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Hydrogen-induced amorphization of C15 Laves $TbFe_2$ compound

K. Aoki[1,*], K. Mori[2], H. Onodera, T. Masumoto

Institute for Materials Research, Tohoku University, Sendai, 980-77, Japan

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Abstract

Structural changes of the C15 Laves compound $TbFe_2$ have been investigated to study the origins of thermal effects during differential thermal analysis (DTA) in a hydrogen atmosphere by means of hydrogen analysis, X-ray diffractometry, differential scanning calorimetry, transmission electron microscopy, ^{57}Fe Mössbauer spectrometry and the magnetization measurements. The origin of the four exothermic peaks in the DTA curve was found to be due to (1) hydrogen absorption in the crystalline state, (2) hydrogen-induced amorphization, (3) the precipitation of TbH_2 in the amorphous phase and (4) the decomposition of the remaining amorphous phase into TbH_2 and α-Fe with increasing temperature. The amorphous nature of the hydrogen-induced amorphous alloy was supported by the Mössbauer data.

Keywords: Amorphous; Hydrogen; Intermetallic compound; Laves phase

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1. Introduction

It has been demonstrated that crystalline RFe_2H_x (c-RFe_2H_x; R=rare earth metal), amorphous RFe_2H_x (a-RFe_2H_x) and RH_2+α-Fe phases are formed with increasing temperature by differential thermal analysis (DTA) in a hydrogen atmosphere or hydrogenation of C15 Laves RFe_2 [1–3]. So far the amorphous nature of a-RFe_2H_x prepared by hydrogenation has been examined by powder X-ray diffractometry (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and other methods [4,5]. Although Mössbauer spectroscopy, which gives information on the magnetic states of the Fe sites and the ^{57}Fe hyperfine field, is useful for a study of the structural changes in Fe containing alloys, there is no report on the Mössbauer effect of the hydrogen-induced a-RFe_2H_x alloys. We are particularly interested in the Mössbauer effect among three states of hydrogenated $TbFe_2$, i.e., a- and c-$TbFe_2H_x$ and RH_2+α-Fe. During DTA in H_2, RFe_2 absorbs hydrogen and changes to c-RFe_2H_x at the first exothermic peak. Subsequently, c-RFe_2H_x transforms to a-RFe_2H_x. On heating this a-RFe_2H_x phase, third and fourth exothermic peaks appear in the DTA curve. However, it is difficult to study the origin of these exothermic peaks by means of XRD and TEM alone. It was hoped that the origin of these peaks could be determined by Mössbauer spectroscopy and magnetic property measurements. In the present work, the C15 type Laves phase $TbFe_2$ was thermally analyzed to clarify the origin of the exothermic peaks during DTA in hydrogen atmosphere.

2. Experimental

A $TbFe_2$ compound was arc melted using 99.9% Tb and 99.99% Fe in an argon atmosphere. The ingot was homogenized to obtain a single phase at 1073 K for 605 ks in an evacuated quartz tube. Pulverized crystalline samples (below 100 mesh) were heated using DTA at a heating rate of 20 K/min in a hydrogen atmosphere of 1 MPa. The structures of the samples heated to the distinct stages of DTA were examined by XRD using monochromated CuKα radiation. The microstructures of the hydrogenated samples were observed by TEM. The hydrogen content in the samples was determined by the high temperature gas extraction-gas chromatographic technique. Thermal properties and hydrogen desorption behaviors were examined by DSC at a heating rate of 40 K/min in a flowing Ar atmosphere. ^{57}Fe Mössbauer spectroscopy was carried out at 293 K using a conventional constant acceleration spectrometer in the transmission mode. The temperature dependence of the magnetization was measured with a vibrating sample magnetometer in the range of 4.2 to 860 K in an applied field of 10 kOe.

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[*] Corresponding author.

[1] Present address: Kitami Institute of Technology, Kitami, Hokkaido, 090 Japan.

