# Pressure dependence of hydrogen-induced amorphization in C14 Laves phase $NdMn_2$

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## Abstract

Structural changes in C14 Laves phase $NdMn_2$ in a hydrogen atmosphere of 0.1–5.0 MPa were investigated using a pressure differential scanning calorimeter (PDSC), a powder X-ray diffractometer (XRD), a conventional differential scanning calorimeter (Ar-DSC), a transmission electron microscope (TEM) and a hydrogen analyzer. Three exothermic peaks resulting from (1) hydrogen absorption in the crystalline state, (2) hydrogen-induced amorphization (HIA) and the precipitation of $BiF_3$-type $NdH_3$ which occur simultaneously, and (3) the decomposition of the remaining amorphous phase into $\alpha$-Mn and $NdH_3$ were observed with increasing temperature between 0.1 and 1.0 MPa $H_2$. HIA and the precipitation of $NdH_3$ occurred separately above 2.0 MPa $H_2$. The peak temperature for HIA of C14 Laves phase $NdMn_2$ and its pressure dependence is higher and smaller than those of C15 Laves phases $RFe_2$. HIA of $NdMn_2$ occurred for every hydrogen pressure, although the single phase amorphous hydride is not formed below 1.0 MPa $H_2$.
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## 1. Introduction

The formation of amorphous hydrides by hydrogenation of intermetallic compounds is called hydrogen-induced amorphization (HIA). HIA is a novel method to prepare amorphous hydrides without rapid quenching, and closely related to the disproportionation that dominates a lifetime of hydrogen storage alloys. Therefore, it is important to make clear the controlling factors for the occurrence of HIA. HIA has been observed in the intermetallic compounds consisting of hydride forming and non-hydride forming ones with the specific crystal structures such as C15, $B8_2$, C23, $D0_{19}$, B2 and $L1_2$ [1–9]. Aoki et al. [10] have investigated the hydrogen-induced structural changes in C15 Laves phases $AB_2$ and showed that HIA occurs in the compounds with the atomic size ratio larger than 1.37. Then, it is interesting whether the C14 Laves $RM_2$ with the atomic size ratio larger than 1.37

amorphize or not by hydrogenation. Recently, the present authors have demonstrated that C14 Laves phase $NdMn_2$ with $R_{Nd}/R_{Mn} = 1.45$ amorphizes by hydrogenation at 5.0 MPa $H_2$ [11].

That is, four exothermic peaks resulting from (1) hydrogen absorption in the crystalline state, (2) hydrogen-induced amorphization (HIA), (3) the precipitation of $NdH_3$ in the amorphous hydride, (4) the decomposition of the remaining amorphous phase into $\alpha$-Mn and $NdH_3$ are observed with increasing temperature. However, Chung et al. reported that $NdMn_2$ does not amorphize by hydrogenation at 0.14 MPa $H_2$ [12]. Aoki et al. have reported that HIA of the C15 Laves phases $RFe_2$ (R = Dy, Tb and Er) occurs above the critical hydrogen pressure [13–15]. Then, there is a possibility that $NdMn_2$ does not amorphize at the low hydrogen pressure in the same way as C15 Laves $RFe_2$. In the present work, we investigate the hydrogen pressure dependence of structural changes in C14 Laves phase $NdMn_2$ and compare it with that of the C15 Laves $RFe_2$ in order to make clear the formation conditions

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of the amorphous hydrides in the C15 and C14 Laves compounds.

## 2. Experimental

NdMn$_2$ was prepared by arc melting under an argon atmosphere. This alloy ingot was homogenized at 1073 K for 7 days in an evaluated quartz tube and then quenched into ice water. The NdMn$_2$ alloy was pulverized and sieved through #100 screen. Thermal analysis of powder sample was carried out using a pressure differential scanning calorimeter (PDSC) in a high purity hydrogen (99.99999%) atmosphere at 0.1–5.0 MPa and at a heating rate of 0.17 K/s. Structures of the samples before and after thermal analysis were identified by a powder X-ray diffractometer (XRD) using monochromated Cu Kα radiation. Microstructural observation and structural characterization were carried out using a transmission electron microscope (TEM). The hydrogen content was measured using a hydrogen analyzer. Thermal stability and crystallization behaviors were measured using a conventional Ar-flow differential scanning calorimeter (Ar-DSC).

