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Hydrogenation of Amorphous and Crystalline Gd-Co Alloys*

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Synopsis

Amorphous Gd-Co alloys were prepared over a wide composition range from 45 to 70 at % Gd by melt-quenching. These alloys absorbed a large amount of hydrogen in the amorphous state below 423 K. The hydrogen absorption capacity for the amorphous alloys was lower than that for the corresponding crystalline alloys and it increased with increasing Gd content in the alloy. The number of hydrogen atom absorbed per one gadolinium atom was approximately two with regardless to the alloy composition.

On the other hand, the Laves phase compound $GdCo_2$ was changed to an amorphous phase after reaction with hydrogen below about 700 K, among all of intermetallic compounds formed in Gd-Co system. This amorphous alloy did not show a pressure plateau in the pressure-composition isotherm, in the same manner as other melt-quenched amorphous alloys.

I. Introduction

It has been reported that the gadolinium-rich Gd-Co amorphous alloys prepared by melt- quenching exhibit remarkable magnetovolume effects such as a large thermal expansion anomaly [1] and a significant pressure dependence on the Curie temperature [2)3)]. In the crystalline alloys, moreover, it has been found that the magnetovolume effect is very sensitive to hydrogen [4] . From this point of view it is interesting to know the effect of hydrogen on the magnetovolume effect in amorphous state.

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In recent the present authors have found that the Laves phase compound $SmNi_2$ becomes amorphous by hydrogenation [5]. From subsequent works, we have known that an amorphous phase can be synthesized by hydrogenation of $RENi_2$ type alloys including $GdCo_2$. The aims of the present work are twofold; the first is to make clear the hydrogen absorption behavior of melt- quenched Gd-Co amorphous alloys and the second is to examine the structural change of the crystalline Gd-Co alloys by hydrogenation treatment. A basic information on the hydrogen absorption behavior of the amorphous and crystalline Gd-Co alloys are described in the present paper. The results of the effect of hydrogen on the magnetization and the Curie temperature of the amorphous Gd-Co alloys are also presented in another paper[6].

II. Experimental

Gd-Co mother alloys were prepared from pure metals [Gd(99.9%) and Co(99.95%)] by arc melting under an argon atmosphere. These mother alloys were rapidly quenched using a single roller-type melt-quenching apparatus under an argon atmosphere. The quenched samples obtained were in the form of ribbon with 0.02-0.03 mm thick and 1-2 mm wide. Structures of the as-quenched samples were identified by X-ray diffraction using Cu- K_α radiation in combination with an X-ray monochromator. The crystallization temperature, T_x, of the amorphous samples was determined with a differential scanning calorimeter(DSC) at the heating rate of 40 K/min or with a differential thermal analyzer(DTA) at the heating rate of 10 K/min. The hydrogenation treatment was conducted in a constant temperature reactor. Pulverized amorphous and crystalline samples were exposed to high pure hydrogen (7N) of 5 MPa in a stainless steel reactor. The amount of hydrogen absorbed was determined from the pressure drop in the known volume reactor. The structures of the hydrogenated samples were examined with the X-ray diffractomator.

III. Results and discussion

1. Formation range of the melt-quenched amorphous phase and its crystallization temperature

Prior to hydrogen absorption experiment, the composition range of amorphous phase formed by melt-quenching was examined. The structures of as-quenched Gd-Co samples are displayed on the

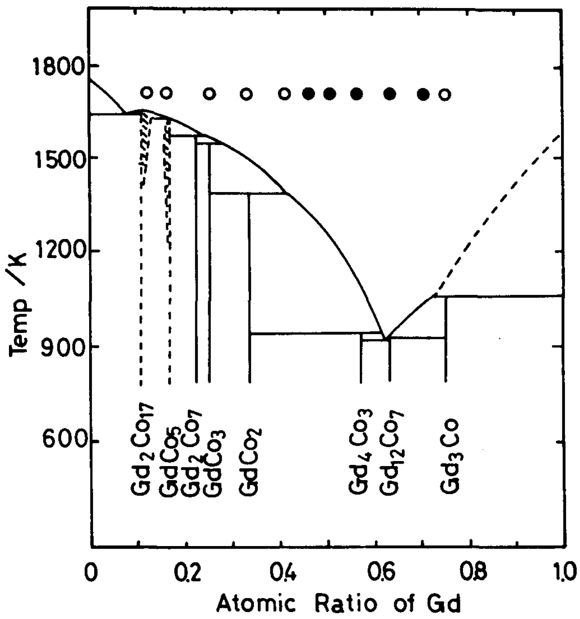

Fig. 1 The structure of Gd-Co samples obtained by melt-quenching. Closed circle shows the amorphous phase and open circle the crystalline phase.

