K) shows the Bragg peaks of a rhombohedral structure. The Ar-DSC curve of this sample does not show any exothermic peak of crystallization. Consequently, the first exothermic peak results from hydrogen absorption in the crystalline state. The hydrogen content of this sample is 1.33 (H/M), so that this crystalline hydride is expressed as c -TbFe₂H_{4.0}. The XRD pattern of the sample heated to above the second exothermic peak (659 K) shows broad Bragg peaks of TbH₂ overlapping with the broad peak of the amorphous phase. The Ar-DSC curve of this sample shows an exothermic peak of decomposition at around 750–900 K. Consequently, the second exothermic peak results from the simultaneous occurrence of HIA and precipitation of TbH₂. Single-phase a -TbFe₂H_x is

Fig. 6 XRD patterns of TbFe₂ after heating to respective stages of PDSC at a rate of 0.17 K/s and H₂ pressure of 0.1 MPa.

Fig. 7 Ar-DSC curves of TbFe₂ after heating to respective stages of PDSC at a rate of 0.17 K/s in 0.1 MPa H₂ (a) and at a rate of 0.33 K/s in 0.1 MPa H₂ (b).

not formed under this experimental condition. The XRD pattern of the sample heated to above the third exothermic peak (775 K) is indexed on the basis of α -Fe and TbH₂. Consequently, the third exothermic peak results from decomposition of the remaining amorphous phase into α -Fe and TbH₂ similarly to the fourth exothermic peak of TbFe₂ heated in 1.0 MPa H₂ (0.17 K/s). The reaction sequence of TbFe₂ during heating in a hydrogen atmosphere is expressed as follows.

(ii) 0.17 K/s in 0.1 MPa H₂

Figure 8(a) shows TDS of TbFe₂ heated in 0.1 MPa H₂ (0.17 K/s). Considering the origins of each thermal peak, we can readily understand that TDS of the samples heated above the second and the third peak in 0.1 MPa H₂ (0.17 K/s) are almost the same as those of the samples heated above the third and the fourth exothermic peaks in 1.0 MPa H₂ (0.17 K/s), respectively.

Figure 9 and Fig. 7(b) show XRD patterns and Ar-DSC curves of TbFe₂ heated to respective stages of PDSC in 0.1 MPa H₂ (0.33 K/s), respectively. The XRD pattern of the sample heated to above the first exothermic peak (to 528 K) shows the Bragg peaks of a rhombohedral structure. The Ar-DSC curve of this sample does not show any exothermic peak of crystallization. Consequently, the first exothermic peak results from hydrogen absorption in the crystalline state. The hydrogen content of this sample is 1.17 (H/M), so that this crystalline hydride is expressed as $c\text{-TbFe}_2\text{H}_{3.5}$.

Fig. 8 TDS of TbFe₂ heated at a rate of 0.17 K/s and H₂ pressure of 0.1 MPa (a) and at a rate of 0.33 K/s and H₂ pressure of 0.1 MPa (b).

Fig. 9 XRD patterns of TbFe₂ heated to respective stages of PDSC at a rate of 0.33 K/s and H₂ pressure of 0.1 MPa.

We note that the second exothermic peak T_p shifts prominently to higher temperatures in comparison with those of the other alloys shown in Figs. 1 and 2. The XRD patterns of the samples heated to 668 K and to above the second exothermic peak (745 K) are indexed on the basis of $c\text{-TbFe}_2\text{H}_x + \alpha\text{-Fe} + \text{TbH}_2$ and $\alpha\text{-Fe} + \text{TbH}_2$, respectively. Fur-

thermore, the Ar-DSC curves of these samples do not show any exothermic peak of crystallization, indicating that the second exothermic peak is due to direct decomposition of *c*-TbFe₂H_{3.5} into α -Fe + TbFe₂, *i.e.*, disproportionation occurs at the second exothermic peak; no amorphous phase is formed by heating of TbFe₂ in 0.1 MPa H₂ (0.33 K/s). The reaction sequence of TbFe₂ during heating in a hydrogen atmosphere is expressed as follows.

(iii) 0.33 K/s in 0.1 MPa H₂

Figure 8(b) shows TDS of TbFe₂ heated in 0.1 MPa H₂ (0.33 K/s). Since the phases heated above the second exothermic peak are α -Fe + TbH₂, TDS of the samples heated under the above-mentioned conditions are almost the same as that of α -Fe + TbH₂ which is heated above the higher temperature.

