Pressure Dependence of Hydrogen-Induced Transformations in C15 Laves Phase DyCo2

Haiwen Li*1, Kazuhiro Ishikawa and Kiyoshi Aoki*2

Department of Materials Science, Kitami Institute of Technology, Koen-cho 165, Kitami 090-8507, Japan

Structural changes in C15 Laves phase DyCo2 heated in a hydrogen atmosphere between 0.1 and 5.0 MPa were investigated using a pressure differential scanning calorimeter (PDSC) and were compared with those of DyFe2. Four exothermic reactions resulting from 1) hydrogen absorption forming crystalline and amorphous hydrides, 2) hydrogen-induced amorphization (HIA), 3) the precipitation of BiFe2-type DyH3 in the amorphous hydride and 4) the decomposition of the remaining amorphous hydride into DyH4 + β-Co were observed with increasing temperature. HIA in DyCo2 occurred for every hydrogen pressure in contrast to DyFe2, because the pressure dependence of it is small.

The mechanism of the phase transformations for DyCo2 in a hydrogen atmosphere was discussed on the basis of the experimental results such as the pressure dependence of Tp and Tm/Tm (the peak temperature/the melting point of DyCo2), the enthalpy change ΔH, the activation energy EA and so on.

In the present work, we investigate the hydrogen pressure dependence of the structural changes in C15 Laves phase DyCo2 and compare it with that of DyFe2. The mechanism of the phase transformations for DyCo2 in a hydrogen atmosphere is discussed on the basis of the experimental results such as the pressure dependence of Tp and Tm/Tm (the peak temperature/the melting point of DyCo2), the enthalpy change ΔH, the activation energy EA and so on.

1. Introduction

Hydrogen storage alloys are usually prepared by the combination of a hydride forming (A) and a non-hydride forming metallic element (B), and absorb and desorb hydrogen at near room temperature keeping the crystalline state. On the other hand, it has been known that intermetallic compounds A1B1−x with the C15, B82, C23, D010 and L12 structures amorphize by hydrogenation,1−14 which is called hydrogen-induced amorphization (HIA). HIA is a practically important phenomenon, because it is closely related to the disproportional reaction that determines the lifetime of hydrogen storage alloys. Therefore, it is important to make clear what factors determine the occurrence of HIA. Among the amorphizing alloys, HIA of the C15 Lave phase compounds RM2 (R = rare earth metals, M = Fe, Co, Ni) is especially interesting, because the formation of both crystalline and amorphous hydrides depends on the hydrogenation temperature. For instance, HIA in TbFe215−17 and ErFe218 occurs above the critical hydrogen pressure, but that of CeFe2 does independent of the hydrogen pressure, i.e., no crystalline hydride is formed.17 More recently, it has been found by thermal analysis of C15 Laves phase DyFe2 in a hydrogen atmosphere that hydrogen absorption forming a crystalline hydride, HIA and the decomposition of the amorphous hydride show a negative pressure dependence, but that for the precipitation of DyH3 shows a positive one.19 As a consequence of such pressure dependence, HIA and the precipitation of DyH3 occur simultaneously at 0.2 MPa H2 and the crystalline hydride decomposes directly into DyH3 and α-Fe at 0.1 MPa H2. That is, HIA of DyFe2 occurs above the critical hydrogen pressure. Furthermore, Tp of HIA for C15 Laves RFe2 (R = Tb, Er) shows also a same strong negative pressure dependence.15−18 It has been proposed that HIA of C15 Laves RM2 occurs by the short-range diffusion of R and M atoms. Therefore, it is interesting to compare the pressure dependence of HIA for DyCo2 with that for DyFe2.

