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Low temperature formation of MgH_2 in $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}/Mg$

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Abstract

We have investigated the hydriding properties and microstructures of the new composite material $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}/Mg$ which contains elemental Mg as a binder. The hydriding properties of the host compound are improved owing to the Mg reduction effect in the process of heat treatment. In addition, we observed that in the process of heat treatment the Cu in the host compound $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ diffuses into the Mg region and Mg_2Cu is formed. After hydriding and dehydriding cycles, hydrogen in the host compound diffuses into the Mg region through the Mg_2Cu phase. Consequently, MgH_2 is formed even at temperatures below 373 K under hydrogen pressures of less than 1 MPa.

1. Introduction

In connection with environmental pollution problems, much attention has been paid recently to metal hydrides, which can be used as materials for hydrogen heat pumps, hydrogen batteries, hydrogen and thermal storage and hydrogen compressors. One of the severe problems to be resolved is the breaking down of the materials into a very fine powder upon hydrogenation, which leads to poor thermal conductivity and also contamination of equipment. Incorporation of the hydride into a composite form can help to solve or mitigate the above problem. The possibility of producing composite metal hydride compacts was first suggested by Ron in 1976 [1]. In his paper metallic Mg was considered as a suitable highly porous metallic matrix to be used for improving thermal conductivity.

In previous papers [2, 3] we reported the following experimental results.

(1) A new composite material for hydrogen storage in which $ZrFe_{1.4}Cr_{0.6}$ is the host storage material (host compound) and Mg is the metallic binder was developed.

(2) In the process of heat treatment of this composite pellet, oxygen in the host compound (especially on the surface) diffuses into the Mg region. This so-called Mg reduction makes the surface of the host compound clean.

(3) The Mg reduction therefore helps to form another composite (solid solution) phase at the interface between the host compound and Mg.

(4) Because of these effects, the hydriding rate and cyclic durability of the host compound can be improved without any change in its pressure–composition isotherms.

We are now continuing investigations to apply this method to other storage materials and the same effective influence on hydrogen storage properties is expected. In this paper we selected the $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ system as the host hydrogen storage compound, which is based on the $TiMn_2$ (C14 Laves) structure. It has been reported [4–6] that Zr substitution for Ti lowers the equilibrium pressure and that Cr substitution for Mn narrows the hysteresis width. Cu addition flattens the plateau region.

In the composite material $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}/Mg$ a more dramatic improvement in hydriding properties was found than before, which cannot be easily predicted from the previous results on $ZrFe_{1.4}Cr_{0.6}/Mg$.

We would like to emphasize that MgH_2 is formed by hydriding $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}/Mg$ at temperatures below 373 K. This phenomenon was not found in the previously studied material. Therefore it is concluded that the Cu in the host compound (partially existing in the form of Mg_2Cu at host–Mg interface after treatment) plays some important role on the diffusion of hydrogen from the host compound region into the Mg region.

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As is well known, the MgH_2 phase can be effectively formed only at temperatures higher than 473 K. Many attempts have been made to improve the reaction of Mg and Mg-based alloys with hydrogen [7, 8]. Several researchers have succeeded in getting Mg to react with hydrogen at temperatures below 473 K (in some cases the reaction occurring at around room temperature or below) using *e.g.* chemical treatments of the surface of Mg-containing materials [9–17], Pd coatings on Mg [18–20], evaporation of Mg onto PdH_x substrates [21] and composite materials of Mg with other hydrides [22].

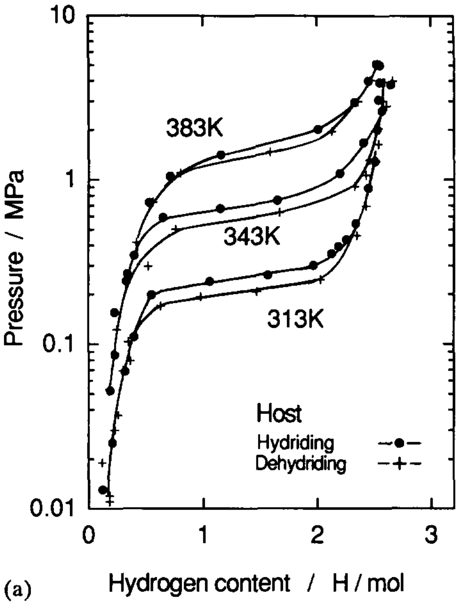
Compared with these attempts, our method using the composite technique seems to be relatively simple. In this paper we mainly describe the formation of MgH_2 under such a moderate condition.