## 3. Results and discussion

Fig. 1 shows PDSC curves of NdMn$_2$ heated at 0.1–5.0 MPa H$_2$ and at the rate of 0.17 K/s. Three exothermic peaks are observed between 0.1 and 1.0 MPa H$_2$ and four ones are observed above 2.0 MPa H$_2$. The origins for these exothermic peaks are investigated as follows.

Fig. 2 shows a PDSC curve and the change in the hydrogen content (the broken line) in NdMn$_2$ heated at 1.0 MPa H$_2$. The thin broken line indicates a base line of the PDSC curve. Three exothermic peaks, i.e. the first sharp and large, the second broad and the third weak peaks are observed on this PDSC curve.

Figs. 3 and 4 show XRD patterns and Ar-DSC curves of the samples heated to above the exothermic peaks (to the points indicated by the arrows in Fig. 2), respectively. The Bragg peaks of the original sample are indexed on the basis of the C14 Laves phase. The Bragg peaks shift to the lower angle side on heating the sample to above the peak I (to 424 K). Correspondingly, the hydrogen content of this sample increases rapidly to 1.92 (H/M). The Ar-DSC curve of this sample shows two endothermic peaks of hydrogen desorption, but do not show any exothermic peak of crystallization. Consequently, the first exothermic peak of the PDSC curve is concluded to result from hydrogen absorption in the crystalline state, and this alloy is expressed as crystalline c-NdMn$_2$H$_{5.76}$.

Broad Bragg peaks, which are overlapped with the wide XRD maximum, are observed in the XRD pattern of the sample heated to above the peak II (to 650 K). Its Ar-DSC curve shows an exothermic peak suggesting the presence of an amorphous hydride together with an endothermic peak of
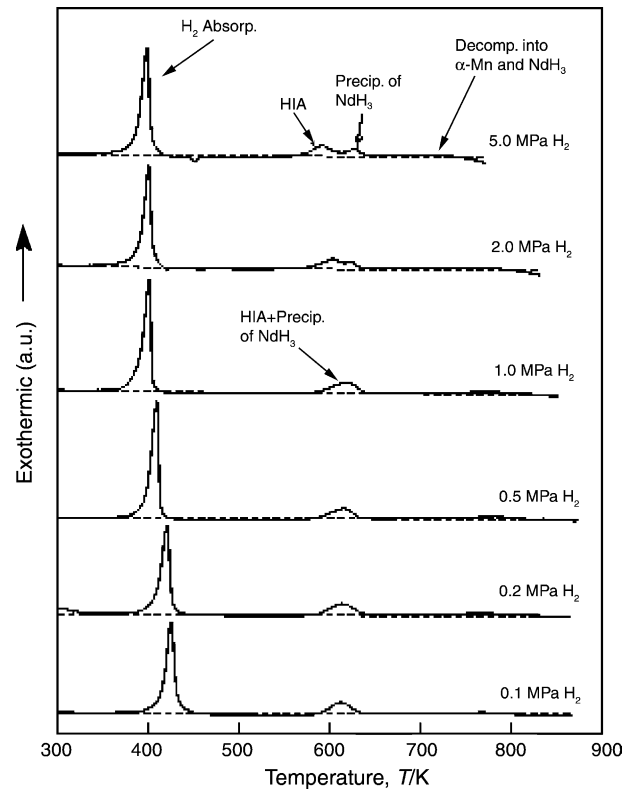


Fig. 1. PDSC curves of C14 Laves phase NdMn$_2$ heated at 0.1–5.0 MPa H$_2$ and at the rate of 0.17 K/s.

hydrogen desorption. The bright field image (BFI) of TEM for this sample is shown in Fig. 5. Small crystalline hydrides below 10 nm size, surrounded by white circles, are embedded in the amorphous hydride. Debye–Scherrer rings are also observed in the selected area electron diffraction pattern (SADP) of TEM for this sample. From XRD, Ar-DSC and TEM experiments, we can see that the sample heated to above the peak II consists of the amorphous hydride and Nd-hydride. That is, hydrogen-induced amorphization (HIA)
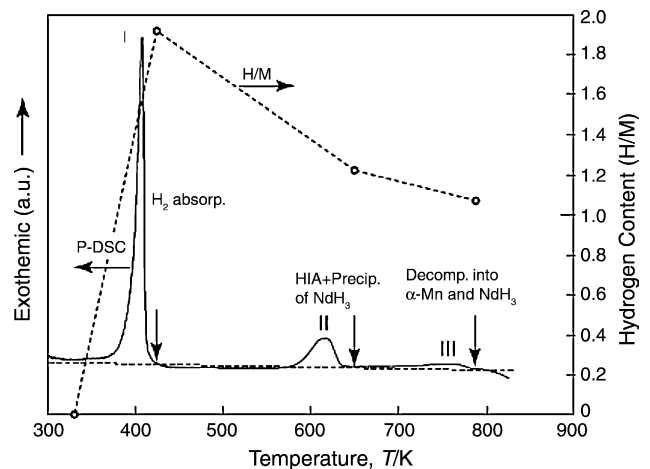