2. Experimental

A DyCo2 alloy was prepared by arc melting using high-purity metals (99.9%) in a purified argon atmosphere. The alloy ingot was homogenized at 1073 K for 1 week in an evacuated quartz tube. Subsequently, it was pulverized under 100 mesh in acetone to prevent oxidation and ignition. The alloy powder was thermally analyzed using a pressure differential scanning calorimeter (PDSC) at heating rates of 0.08, 0.17, 0.33 and 0.67 K/s in a flowing argon atmosphere of 0.1−5.0 MPa. To make clear the origin of thermal peaks, the sample was heated to the respective stages in PDSC, followed by rapid cooling to room temperature and was subjected to a powder X-ray diffraction (XRD) analysis with monochromatic CuKα radiation and to a conventional differential scanning calorimetry (Ar-DSC) at a heating rate of 0.67 K/s in a flowing argon atmosphere. The amount of desorbed hydrogen was measured by heating the sample at a rate of 2 K/s in an argon atmosphere using a hydrogen analyzer. Some samples were further examined by a transmission electron microscope (TEM).

3. Results

3.1 Structural changes of DyCo2 heated in a hydrogen atmosphere

Figure 1 shows examples of PDSC curves and the change of the hydrogen content (H/M) in DyCo2 heated at the rate of 0.17 K/s at 1.0 and 0.1 MPa H2. The broken lines and the arrows indicate the base line and the temperature to which the samples were heated and then cooled, respectively. Four
exothermic peaks, i.e., one large and sharp and subsequent three small and broad peaks are observed in these PDSC curves. We can notice that the second exothermic peak of DyCo$_2$ is prominently smaller than that of DyFe$_2$.19)

3.1.1 Structural changes of DyCo$_2$ heated at 1.0 MPa H$_2$

XRD patterns, TEM photographs and Ar-DSC curves of DyCo$_2$ heated to above the respective exothermic peaks of PDSC at 1.0 MPa H$_2$ are shown in Fig. 2(a), Figs. 3(a)–(e) and Fig. 4(a), respectively. The XRD pattern of original DyCo$_2$ indicates that this sample consists of the C15 Laves phase (Fd3m) [Fig. 2(1)]. The Bragg peaks shift to the lower angle side and become very small, which are indexed on the basis of a rhombohedral structure (R3m), when the sample is heated to above the first exothermic peak [Fig. 2(2)]. The hydrogen content of this sample increases to 1.31 (H/M). Consequently, the first large and sharp exothermic peak is considered to result from hydrogen absorption to form the crystalline hydride, c-DyCo$_2$H$_x$. Since the intensity of these Bragg peaks is very low, it is suggested that this sample contains also the amorphous hydride a-DyCo$_2$H$_y$, which is confirmed as follows.

The bright field images of TEM for DyCo$_2$ heated to above the first exothermic peak and its selected area diffraction patterns (SADP) are shown in Fig. 3(a) and Fig. 3(b). This sample is heterogeneous, i.e., some region shows the crystalline hydride nature [Fig. 3(a)] and the other one does the amorphous one [Fig. 3(b)] implying that this sample consists of both crystalline c- and amorphous hydride a-DyCo$_2$H$_x$. Since the Ar-DSC curve of DyCo$_2$ heated to above the first exothermic peak [Fig. 4(1)] is very complex, it is difficult to distinguish between the exothermic and endothermic peak. In Fig. 4, the broken lines indicate the estimated base lines. It has been reported that crystalline hydrides c-RM$_2$H$_x$ can desorb hydrogen in the crystalline state and their Ar-DSC curves show only endothermic peaks at relatively low temperatures without exception.14,15,18,19) The Ar-DSC curve of DyCo$_2$ heated to above the first

![Fig. 1 PDSC curves of DyCo$_2$ and the change of the hydrogen content (H/M) heated at the rate of 0.17 K/s at 1.0 and 0.1 MPa H$_2$.](image1)

![Fig. 2 XRD patterns of DyCo$_2$ heated to above respective peaks of PDSC at the rate of 0.17 K/s at 1.0 MPa H$_2$ (a) and 0.1 MPa H$_2$ (b). The original sample (1), the samples heated to the following temperatures: (2) to 400 K, (3) to 623 K, (4) to 723 K, (5) to 798 K, (6) to 453 K, (7) to 623 K, (8) to 723 K and (9) to 863 K.](image2)