Figure 10 shows the relationship between the peak temperature, T_p , of each reaction and the hydrogen pressure for two heating rates 0.17 K/s (open symbols and dotted line) and 0.33 K/s (solid symbols and solid line). As the heating rate increases, the peak temperature shifts to higher temperatures. Therefore, it is expected that all reactions, *i.e.*, hydrogen absorption, HIA, precipitation of TbH₂ and decomposition of the amorphous alloy, are controlled by the thermally activated process. The activation energy for each reaction will be evaluated from the peak shift by the Kissinger method. As the hydrogen pressure increases, T_p for hydrogen absorption, HIA and decomposition of the amorphous phase become low, but T_p for precipitation of TbH₂ becomes high. It is worth noting that T_p for precipitation of TbH₂ increases with increasing hydrogen pressure, which suggests that precipitation of TbH₂ is not controlled by the diffusion of hydrogen or Tb, but by the diffusion of Fe which does not interact with hydrogen. The difference in T_p between HIA and precipitation of TbH₂ decreases with decreasing hydrogen pressure, as shown in Figs. 1, 2 and 10. As a result, HIA and precipitation of TbH₂ occur simultaneously in 0.1 MPa H₂ (0.17 K/s). T_p for this reaction falls on the extrapolated lines of T_p values for

HIA and for precipitation of TbH₂. As mentioned in Introduction, HIA and precipitation of ErH₂ occur simultaneously by heating ErFe₂ in 1.0 MPa H₂ (0.17 K/s).¹³⁾ If the peak temperature of HIA of ErFe₂ and precipitation of ErH₂ decreases and increases, respectively, with increasing hydrogen pressure in the same way as TbFe₂, it is expected that HIA of ErFe₂ occurs above 1.0 MPa H₂.

The present work clearly indicates that HIA in TbFe₂ occurs above the critical hydrogen pressure and below the critical heating rate. The amorphous single-phase α -TbFe₂H_x is formed above 0.2 MPa H₂ and at the heating rate of 0.17 K/s. On the contrary, no HIA is observed upon heating of TbFe₂ in 0.1 MPa H₂ (0.33 K/s). It is noteworthy that HIA does not occur in the conventional DSC experiments in 0.1 MPa H₂. We discuss why HIA does not occur at low hydrogen pressures. As the hydrogen pressure increases, the amount of hydrogen absorbed in the crystalline phase increases, which gives rise to the strain. If HIA, *i.e.*, the transformation from *c*-TbFe₂H_x to α -TbFe₂H_x, is triggered by the strain due to hydrogen in the interstitial sites, HIA occurs readily at a high hydrogen pressure, because much hydrogen is absorbed. Actually, HIA occurs readily at high hydrogen pressures as shown in Figs. 1, 2 and 10. Therefore, if the hydrogen content is lower than the critical value, HIA does not occur. The critical hydrogen content for HIA of TbFe₂ is estimated to be approximately 1.2 (H/M) from Fig. 2.

4. Summary and Conclusions

In order to clarify the formation conditions of amorphous α -TbFe₂H_x by hydrogenation and the mechanism of HIA, its structural changes upon heating using a PDSC in a hydrogen atmosphere of 0.1–5.0 MPa and at heating rates of 0.17 and 0.33 K/s were investigated by XRD, Ar-DSC and hydrogen analyses. Hydrogen absorption, HIA, precipitation of TbH₂ and decomposition of the amorphous alloy into α -Fe and TbH₂ occur exothermally with increasing temperature of TbFe₂ above 0.5 MPa H₂. As the heating rate increases, the peak temperature shifts to higher temperatures. As the hydrogen pressure increases, the peak temperatures of hydrogen absorption, HIA and decomposition of the remaining amorphous alloys shift to lower temperatures, but that of precipitation of TbH₂ shifts to higher temperatures. As a result, HIA and precipitation of TbH₂ overlap each other at low hydrogen pressures. HIA may be triggered by the strain due to hydrogen in the interstitial sites. No amorphous phase is formed at low hydrogen pressures and at a high heating rate because the hydrogen content is lower than the critical value.

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Fig. 10 Relationship between the peak temperature, T_p , of each reaction and the hydrogen pressure at two heating rates, 0.17 K/s (open symbols and dotted line) and 0.33 K/s (solid symbols and solid line).

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