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-TbFe3H3 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 content absorbed in the crystalline state of TbFe2 was discussed on the basis of the hydrogen content absorbed in the crystalline state of TbFe2.

(Received November 16, 2001; Accepted January 24, 2002)

Keywords: hydrogen absorption, amorphous, amorphization, intermetallic compounds

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, B2, C23, D02 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 exothermically 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-RFe2Hx and amorphous a-RFe2Hx 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-CeFe2Hx and amorphous a-ErFe2Hx 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

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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 $c$-TbFe$_2$ changes to $c$-TbFe$_2$H$_4$.

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 $a$-TbFe$_2$H$_{3.6}$. In the XRD pattern of the sample heated to above 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 $\alpha$-Fe and TbH$_2$. 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 $\alpha$-Fe and TbH$_2$. Thus, the amorphous hydride $\alpha$-TbFe$_2$H$_x$ crystallizes via two steps, i.e., precipitation of TbH$_2$ and decomposition into $\alpha$-Fe+TbH$_2$.

The reaction sequence of TbFe$_2$ during heating in a hydrogen atmosphere is expressed as follows.

(i) 0.17 K/s in 1.0 MPa H$_2$

\[
c\text{-TbFe}_2 \rightarrow c\text{-TbFe}_2\text{H}_{4.8} \rightarrow \alpha\text{-TbFe}_2\text{H}_{3.6} \rightarrow \alpha\text{-Fe} + \text{TbH}_2
\]

(peak I) (peak II) (peak III) (peak IV)

Figure 5 shows TDS of $c\text{-TbFe}_2\text{H}_{4.8}$, $\alpha\text{-TbFe}_2\text{H}_{3.6}$, $\alpha\text{-Tb}_{1-y}\text{Fe}_2\text{H}_x$ + TbH$_2$, and $\alpha$-Fe + TbH$_2$, which were obtained using the hydrogen analyzer after heating TbFe$_2$ to respective stages of the PDSC at 1.0 MPa H$_2$ (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 $c\text{-TbFe}_2\text{H}_{4.8}$ implies that hydrogen in the crystalline hydride is weakly trapped in tetrahedral sites with a narrow energy variation. Some hydrogen in $\alpha$-$\text{TbFe}_2\text{H}_{3.6}$ 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 $\alpha$-$\text{TbFe}_2\text{H}_{3.6}$, which indicates that some hydrogen is strongly trapped in the amorphous hydride. The spectra of $\alpha$-$\text{Tb}_{1-y}\text{Fe}_2\text{H}_x$ + TbH$_2$ and $\alpha$-Fe + TbH$_2$ are similar to the spectrum of $\alpha$-$\text{TbFe}_2\text{H}_{3.6}$, which implies that the local environments of hydrogen atoms in $\alpha$-$\text{TbFe}_2\text{H}_{3.6}$ are similar to those in TbH$_2$. The present authors previously investigated the structures, e.g., the interatomic distance $r$ and the coordination number $N$ of Gd–Gd pairs, in $\alpha$-$\text{GdFe}_2\text{H}_{3.0}$ prepared by hydrogenation and suggested that the short-range order in $\alpha$-$\text{GdFe}_2\text{H}_{3.0}$ is similar to that in $c$-$\text{GdH}_2$. The present TDS data strongly support this previous suggestion.

Figure 6 and Fig. 7(a) show XRD patterns and Ar-DSC curves, respectively, of TbFe$_2$ heated to corresponding stages of PDSC at 0.1 MPa H$_2$ (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 $c\text{-TbFe}_2\text{H}_{4.0}$. The XRD pattern of the sample heated to above the second exothermic peak (659 K) shows broad Bragg peaks of TbH$_2$ 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 TbH$_2$. Single-phase $\alpha$-$\text{TbFe}_2\text{H}_{3.6}$ is

![Fig. 5 TDS of TbFe$_2$ heated at a rate of 0.17 K/s and H$_2$ pressure of 1.0 MPa.](image1)

![Fig. 6 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 0.1 MPa.](image2)
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 \(\alpha\)-Fe and \(\mathrm{TbH}_2\). Consequently, the third exothermic peak results from decomposition of the remaining amorphous phase into \(\alpha\)-Fe and \(\mathrm{TbH}_2\) similarly to the fourth exothermic peak of \(\mathrm{TbFe}_2\) heated in 1.0 MPa \(\mathrm{H}_2\) (0.17 K/s). The reaction sequence of \(\mathrm{TbFe}_2\) during heating in a hydrogen atmosphere is expressed as follows.