![Fig. 3 TEM bright field images and corresponding SADP of DyCo$_2$ heated to respective stages at the rate of 0.17 K/s at 1.0 MPa H$_2$. The sample heated to above the first exothermic peak (to 400 K) (a,b), the second peak (to 623 K) (c), the third peak (to 723 K) (d) and to the fourth peak (to 798 K) (e).](image3)
The Bragg peaks disappear and are replaced by a broad maximum when DyCo$_2$ is heated to above the second exothermic peak [Fig. 2(3)]. The bright field image of TEM for this sample shows a featureless microstructure and its SADP shows a broad halo characteristic of the amorphous phase [Fig. 3(c)]. The Ar-DSC curve of this sample supports its amorphous nature, because the exothermic peaks are also observed above about 700 K [Fig. 4(2)]. Consequently, DyCo$_2$ sample heated to above the second exothermic peak is amorphous, i.e., the second exothermic peak results from hydrogen-induced amorphization (HIA). The hydrogen content of this sample is 1.03 (H/M), so that the alloy is expressed as amorphous $a$-DyCo$_2$H$_3$. Since a part of $c$-DyCo$_2$H$_3$ has transformed to $a$-DyCo$_2$H$_3$ at the first exothermic peak, HIA at the second exothermic peak is very limited, which leads to the small second exothermic peak of PDSC.

In the XRD pattern of the sample heated to above the third exothermic, weak and broad Bragg peaks of Dy hydride appear overlapping with the broad maximum [Fig. 2(4)]. The bright field image of TEM [Fig. 3(d)] for this sample shows the crystalline phase along with the amorphous hydride and its SADP shows the Debye-Scherrer rings of Dy hydride overlapped with a broad halo. At first glance, these Bragg peaks are indexed on the basis of the CaF$_2$-type DyH$_2$. However, this hydride is not di-hydride DyH$_2$, but is tri-hydride DyH$_3$ as shown below. The hydrogen content of the Dy hydride for this sample cannot be determined, because it consists of a mixture of the Dy hydride and the amorphous hydride. However, its hydrogen content is determined using a sample heated above the fourth exothermic peak. The XRD pattern of the sample [Fig. 2(5)] heated to above the fourth exothermic peak is indexed on the basis of Dy hydride + $\beta$-Co. The hydrogen content of this sample is 0.95(H/M), so that this hydride is the tri-hydride DyH$_3$. DyH$_3$ generally takes the HoH$_3$ type structure, but the Bragg peaks of this sample are not indexed on the basis of it. They are indexed on the basis of BiF$_3$-type hydride [Fm$\overline{3}$m]. The bright field image of TEM for this sample shows the crystal lattice image and its SADP shows the Debye-Scherrer rings of $\beta$-Co and BiF$_3$-type DyH$_3$ [Fig. 3(e)]. Consequently, the fourth exothermic peak results from the decomposition of the remaining amorphous hydride into BiF$_3$-type DyH$_3$ and $\beta$-Co. Then, the third exothermic peak of PDSC may result also from the precipitation of BiF$_3$-type DyH$_3$ in the amorphous hydride.

The reaction sequence of DyCo$_2$ heated at the rate of 0.17 K/s at 1.0 MPa H$_2$ is expressed below.

\[
\begin{align*}
  c \text{-DyCo}_2 & \rightarrow c \text{-DyCo}_2 \text{H}_3 \\
  + a \text{-DyCo}_2 \text{H}_3 & \rightarrow a \text{-DyCo}_2 \text{H}_3 & \rightarrow & DyH_3 \\
  + a \text{-Dy}_{1-x} \text{Co}_2 \text{H}_3 & \rightarrow DyH_3 + \beta \text{-Co}
\end{align*}
\]

### 3.1.2 Structural changes of DyCo$_2$ heated at 0.1 MPa H$_2$

Four exothermic peaks are also seen in the PDSC curve of DyCo$_2$ heated at 0.1 MPa H$_2$ [Fig. 1]. The XRD patterns and Ar-DSC curves of the sample heated to the respective stages are shown in Fig. 2(b) and Fig. 4(b), respectively. The bright field image of TEM shows a featureless microstructure and its SADP shows a broad halo indicating that the sample heated to above the second exothermic peak is an amorphous hydride. Furthermore, XRD, TEM and Ar-DSC experiments of the DyCo$_2$ sample heated at 0.1 MPa H$_2$ indicate the same structural changes with those of the samples heated at 1.0 MPa H$_2$. That is, as the temperature increases, 1) hydrogen absorption forming a crystalline and an amorphous hydride, 2) HIA, 3) the precipitation of BiF$_3$-type DyH$_3$, 4) the decomposition of the remaining amorphous hydride into BiF$_3$-type DyH$_3$ + $\beta$-Co occur exothermically.