[2] Present address: Central Research Institute, Mitsubishi Materials Corporation, Omiya, Saitama, 330 Japan.

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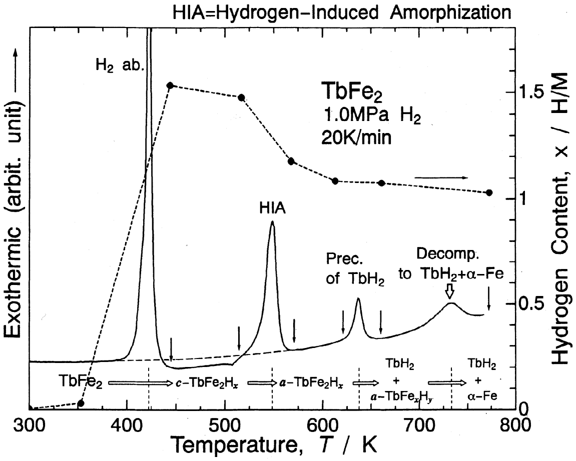

Fig. 1. A differential thermal analysis (DTA) curve of $TbFe_2$ heated at a heating rate of 20 K/min in 1 MPa H_2 and the change of the hydrogen content in the sample.

3. Results and discussion

Fig. 1 shows a DTA curve of $TbFe_2$ heated in a hydrogen atmosphere of 1 MPa. The amount of hydrogen (H/M) in the sample heated below and above the exothermic peaks is also plotted in this figure. Four exothermic peaks are clearly observed in the DTA curve. The hydrogen content increases drastically to 1.5 (H/M) on heating to 445 K, so that we see that the first exothermic peak is due to hydrogen absorption in agreement with previous work [3,6]. In order to clarify the origin of the peaks, XRD, DSC, TEM, Mössbauer spectroscopy and the magnetization measurement were carried out for the samples heated to the temperatures marked by the arrows.

Figs. 2–4 show XRD patterns, DSC curves and the Mössbauer spectra of $TbFe_2$ heated to the distinct stages of DTA in 1 MPa H_2. The XRD pattern of the original sample indicates this consisting of the single C15 Laves phase. The XRD pattern of the sample heated above the first peak (to 445 K) shows Bragg peaks which are indexed on the basis of a rhombohedral structure. The DSC curve of this sample shows endothermic peaks (below the broken line) resulting from hydrogen desorption, but does not show an exothermic peak of crystallization, indicating that no amorphous phase is contained in this sample. The Mössbauer spectrum of this sample shows a sharp doublet and broad and weak sextet characteristic of the crystalline phase. From the hydrogen analysis, XRD, DSC and Mössbauer spectroscopy, it is concluded that the first exothermic peak in the DTA curve is due to hydrogen absorption in the crystalline phase. That is, the C15 Laves $TbFe_2$ phase changes to the rhombohedral c-$TbFe_2H_x$ phase exothermally.

In the XRD patterns of the samples heated to 570–620 K, the Bragg peaks disappear and are replaced by a broad maximum. The DSC curves of these samples show two exothermic peaks of crystallization at 650 K and 830 K