Fig. 2. A PDSC curve and the change in the hydrogen content of NdMn$_2$ heated at 1.0 MPa H$_2$ and at the rate of 0.17 K/s.
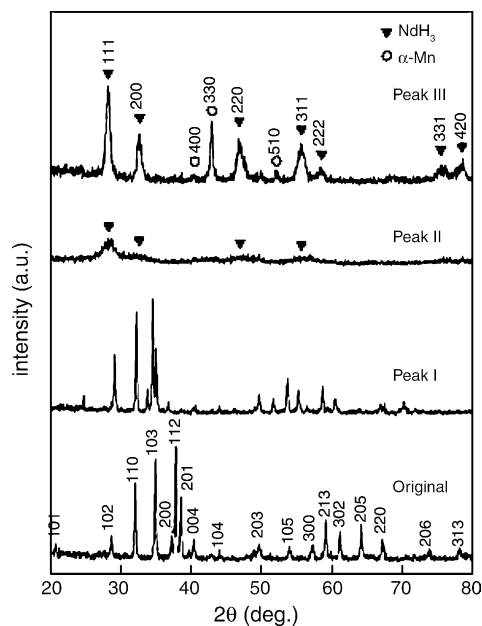
Fig. 3. XRD patterns of NdMn$_2$ heated to distinct temperatures in PDSC at 1.0 MPa H$_2$.

and the precipitation of Nd-hydride occur simultaneously at the second peak. However, the crystal structure of this Nd hydride cannot be identified, because its hydrogen content is unknown, although the total hydrogen content of this sample is 1.22 (H/M).

The XRD pattern of the sample heated to above the peak III (to 787 K) consists of α-Mn and the Nd hydride. Its Ar-DSC
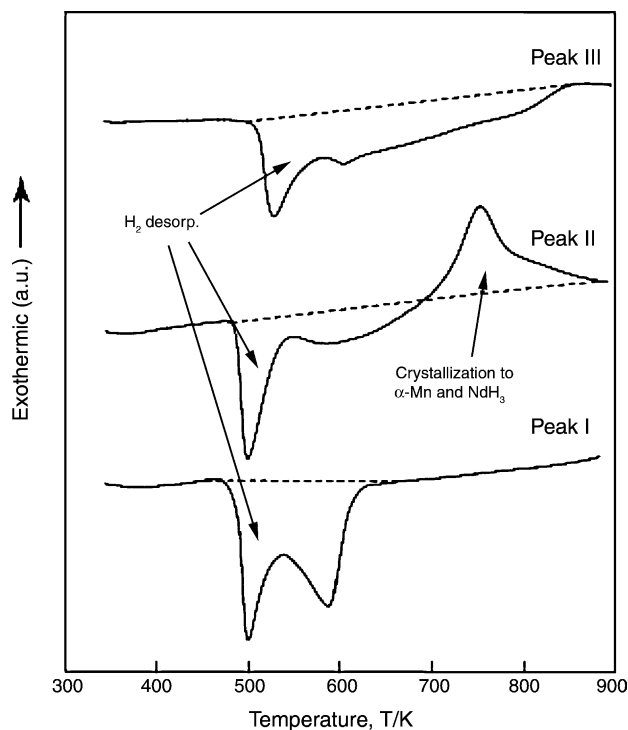


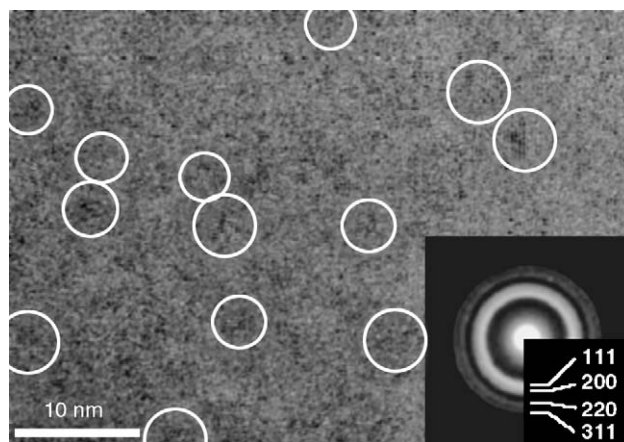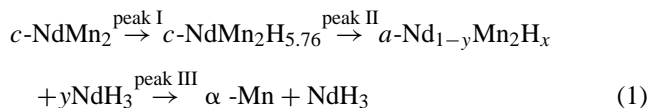Fig. 4. Ar-DSC curves of NdMn$_2$ heated to distinct temperatures in PDSC at 1.0 MPa H$_2$.