### 3.2 Pressure dependence of peak temperature $T_p$ for thermal reactions

Figure 6 shows PDSC curves of DyCo$_2$ heated at the rates of 0.08, 0.16, 0.33 and 0.67 K/s in the hydrogen atmosphere of 0.1–5.0 MPa. From these PDSC curves, the peak temperature $T_p$ for each thermal peak is determined and is plotted against the hydrogen pressure as shown in Fig. 7. As the hydrogen pressure increases, $T_p$ for the formation of the crystalline and the amorphous hydrides, and for the decomposition of the amorphous hydride shifts to the lower pressures.
temperature side, i.e., show the negative pressure dependence. On the contrary, \( T_p \) for HIA and for the precipitation of BiF\(_3\)-type DyH\(_3\) is almost independent of the hydrogen pressure. As a consequence of such pressure dependence, the amorphous hydride is formed even at the low hydrogen pressure in contrast to DyFe\(_2\).\(^{19}\)

Figure 8 shows the relation between \( T_p/T_m \) \((T_m\) is the melting point of DyCo\(_2\)) and the hydrogen pressure for the exothermic reactions for DyCo\(_2\).

3.3 The enthalpy change \( \Delta H \) and the activation energy \( E_A \) of thermal reactions

The enthalpy change \( \Delta H \) for the thermal reactions of DyFe\(_2\) heated at 1.0 MPa H\(_2\) was calculated from the area of the thermal peaks. On the other hand, the activation energy \( E_A \) for the thermal reactions is evaluated by Kissinger’s peak shift method.\(^{16}\) The method includes the application of the following equation.
4.1 Formation of crystalline and amorphous hydrides at the first exothermic peak

The PDSC curves of C15 Laves phase DyCo2 show four exothermic peaks, i.e., 1) hydrogen absorption forming both crystalline and amorphous hydrides, 2) HIA, 3) the precipitation of BiF3-type DyH3 in the amorphous hydride and 4) the decomposition of the remaining amorphous hydride into BiF3-type DyH3 + β-Co with increasing temperature. These experimental results imply that HIA occurs at the first and the second exothermic peaks. It has been reported that the first exothermic peak of PDSC is caused by hydrogen absorption forming the crystalline hydride in C15 Laves phase TbFe2 and ErFe2[15-18] or the amorphous hydride in CeFe2.[17] The formation of crystalline and amorphous hydrides at the first exothermic peak is the first finding in the present work. First, we discuss the reason why both crystalline and amorphous hydrides are formed at the first exothermic peak.  

\[
\text{Time (s)}
\]

\[
\text{Temperature (°C)}
\]

\[
\text{Fig. 9} \quad \text{The schematic illustration of} \; \Delta H \; \text{and} \; E_A \; \text{for thermal reactions of} \; \text{DyCo2} \; \text{heated at} \; 1.0 \; \text{MPa} \; \text{H}_2 \; \text{in the reaction sequence.}
\]

\[
\ln(C/T_p^2) = -(E_A/R T_p) + A
\]

Where \( C \) is the heating rate, \( T_p \) is the peak temperature, \( E_A \) is the activation energy, \( R \) is the gas constant, and \( A \) is a constant.