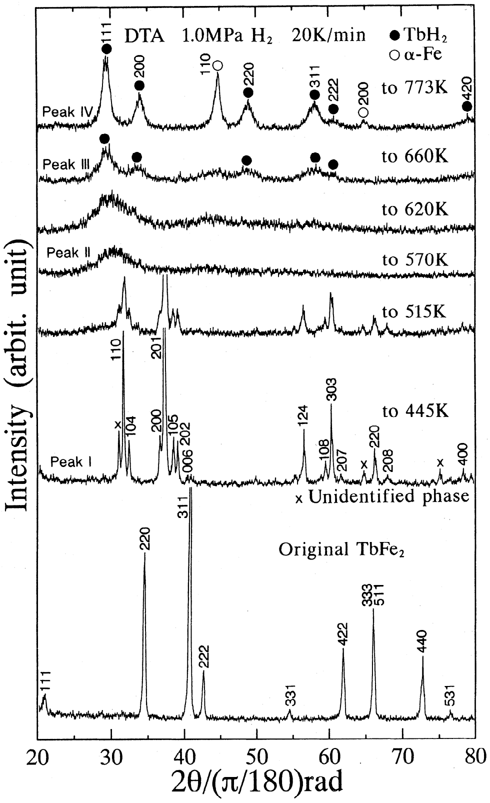

Fig. 2. X-ray diffraction (XRD) patterns of $TbFe_2$ heated to the distinct stages of DTA in 1 MPa H_2.

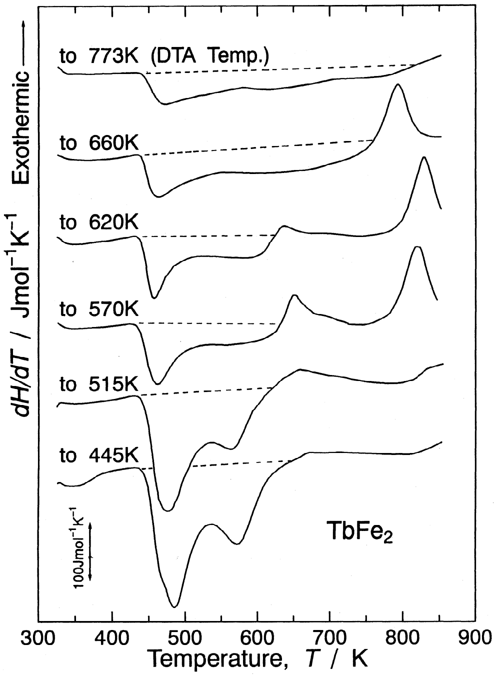

Fig. 3. DSC curves of $TbFe_2$ heated to the distinct stages of DTA in 1 MPa H_2.

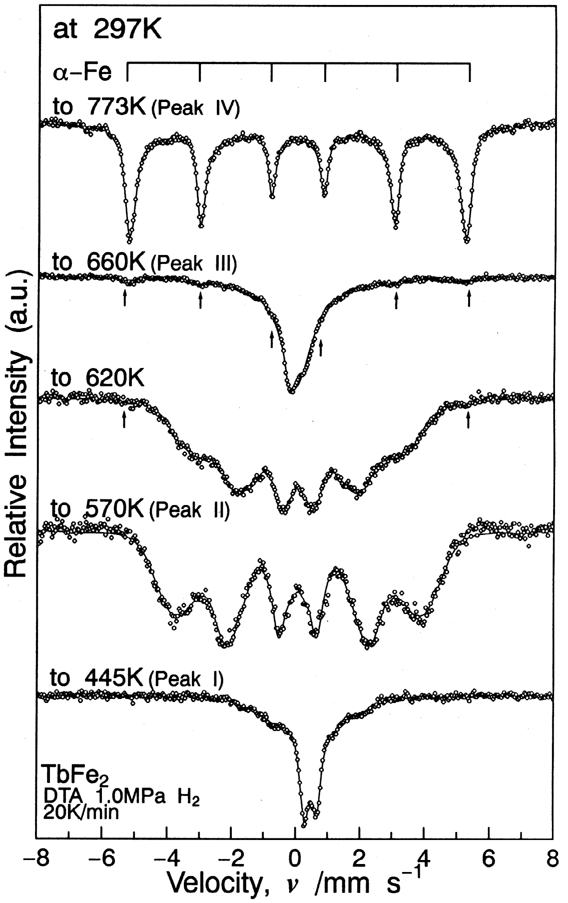

Fig. 4. The Mössbauer spectra of $TbFe_2$ heated to the distinct stages of DTA in 1MPa H_2.