2. Experimental procedures

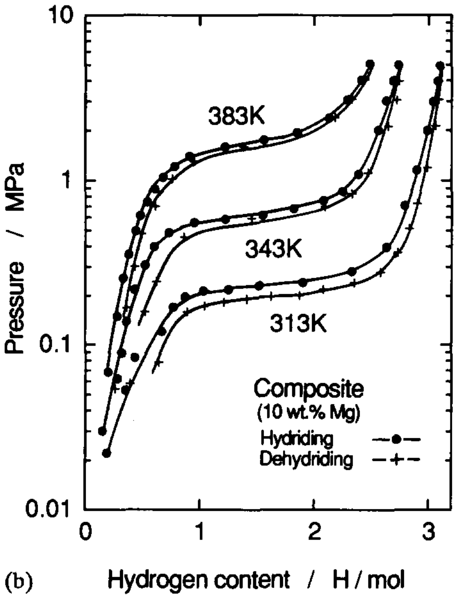
The host compound $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ was prepared by r.f. melting of stoichiometric amounts of the elements of 99.9% purity under an Ar atmosphere and then pulverized into powder of diameter less than 200 μm. The powdered sample was mixed with fixed amounts of Mg powder (10 and 20 wt.% of the composite material) of diameter less than 1 mm and hot isostatically pressed (HIPped) under an Ar gas pressure of 100 MPa at 973 K for 0.5 h. Finally it was sintered at 773 K for 2 h under an Ar gas pressure of 0.2–0.3 MPa.

The pressure–composition isotherms of the samples obtained were determined using a standard Sieverts apparatus. The hydriding rate was measured using a pressure-induced process in which the hydrogen pressure was changed from 1.0 Pa to 1.0 MPa at a constant temperature of 313 K. The cyclic durability was tested using a thermally induced process in which the temperature was changed from 373 K to room temperature and back to 373 K again in 0.5 h under a hydrogen pressure of 1.0 MPa. Using this process, hydriding and dehydriding were repeated for 500 cycles.

The samples thus tested were then characterized by X-ray diffraction and the electron probe microanalysis (EPMA) line profile method.



(a)



(b)

Fig. 1. Pressure–composition isotherms of hydriding and dehydriding processes for (a) $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ and (b) its composite with 10 wt.% Mg after heat treatment. Here it is assumed that Mg absorbs no hydrogen and only acts as a binder.

3. Hydriding properties

3.1. Pressure–composition isotherms

Figures 1(a) and 1(b) show the pressure–composition isotherms for the hydriding and dehydriding processes for the host compound and the composite material with 10 wt.% Mg respectively after the heat treatment described above. The equilibrium pressure and the width of the hysteresis are almost the same except for the width of the plateau region. We can see a slight increase (about 20%) in hydrogen uptake in the composite material compared with the host compound.

From these figures the changes in enthalpy, ΔH, and entropy, ΔS, due to hydride formation were evaluated according to the van't Hoff equation. The values are listed in Table 1 for the host compound and the composite material with 10 wt.% Mg. The data for the host and composite are close to each other.

TABLE 1. Values of enthalpy ΔH and entropy ΔS

	Host	Composite (10 wt.% Mg)
$-\Delta H$ (kJ (mol H_2)$^{-1}$)	27.1	28.0
$-\Delta S$ (J (mol H_2)$^{-1}$)	93.5	95.8

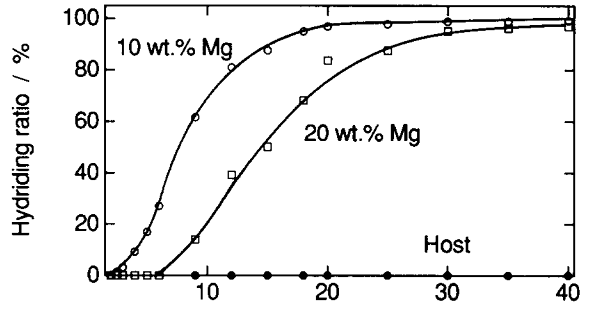


Fig. 2. Initial hydriding ratio at 313 K under 1 MPa hydrogen pressure as a function of time for $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ (practically the horizontal axis) and its composites with 10 and 20 wt.% Mg after heat treatment.