equilibrium phase diagram[7] shown in Fig.1. It can be seen from this figure that the amorphous phase is obtained over a composition range from 45 to 70 at % Gd in Gd-rich alloys around the eutectic point, where includes two intermetallic compounds corresponding to Gd_4Co_3 and $Gd_{12}Co_7$. These amorphous samples were so brittle that could not be bent in contrast to usual melt- quenched amorphous ribbons.

Representative DSC curves for amorphous Gd-Co ribbons are shown in Fig. 2. As seen from the figure, a well defined exothermic peak is observed around 600 K. In addition to the exothermic crystallization peak, an endothermic peak due to the glass transition is also clearly observed in the amorphous $Gd_{60}Co_{40}$ alloy and its transition temperature, T_g is 563 K. From the DSC curves, the crystallization temperature,T_x is determined and is shown as a function of alloy compositions in Fig. 3. In the present work, T_x was defined as the temperature corresponding to the intersection of the extrapolated base line and the steepest tangent of the first exothermic peak. As seen from this figure, T_x is in the temperature range of 561-581 K, showing a slight composition dependence.

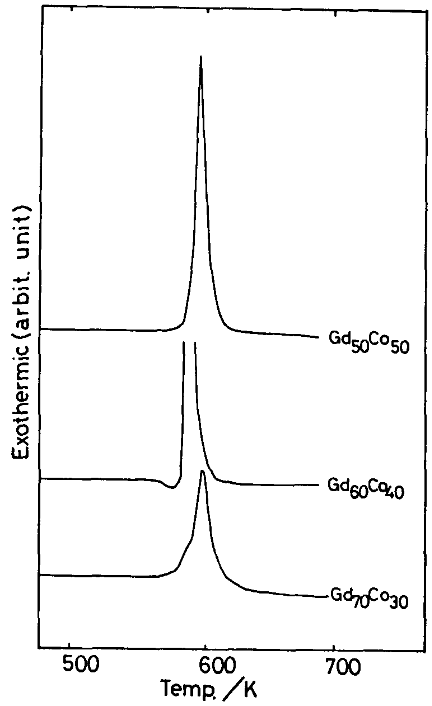

Fig. 2 DSC curves for melt-quenched Gd-Co amorphous alloys.

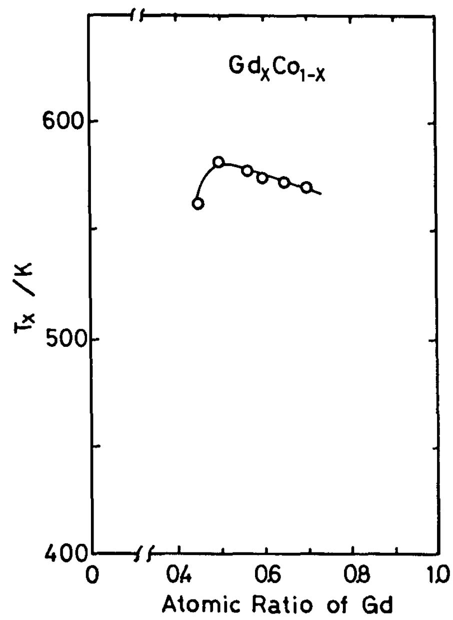

Fig.3 Crystallization temperature of Gd-Co amorphous alloys.