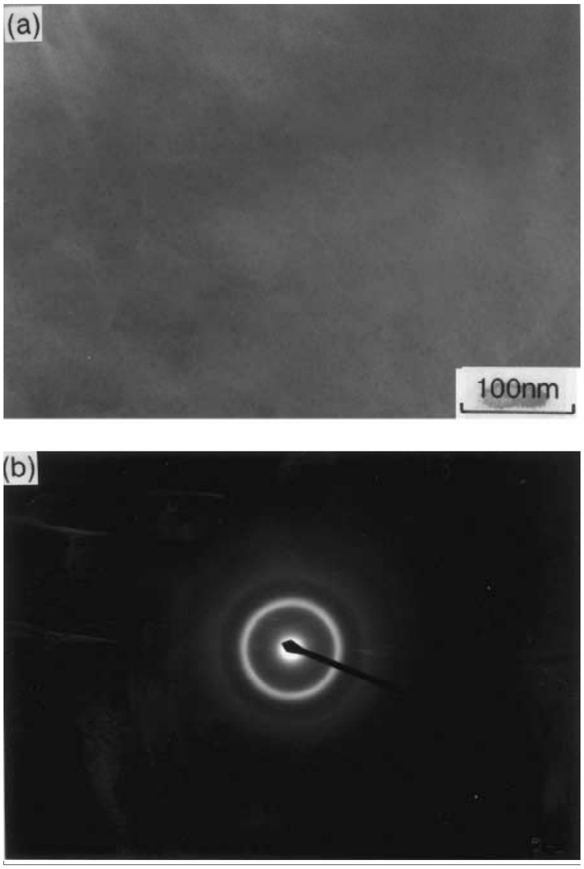

Fig. 5. A transmission electron micrograph (a) and the corresponding diffraction pattern (b) of $TbFe_2$ heated to 570 K in DTA in 1 MPa H_2.

along with the endothermic peak of hydrogen desorption. An electron micrograph of the sample heated to 570 K is featureless [Fig. 5(a)] and the corresponding selected area diffraction pattern shows a broad halo characteristic of an amorphous phase [Fig. 5(b)]. The Mössbauer spectrum of this sample shows a broad sextet due to the distributed hyperfine fields. The hyperfine field distribution is a characteristic feature of magnetically disordered amorphous materials. Thus the amorphous nature of this sample is supported by the Mössbauer effect. From XRD, DSC, TEM and Mössbauer spectroscopy, $TbFe_2$ heated to 570 K in 1 MPa H_2 is concluded to be amorphous. These observations indicate that the second exothermic peak in the DTA curve is due to the transformation of c-$TbFe_2H_x$ to a-$TbFe_2H_x$, i.e., a hydrogen-induced amorphization (HIA).

Broad Bragg peaks of TbH_2 are clearly observed in the XRD pattern of the sample heated above the third peak (to 660 K) in DTA. Correspondingly, the first exothermic DSC peak of the precipitation of TbH_2 disappears. Consequently, it is sure that TbH_2 precipitates at the third DTA peak. However, it is uncertain whether a-$TbFe_2H_x$ decomposes into TbH_2+α-Fe at the third DTA peak, although a faint Bragg peak is apparently observed at the position of (110) of α-Fe. In such a case, Mössbauer spectroscopy is useful to detect α-Fe. The Mössbauer spectrum of the sample heated above the third peak (to 660 K) shows a broad doublet, which is quite different from that of the sample heated above the fourth peak (to 773 K) which shows a sharp sextet of α-Fe. A very weak sextet of α-Fe overlapping with the doublet (see arrow marks) is observed, indicating that a small amount of α-Fe is present in the sample heated above the third peak. However, a small amount of α-Fe is also seen in the sample heated to 620 K. Therefore, it is concluded that α-Fe is not concerned by the third DTA peak. In order to identify the phase(s) other than TbH_2, the temperature dependence of magnetization was measured.