According to Hess’s rule, \( \Delta H \) for a reaction is independent of the reaction route. When DyCo2 is heated at 1.0 MPa H2, its final product is DyH2 + β-Co. Therefore, the total \( \Delta H \) should be equal to the formation \( \Delta H \) of DyH3. Here, the physical mixture of Dy, 2Co and 3/2H2 is a starting point of the reactions and \( \Delta H \) is 0. The formation \( \Delta H \) of DyH3 and DyCo2 are \(-138, -34 \text{kJ/mol Dy, respectively.}^{20,21}\) The \( \Delta H \) value of hydrogen absorption, HIA, the precipitation and the decomposition for DyCo2 heated at 1.0 MPa H2 is calculated to be \(-62, -7, -6 \) and \(-3 \text{kJ/mol Dy, respectively. The sum of} \; \Delta H \; \text{for these reactions is in good agreement with the formation} \; \Delta H \; \text{of DyH3, which strongly supports the formation of BiF3-type DyH3.}

4.2 The pressure dependence of thermal reactions and the mechanism of HIA

The pressure dependence of thermal reactions of MFe2 and DyCo2 at 1.0 MPa are calculated to be 36, 175, 336, 493 kJ/mol Dy, respectively. 20,21) The activation energy, \( E_A \), for the thermal reaction at the first exothermic peak is 36 kJ/mol Dy. Consequently, \( E_A \) for hydrogen absorption forming only c-DyCo2Hx should be much smaller than 36 kJ/mol Dy. On the other hand, it has been reported that \( E_A \) for hydrogen absorption forming c-DyCo2Hx is 56 kJ/mol Dy.[19] Such large difference in the activation energy implies that hydrogen absorption occurs very easily in DyCo2. Hydrogen is absorbed exothermically in DyCo2, which gives rise to rapid increase of the temperature. When the temperature of c-DyCo2Hx exceeds the temperature of HIA, the transformation from c-DyCo2Hx to a-DyCo2Hx occurs. Since hydrogen absorption and subsequent HIA occur simultaneously, the first exothermic peak becomes very large and the second exothermic peak becomes very small as seen in Fig. 1.

4. Discussion

4.1 Formation of crystalline and amorphous hydrides at the first exothermic peak

The PDSC curves of C15 Laves phase DyCo2 show four exothermic peaks, i.e., 1) hydrogen absorption forming both crystalline and amorphous hydrides, 2) HIA, 3) the precipitation of BiF3-type DyH3 in the amorphous hydride and 4) the decomposition of the remaining amorphous hydride into BiF3-type DyH3 + β-Co with increasing temperature. These experimental results imply that HIA occurs at the first and the second exothermic peaks. It has been reported that the first exothermic peak of PDSC is caused by hydrogen absorption forming the crystalline hydride in C15 Laves phase TbFe2 and ErFe2[15-18] or the amorphous hydride in CeFe2.[17] The formation of crystalline and amorphous hydrides at the first exothermic peak is the first finding in the present work. First, we discuss the reason why both crystalline and amorphous hydrides are formed at the first exothermic peak.  

\[
\text{Time (s)}
\]

\[
\text{Temperature (°C)}
\]

\[
\text{Fig. 9} \quad \text{The schematic illustration of} \; \Delta H \; \text{and} \; E_A \; \text{for thermal reactions of} \; \text{DyCo2} \; \text{heated at} \; 1.0 \; \text{MPa} \; \text{H}_2 \; \text{in the reaction sequence.}
\]

\[
\ln(C/T_p^2) = -(E_A/R T_p) + A
\]

Where \( C \) is the heating rate, \( T_p \) is the peak temperature, \( E_A \) is the activation energy, \( R \) is the gas constant, and \( A \) is a constant.

According to Hess’s rule, \( \Delta H \) for a reaction is independent of the reaction route. When DyCo2 is heated at 1.0 MPa H2, its final product is DyH2 + β-Co. Therefore, the total \( \Delta H \) should be equal to the formation \( \Delta H \) of DyH3. Here, the physical mixture of Dy, 2Co and 3/2H2 is a starting point of the reactions and \( \Delta H \) is 0. The formation \( \Delta H \) of DyH3 and DyCo2 are \(-138, -34 \text{kJ/mol Dy, respectively.}^{20,21}\) The \( \Delta H \) value of hydrogen absorption, HIA, the precipitation and the decomposition for DyCo2 heated at 1.0 MPa H2 is calculated to be \(-62, -7, -6 \) and \(-3 \text{kJ/mol Dy, respectively. The sum of} \; \Delta H \; \text{for these reactions is in good agreement with the formation} \; \Delta H \; \text{of DyH3, which strongly supports the formation of BiF3-type DyH3.}