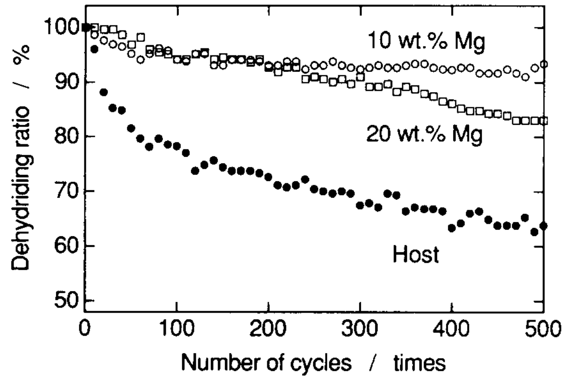


Fig. 3. Dehydriding capacity as a function of number of hydriding and dehydriding cycles for $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ and its composites with 10 and 20 wt.% Mg after heat treatment.

3.2. *Kinetic characteristics and cyclic durabilities*

Figure 2 shows the initial hydriding ratio as a function of time at a temperature of 313 K under a hydrogen pressure of 1 MPa. The host compound hardly reacts with hydrogen without special activation treatment. In contrast, the composite materials with 10 and 20 wt.% Mg content can readily react with hydrogen.

The dehydriding capacities of the host and composites are shown in Fig. 3 as a function of the number of hydriding and dehydriding cycles. The capacity of the host compound without Mg decreases with increasing number of cycles and reaches 60% of the initial dehydriding capacity after applying 500 cycles, while the capacities of the Mg composites retain more than 80%–90%.

4. Microanalysis

4.1. *Before hydriding*

In Fig. 4(a) the X-ray diffraction pattern before hydriding at room temperature is shown for the composite material containing 20 wt.% Mg. This pattern consists of three sets of peaks. The two main sets of peaks correspond to the phases of $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ (C14 Laves, hexagonal) and Mg (h.c.p.). In addition to these peaks, there are several other peaks corresponding to the Mg_2Cu phase which was formed in the process of heat treatment.

To clarify the local composition around the interface between the host compound and the Mg region, we examined the EPMA line profiles for all the elements along the direction perpendicular to the interface. In Fig. 5 the intensities of the EPMA line profiles corresponding to the Ti, Cu and Mg components are shown as representatives, the profiles of other components such as Zr, Mn and Cr being almost the same as that of the Ti component. However, only Cu diffuses into the Mg region and then accumulates in that region close to the interface. This result corresponds to the formation of Mg_2Cu due to the diffusion reaction of Cu as seen in Fig. 4(a).

4.2. *After hydriding*

Figure 4(b) shows the X-ray diffraction pattern of the 20 wt.% composite material after hydriding. The peaks corresponding to $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$ shift to lower angles than those in Fig. 4(a), indicating the

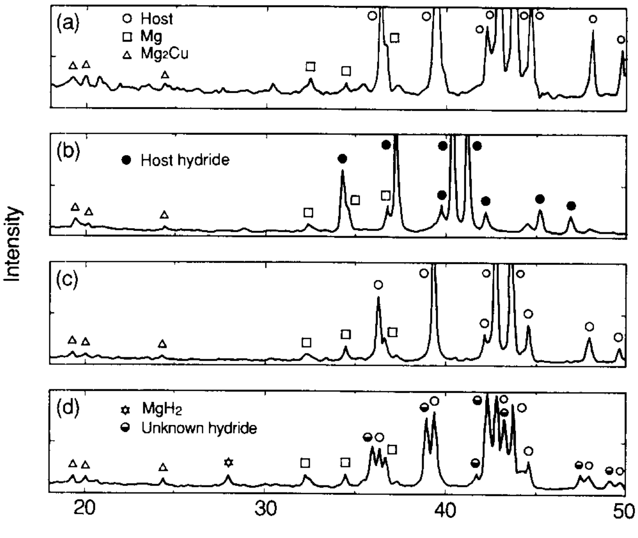


Fig. 4. Room temperature Cu Kα X-ray diffraction patterns of heat-treated $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}/Mg$ (20 wt.%) composite (a) before hydriding, (b) after initial hydriding without degassing treatment, (c) after five hydriding and dehydriding cycles with degassing treatment and (d) after 500 cycles with degassing treatment.