The thermomagnetizations of the samples heated above the second (solid line), third (dotted line) and fourth peak (broken line) in the DTA curves are shown in Fig. 6. Hydrogen-induced amorphous a-$TbFe_2H_{3.5}$ is a ferrimagnet with the compensation temperature T_{comp}=53 K and the Curie temperature T_C=450 K. On the other hand, the magnetization of the sample heated above the fourth peak shows the high value of α-Fe. The sample heated above the third peak shows a similar temperature dependence as that of a-$TbFe_2H_x$. This phase is also a ferrimagnet with T_{comp}=22 K and T_C=410 K. These thermomagnetization

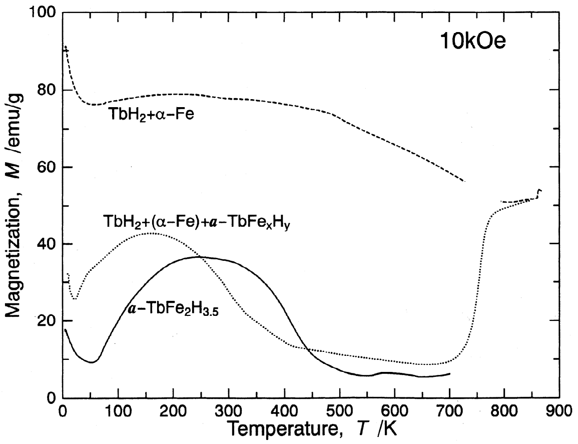

Fig. 6. Thermomagnetization curves of the samples heated above the second (solid line), third (dotted line) and fourth peak (broken line) in DTA.

data indicate that a phase other than TbH_2 is amorphous. This amorphous phase should be the Fe-rich one from a material balance point of view, because the TbH_2 phase has been precipitated in this sample. From XRD, DSC, Mössbauer spectroscopy and the temperature dependence of magnetization, it is concluded that the third DTA peak is due to the precipitation of TbH_2 in the amorphous phase.

The XRD pattern of the sample heated above the fourth peak (to 773 K) in DTA is indexed on the basis of TbH_2 and α-Fe. Furthermore, the presence of α-Fe is supported by Mössbauer spectroscopy as shown above. Since the amorphous phase remained in the sample which was heated above the third exothermic peak in DTA, we conclude that the fourth exothermic peak results from the decomposition (crystallization) of the remaining amorphous phase.

The origins of the exothermic peaks and the regions of each phase are presented in Fig. 1. The first, second, third and fourth DTA exothermic peaks are due to hydrogen absorption in the crystalline state, HIA, precipitation of TbH_2 and decomposition of the remaining amorphous phase, respectively. c-$TbFe_2H_x$, a-$TbFe_2H_x$, TbH_2+a-$TbFe_xH_y$ and TbH_2+α-Fe are formed with increasing temperature during DTA in hydrogen. This indicates that the stability of the phases increases in this order. It is important to note that the stability of a-$TbFe_2H_x$ is higher than that of c-$TbFe_2H_x$, which is the driving force for HIA. The driving force for HIA may be explained by the difference in enthalpy resulting from the different hydrogen environments in the a- and c-$TbFe_2H_x$ structures [3].

4. Summary and conclusions

The structural changes of the C15 Laves phase $TbFe_2$ during DTA in a hydrogen atmosphere have been investigated to clarify the origin of thermal effects. The origin of the first and second exothermic peak was determined by means of XRD, TEM and DSC to be due to hydrogen absorption, and HIA, respectively. However, it was impossible to clarify the origin of the third and fourth exothermic peak by these methods alone. The origin of the third and fourth exothermic peak was determined to result from the precipitation of TbH_2 in the amorphous phase and the decomposition (crystallization) of the remaining amorphous phase by means of Mössbauer spectroscopy and the magnetization measurement in addition to the above experimental methods. The Mössbauer data support the amorphous nature of the hydrogen-induced amorphous a-$TbFe_2H_x$ alloy.

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