4.2 The pressure dependence of thermal reactions and the mechanism of HIA

As the hydrogen pressure increases, \( T_p \) for the formation of both c-DyCo2Hx and a-DyCo2Hx, and the decomposition of a-DyCo2Hx into DyH3 + β-Co shift to lower temperature side, which show the negative pressure dependence [Fig. 7]. On the contrary, \( T_p \) for HIA and the precipitation of DyH3 is almost independent of the hydrogen pressure. The line connecting \( T_p \) for HIA does not intersect the line connecting \( T_p \) for the precipitation of DyH3, so that HIA occurs even at the lower hydrogen pressure. On the other hand, \( T_p \) of HIA and the precipitation of DyH3 in DyFe2 show the large negative and the small positive pressure dependence,[19] respectively. As a consequence of such pressure dependence, HIA overlaps with the precipitation of DyH3 at 0.2 MPa H2 and the crystalline hydride decomposes directly into α-Fe and DyH3 at 0.1 MPa H2. Then, HIA of DyFe2 occurs above the critical hydrogen pressure. Thus, the pressure dependence of HIA is a key factor whether HIA occurs or not at the low hydrogen pressure in the C15 Laves RM2. HIA is considered
to occur by the short-range diffusion of both Dy and Co (Fe) for DyCo₂ (DyFe₂). It is interesting to note that the pressure dependences of HIA and the precipitation of DyH₃ depend strongly on the kinds of M metals (Co or Fe). It is a future subject to determine what factors determine the pressure dependence of HIA and the precipitation of BiH₃-type DyH₃.

We discuss the mechanism of HIA in the C15 Laves phase DyCo₂ from the standpoint of the pressure dependence of structural changes. Thermal reactions related with hydrogen are generally controlled by the kinetic and thermodynamic factors. At about 0.3 \( T_m \), where the diffusion of the metallic atoms does not substantially occur, hydrogen is absorbed forming c-DyCo₂Hₓ and a part of it transforms into a-DyCo₂Hₓ by the temperature increase. When c-DyCo₂Hₓ is heated to above the second exothermic peak, \( i.e., \) to about 0.38 \( T_m \), where both Dy and Co atoms can move over a short-range distance, HIA occurs so as to reduce the enthalpy. The driving force for HIA is considered to be the enthalpy difference resulting from the different hydrogen occupation sites. Hydrogen atoms in c-DyCo₂Hₓ occupy tetrahedral sites surrounded by 2Dy + 2Co and Dy + 3Co by the geometric constraint. On the contrary, hydrogen atoms in the amorphous hydride can occupy tetrahedral sites surrounded by 4Dy and 3Dy + 1Co in addition to 2Dy + 2Co and Dy + 3Co, because there is no geometric constraint for the structure. Since the formation enthalpy of the Dy hydride is more negative than that of the Co hydride, hydrogen atoms can stay more stable in the amorphous hydride. Even though the hydrogen pressure increases, the peak temperature can stay more stable in the amorphous hydride. Even though hydrogen absorption forming c-DyCo₂Hₓ occurs very easily at the first exothermic peak and gives rise to the rapid increase of the temperature, a part of c-DyCo₂Hₓ transforms to a-DyCo₂Hₓ. On the contrary, the enthalpy change \( \Delta H \) for hydrogen absorption takes a large absolute value, but the activation energy \( E_a \) for it takes a small absolute one, which indicates that hydrogen absorption occurs easily. Since hydrogen absorption forming c-DyCo₂Hₓ occurs very easily at the first exothermic peak and gives rise to the rapid increase of the temperature, a part of c-DyCo₂Hₓ transforms to a-DyCo₂Hₓ. On the contrary, the enthalpy change \( \Delta H \) for HIA, the precipitation of DyH₃ and the decomposition of the remaining amorphous hydride take small absolute values, but \( E_a \) for them take large absolute ones. The mechanism of HIA in DyCo₂ was discussed on the basis of the experimental results such as the pressure dependence of \( T_P / T_m \) (the peak temperature/the melting point of DyCo₂), the enthalpy change \( \Delta H \), the activation energy \( E_a \) and so on for each reaction.

REFERENCES