2. Structural changes during hydrogenation

(i) Hydrogen absorption and thermal stability of amorphous Gd-Co alloys

X-ray diffraction (XRD) patterns of the as-quenched amorphous(a-) and hydrogenated a-$Gd_{50}Co_{50}$ alloys at different temperatures are shown in Fig. 4. The intensity profile of the sample hydrogenated at 373 K is similar to that of the as-quenched one and characterized by broad peaks which are typically observed in many other amorphous alloys. However, the peak position of the hydrogenated sample shifts towards lower angle side, indicating a volume expansion induced by hydrogenation. After hydrogenation at 473 K, several crystalline peaks of gadolinium hydride, GdH_2 superimpose on the broad peak and they become sharper with increasing temperature. At temperatures higher than 523 K, the peaks of an unknown crystalline phase appear in addition to those of the hydride GdH_2. Namely the amorphous phase of $Gd_{50}Co_{50}$ decomposes finaly into two phases after hydrogenation treatment.

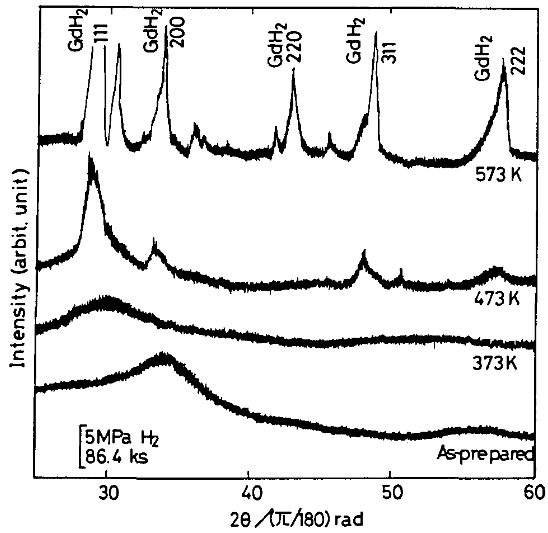

Fig.4 X-ray diffraction patterns of the amorphous $Gd_{50}Co_{50}$ alloy hydrogenated at various temperatures for 86.4 ks under hydrogen pressure of 5 MPa.

Figure 5 shows the phase identified by X-ray diffraction for various amorphous Gd-Co alloys as a function of the hydrogenation temperature. In this figure, it is seen that all the alloys keep the amorphous state by hydogenation at low temperatures below 423 K and above 473 K the gadolinium hydride is formed in amorphous phase.

(ii) Formation of amorphous phase in crystalline Gd-Co alloys by hydrogenation

It has been found that the Laves phase compound $GdNi_2$ with the $MgCu_2$ type structure becomes amorphous by hydrogenation[8). Since the $GdCo_2$ phase has also the $MgCu_2$ type structure, it is interesting to examine whether the $GdCo_2$ phase becomes amorphous or not by hydrogenation. Figure 6 shows XRD patterns of the $GdCo_2$ phase hydrogenated at different temperatures. The XRD pattern of the arc-melted sample indicates that this alloy consists of $GdCo_2$ compound with the $MgCu_2$ structure. In the XRD pattern of the sample hydrogenated at 523 K, however, these sharp peaks of $GdCo_2$ disappear and only a broad peak is observed. At hydrogenation temperatures higher than 723 K, diffraction peaks corresponding to the GdH_2 phase appear overlapping with a broad peak. Among eight intermetallic compounds formed in the Gd-Co alloy system, only the $GdCo_2$ alloy shows the formation of amorphous phase by hydrogenation.

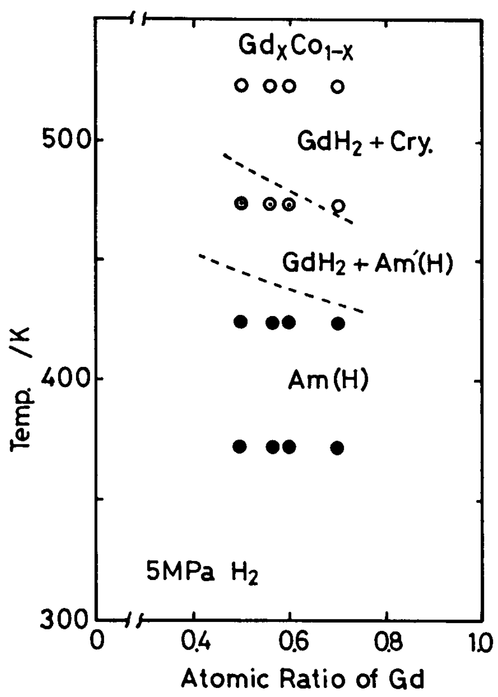

Fig. 5 Structure of amorphous Gd-Co alloys hydrogenated at various temperatures for 86.4 ks under hydrogen pressure of 5 MPa.