Fig. 5. Bright field image (BFI) and selected area electron diffraction pattern (SADP) of NdMn$_2$ heated above peak II in PDSC at 1.0 MPa H$_2$. The small crystalline BiF$_3$-type NdH$_3$ phases, surrounded by white circles, are embedded in amorphous matrix.

curve does not show any exothermic peak of crystallization indicating the absence of any amorphous hydride. Consequently, the third exothermic peak in the PDSC curve results from the decomposition of the amorphous hydride into α-Mn and Nd hydride.

We discuss the crystal structure of the Nd hydride that is formed by the precipitation in the amorphous hydride or the decomposition of it. The peak position of the Bragg peaks for CaF$_2$-type NdH$_2$ is same as that of BiF$_3$-type NdH$_3$, so that it is impossible to distinguish them by the XRD experiments. In both hydrides, Nd atoms occupy both the face center and cube corner sites in the f.c.c. structure. On the other hand, hydrogen atoms in CaF$_2$-type NdH$_2$ occupy the tetrahedral sites and those in BiF$_3$-type NdH$_3$ occupy the octahedral sites in addition to the tetrahedral sites. They are distinguishable by the hydrogen content. The hydrogen content of the sample heated above the peak III is 1.07 (H/M), i.e. 3.21 (H/Nd). Hydrogen is not dissolved in α-Mn, but dissolved in the Nd hydride. Consequently, the Nd hydride formed by heating above the peak III is BiF$_3$-type NdH$_3$. Similarly, the Nd hydride formed by precipitation in the amorphous hydride is considered to be BiF$_3$-type NdH$_3$. Same thermal reactions were observed between 0.1 and 1.0 MPa H$_2$. The reaction sequence of NdMn$_2$ heated at 0.1–1.0 MPa H$_2$ is expressed as follows:

$$c\text{-NdMn}_2 \overset{\text{peak I}}{\to} c\text{-NdMn}_2\text{H}_{5.76} \overset{\text{peak II}}{\to} a\text{-Nd}_{1-y}\text{Mn}_2\text{H}_x$$

$$+y\text{NdH}_3 \overset{\text{peak III}}{\to} \alpha\text{-Mn} + \text{NdH}_3 \qquad (1)$$

The crystalline hydride $c$-NdMn$_2$H$_x$ always changes to $c$-NdMn$_2$H$_x$ + NdH$_3$ at low hydrogen pressure regions.

Four exothermic peaks are observed in the PDSC curves measured above 2.0 MPa H$_2$. In our previous paper [11], the origin of these four exothermic peaks was determined as (1) hydrogen absorption in the crystalline state forming a crystalline hydride, (2) hydrogen-induced amorphization (HIA),
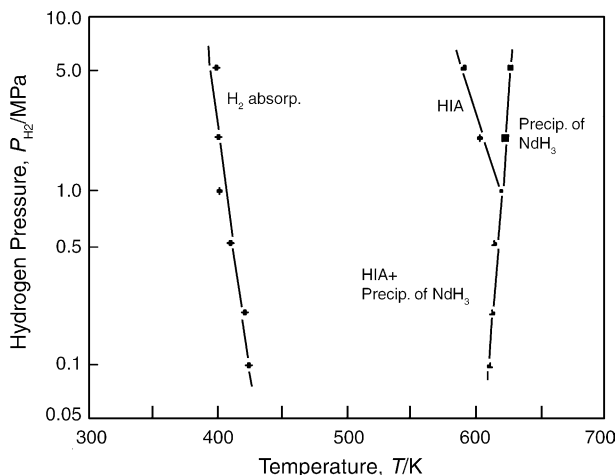
Fig. 6. A pressure dependence of peak temperatures for exothermic reactions of $NdMn_2$.

and nano-crystalline phases by the XRD pattern and SADP of TEM. The presence of the amorphous hydride above peak II below 1 MPa $H_2$ is for the first time confirmed by using a high resolution TEM.