(ii) \(0.17 \, \text{K/s in 0.1 MPa } \mathrm{H}_2\)

\[
\begin{align*}
\text{c-} \mathrm{TbFe}_2 & \rightarrow \text{c-} \mathrm{TbFe}_2 \mathrm{H}_{4.0} \\
\text{(peak I)} & \\
& \rightarrow \alpha \mathrm{Tb}_{1-y} \mathrm{Fe}_2 \mathrm{H}_x + \mathrm{TbH}_2 \rightarrow \alpha \text{-Fe} + \mathrm{TbH}_2 \\
\text{(peak II)} & \\
& \text{(peak III)}
\end{align*}
\]

Figure 8(a) shows TDS of \(\mathrm{TbFe}_2\) heated in 0.1 MPa \(\mathrm{H}_2\) (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 \(\mathrm{H}_2\) (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 \(\mathrm{H}_2\) (0.17 K/s), respectively.

Figure 9 and Fig. 7(b) show XRD patterns and Ar-DSC curves of \(\mathrm{TbFe}_2\) heated to respective stages of PDSC in 0.1 MPa \(\mathrm{H}_2\) (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-\(\mathrm{TbFe}_2\)\(\mathrm{H}_{3.5}\).
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 $c$-$TbFe_2H_{1.5}$ into $\alpha$-Fe + $TbFe_2$, i.e., disproportionation occurs at the second exothermic peak; no amorphous phase is formed by heating of $TbFe_2$ in 0.1 MPa $H_2$ (0.33 K/s). The reaction sequence of $TbFe_2$ during heating in a hydrogen atmosphere is expressed as follows.

(iii) 0.33 K/s in 0.1 MPa $H_2$

\[
c-TbFe_2 \rightarrow c-TbFe_2H_{1.5} \rightarrow \alpha$-Fe + $TbH_2
\]  

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 $TbH_2$ 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 Kissing 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 $TbH_2$ becomes high. It is worth noting that $T_p$ for precipitation of $TbH_2$ increases with increasing hydrogen pressure, which suggests that precipitation of $TbH_2$ 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 $TbH_2$ decreases with decreasing hydrogen pressure, as shown in Figs. 1, 2 and 10. As a result, HIA and precipitation of $TbH_2$ occur simultaneously in 0.1 MPa $H_2$ (0.17 K/s). $T_p$ for this reaction falls on the extrapolated lines of $T_p$ values for HIA and for precipitation of $TbH_2$. As mentioned in Introduction, HIA and precipitation of $ErH_2$ occur simultaneously by heating $Er_2Fe_2$ in 1.0 MPa $H_2$ (0.17 K/s). If the peak temperature of HIA of $Er_2Fe_2$ and precipitation of $ErH_2$ decreases and increases, respectively, with increasing hydrogen pressure in the same way as $TbFe_2$, it is expected that HIA of $Er_2Fe_2$ occurs above 1.0 MPa $H_2$.

The present work clearly indicates that HIA in $TbFe_2$ occurs above the critical hydrogen pressure and below the critical heating rate. The amorphous single-phase $\alpha$-$TbFe_2H_x$ is formed above 0.2 MPa $H_2$ and at the heating rate of 0.17 K/s. On the contrary, no HIA is observed upon heating of $TbFe_2$ in 0.1 MPa $H_2$ (0.33 K/s). It is noteworthy that HIA does not occur in the conventional DSC experiments in 0.1 MPa $H_2$. 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 $c$-$TbFe_2H_{1.5}$ to $\alpha$-$TbFe_2H_x$, 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 $TbFe_2$ 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 $\alpha$-$TbFe_2H_x$ 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 $TbH_2$ and decomposition of the amorphous alloy into $\alpha$-Fe and $TbH_2$ occur exothermally with increasing temperature of $TbFe_2$ above 0.5 MPa $H_2$. 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 $TbH_2$ shifts to higher temperatures. As a result, HIA and precipitation of $TbH_2$ 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.

Acknowledgments

This work was supported in part by a “Grant-in-Aid for Scientific Research on Priority Area A of New Protium Function” from the Ministry of Education, Culture, Sports, Science and Technology.

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