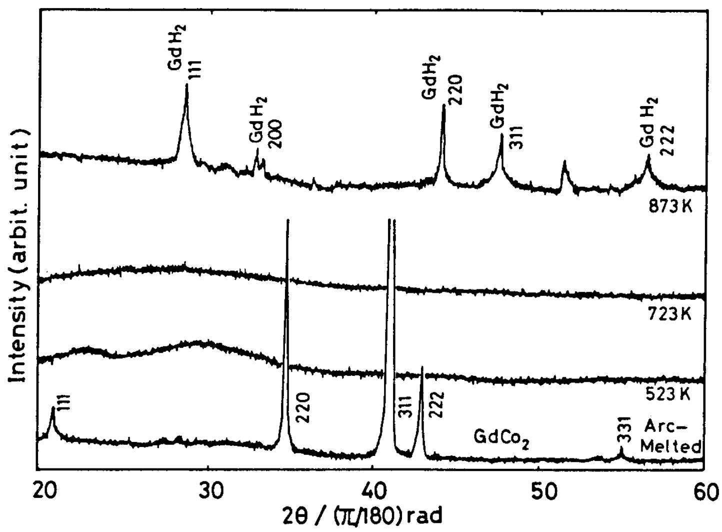

Fig. 6 X-ray diffraction patterns of the crystalline $GdCo_2$ alloys hydrogenated for 86.4 ks at various temperatures.

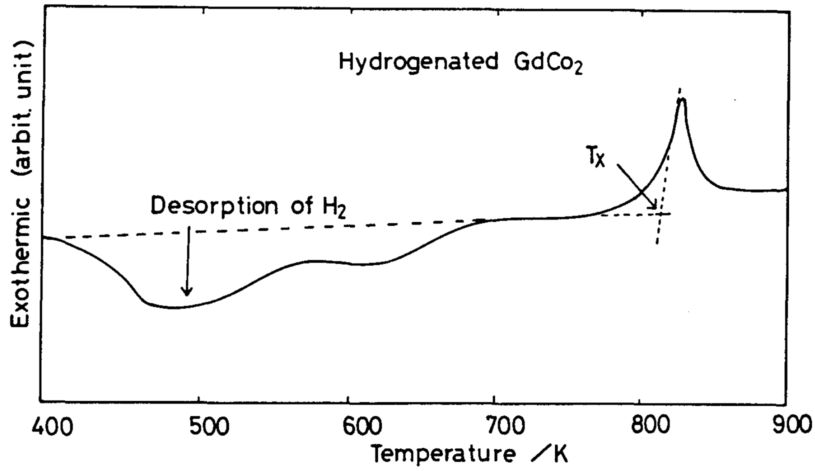

Fig. 7 DTA curve for the hydrogenated $GdCo_2$ alloy.

Figure 7 shows DTA curve of the amorphous phase for the hydrogenated $GdCo_2$ alloy. The curve exhibits a single exothermic peak around 820 K and a broad endothermic peak around 450-700 K. From XRD and DTA data, it can be said that the former peak is induced by crystallization of the amorphous phase and the later one by desorption of hydrogen from the amorphous phase. Thus, the $GdCo_2$ Laves phase also becomes amorphous by hydrogenation.

3. PC isotherm of the $GdCo_2$ alloy

It has been reported that the melt-quenched amorphous alloys do not show any pressure plateau on the pressure-composition isotherm [9)-11)], because no hydride is formed. In the present work, the pressure - composition isotherm for the amorphous alloy synthesized by hydrogenation was examined. The pressure-composition isotherm for the crystalline $GdCo_2$ alloy at 323 K is shown in Fig. 8, where the equilibrium hydrogen pressure is plotted against hydrogen concentration, which is expressed as the number of hydrogen atom per one metal atom (H/M). The hydrogen pressure is found to increase continuously with hydrogen concentration uncompanying with any pressure plateau. Such a phenomenon is in the same manner as other melt-quenched amorphous alloys[11)]. This means that no hydride is formed in the $GdCo_2$ -H system.