The peak temperature for HIA of C14 Laves phase $NdMn_2$ and its pressure dependence are higher and smaller than those of C15 Laves phases $RM_2$. In the case of C15 $TbFe_2$, $ErFe_2$ and $DyFe_2$ [13–15], the peak temperature for HIA is changed widely with the hydrogen pressure. In addition, HIA occurs above the critical hydrogen pressure, i.e. the crystalline hydride decomposes into $\alpha$-Fe and $RH_3$ directly at lower pressures. On the other hand, the peak temperature for HIA of $DyCo_2$ is almost constant and amorphous single phase is formed at 0.1 MPa $H_2$ [16]. Thus, formation conditions of amorphous hydride vary with the alloy systems. We can also expect that it depends on the combination of R and M in C14 Laves structure. Further investigation is required in order to clarify the mechanisms and controlling factor of HIA in C14 Laves phases.

(3) the precipitation of $NdH_2$ in the amorphous hydride and (4) the decomposition of the remaining amorphous phase into $\alpha$-Mn and $NdH_2$. However, the Nd hydride formed by the precipitation or the decomposition is not $CaF_2$-type $NdH_2$, but is considered to be $BiF_3$-type $NdH_3$ as discussed above. The thermal reactions for $NdMn_2$ heated at 5.0 MPa $H_2$ are expressed as follows:

$$c\text{-}NdMn_2 \overset{\text{peak I}}{\rightarrow} c\text{-}NdMn_2H_{5.91} \overset{\text{peak II}}{\rightarrow} a\text{-}NdMn_2H_{3.87}$$

$$\overset{\text{peak III}}{\rightarrow} a\text{-}Nd_{1-y}Mn_2H_x + yNdH_3 \overset{\text{peak IV}}{\rightarrow} \alpha\text{-}Mn + NdH_3$$
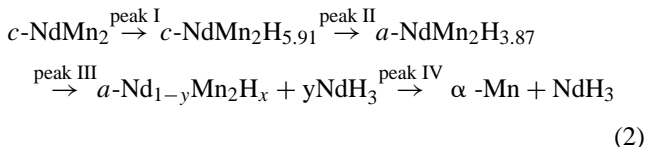
$$(2)$$

Fig. 6 shows the relation between the peak temperatures $T_p$ for the thermal reactions and the hydrogen pressure. $T_p$ for the decomposition of the remaining amorphous hydride into $\alpha$-Mn and $NdH_3$ is not plotted, because these exothermic peaks are too small to determine the peak temperature exactly. $T_p$ for both hydrogen absorption and HIA decrease with increasing hydrogen pressure, i.e. show the negative pressure dependence. On the contrary, that for the precipitation of $NdH_3$ shows the positive one. Furthermore, $T_p$ for the temperature where HIA and the precipitation of $NdH_3$ occur simultaneously also shows the slightly positive pressure dependence. The present work demonstrates that HIA of C14 Laves $NdMn_2$ occurs for every hydrogen pressure, although it has been reported $NdMn_2$ does not amorphize by hydrogenation at 0.14 MPa $H_2$ [12]. This discrepancy may be caused from experimental difficulties for the thermal analysis (PDSC) and structural identification (XRD and TEM). The sample weight is one of the most important factors for PDSC measurement. Detection of the exothermic peaks becomes impossible if not enough sample is used. While, the reaction sequence is abnormally proceeded by the rapid exothermic heat generated from the reaction between the sample and hydrogen, if the sample weight is too great, which gives the same result reported by Chung et al. Furthermore, it should be difficult to distinguish the co-existence of the amorphous

## 4. Summary

The pressure dependence of structural changes in C14 Laves phase $NdMn_2$ were investigated between 0.1 and 5.0 MPa $H_2$ by PDSC, XRD, TEM, Ar-DSC and a hydrogen analyzer. Three exothermic reactions, i.e. (1) hydrogen absorption in the crystalline state, (2) HIA and the precipitation of $NdH_3$ in the amorphous hydride, (3) the decomposition of remaining amorphous hydride into $\alpha$-Mn and $NdH_3$, occurred with increasing temperature between 0.1 and 1.0 MPa $H_2$. HIA and the precipitation of $NdH_3$ occur separately above 2.0 MPa $H_2$. The peak temperatures of the exothermic reactions of HIA and the precipitation of $NdH_3$ show negative and positive dependence to hydrogen pressure, respectively. The peak temperature for HIA of C14 Laves phase $NdMn_2$ and its pressure dependence are higher and smaller than those of C15 Laves $RFe_2$.

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