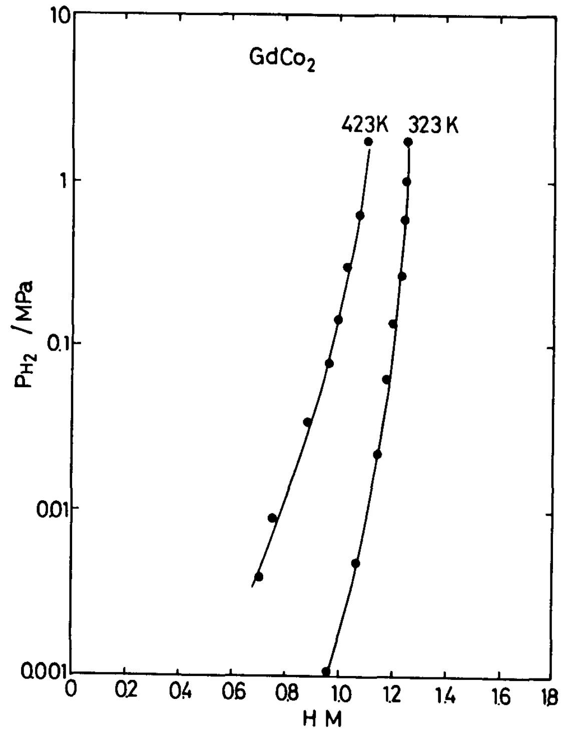

Fig. 8 Pressure-composition isotherm for $GdCo_2$ alloy.

4. Hydrogen absorption capacity

In Fig. 9, hydrogen absorption capacity, M_H , defined as the maximum hydrogen content, is plotted against Gd content for amorphous and crystalline Gd-Co alloys. It is clear that the M_H values of the crystalline Gd-Co alloys irregulary change with the alloy composition and the crystal structures. On the other hnad, the M_H values for the amorphous alloys increase with increasing gadolinium content, and are distributed along the dotted line shown H/Gd = 2. This result indicates that the number of hydrogen atom absorbed per one atom of gadolinium is approximately two, independining on the alloy composition. It is known that gadolinium metal forms dihydride GdH_2 . Consequently, it is suggested that the hydrogen absorption capacity of amorphous Gd-Co alloys depends mainly on the number of the hidride-forming gadolinium metal in the alloy. Such results have also been reported by the present authors in other amorphous alloys such as Ti-Ni, Zr-Ni and Hf-Ni systems[9)-11)].

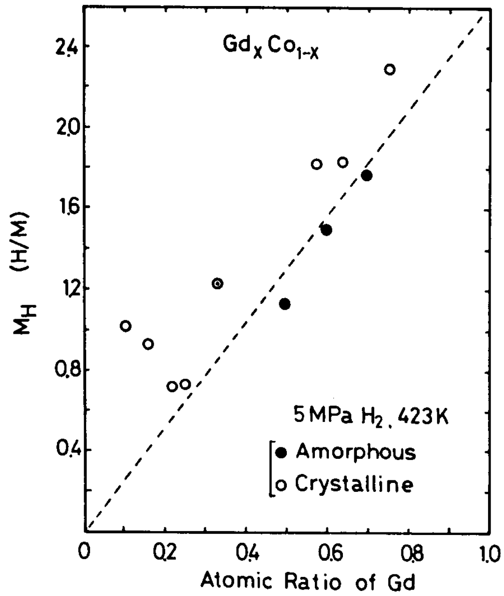

Fig. 9 Composition dependence of hydrogen absorption capacity M_H of amorphous and crystalline Gd-Co alloys hydrogenated at 423 K under hydrogen pressure of 5 MPa.

IV. Summary

Various Gd-Co alloys were rapidly quenched from the melt in an argon atmosphere. Amorphous alloys were obtained in the composition range from 45 to 70 at % Gd. These amorphous alloys absorbed a large amount of hydrogen in the amorphous state below 423 K. On the other hand, the Laves phase compound, $GdCo_2$ became amorphous by hydrogenation below about 700 K. The pressure-composition isotherm of this alloy did not show a pressure plateau in the same manner as the other melt-quenched amorphous alloys. The hydrogen absorption capacity of amorphous alloys was lower than that of the crystalline counterparts, it increased with increasing gadolinium content and approximately two hydrogen atoms were absorbed per gadolinium atom.

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