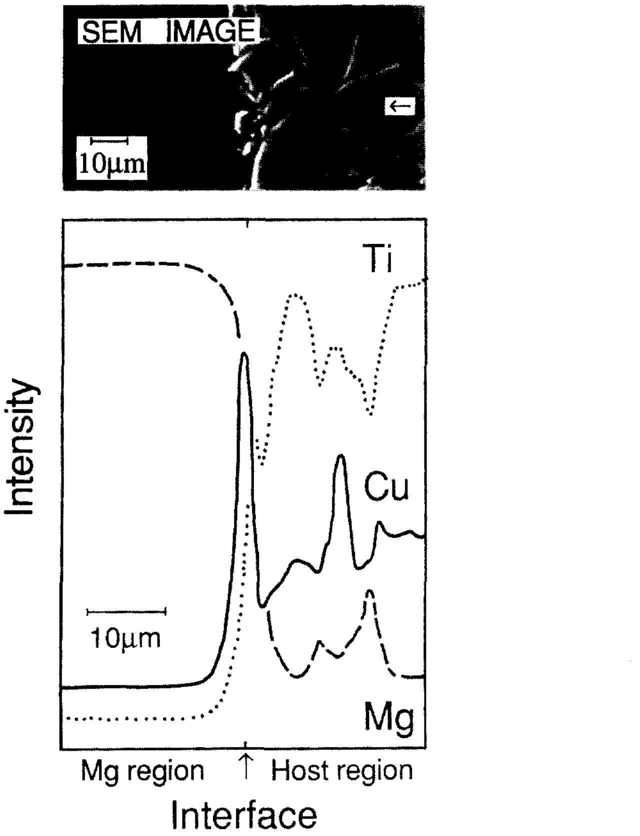


Fig. 5. EPMA line profiles for $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}/Mg$ (20 wt.%) composite after heating treatment (the arrow in the image shows the position of line profiling).

formation of $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}H_3$. The other phases, Mg and Mg_2Cu formed *in situ* in the process of heat treatment, did not change at all during the hydriding process.

After increasing the number of cycles, we again took X-ray diffraction patterns and these are shown in Figs. 4(c) and 4(d). The pattern in Fig. 4(c) is from the composite material after degassing in a vacuum of less than 1.0 Pa for 12 h at room temperature after five hydriding and dehydriding cycles. This pattern looks almost the same as the pattern in Fig. 4(a). In contrast, the degassed pattern in Fig. 4(d), obtained after 500 hydriding and dehydriding cycles, contains two different phases compared with the composite material before hydriding shown in Fig. 4(a). One of the two is a hydride phase related to segregation into a more stable hydride such as a Zr-based alloy hydride, while the other is the MgH_2 phase.

Generally MgH_2 can be effectively formed only at temperatures higher than 473 K. In this work, however, we found that MgH_2 is formed in the composite materials even below 373 K.

5. Discussion

We mainly discuss here the formation process of the MgH_2 phase below 373 K.

The existence of the Mg_2Cu phase is essential for the formation of the MgH_2 phase at low temperature as described above, because there is little indication of the formation of MgH_2 in $ZrFe_{1.4}Cr_{0.6}/Mg$ [2, 3] or $Ti_{0.6}Zr_{0.4}Mn_{0.8}Cr/Mg$ (the composite material containing the host compound without Cu).

In general the reaction of Mg_2Cu with hydrogen at higher temperatures of around 550 K seems to proceed in two ways as follows [7, 23, 24]:

$$2Mg_2Cu + 3H_2 \longrightarrow 3MgH_2 + MgCu_2 \qquad (1)$$

$$Mg_2Cu + 2H_2 \longrightarrow 2MgH_2 + Cu \qquad (2)$$

However, we cannot see the $MgCu_2$ and Cu phases in Fig. 4(d) at all. In addition, the peaks corresponding to Mg_2Cu do not decrease with increasing MgH_2 peak intensity. These results indicate that the Mg in MgH_2 does not originate from the decomposition of Mg_2Cu but from pure Mg metal, which does not react with Cu yet. Also, it is not impossible to express the formation of MgH_2 by the following reaction:

$$Mg_2CuH_4 + 2Mg \longrightarrow Mg_2Cu + 2MgH_2 \qquad (3)$$

However, a hydride phase of Mg_2Cu (such as Mg_2CuH_4) is not stable compared with reaction (1) from a thermodynamic point of view [24]. Therefore a process according to reaction (3) is rather unlikely.

Finally, one might think about the formation of the hydrogen solution phase of Mg_2Cu (α phase). In the case of Mg_2Ni the α phase is easily formed at temperatures of around 373 K within only a few minutes [25]. Although the α phase of Mg_2Cu is less stable than that of Mg_2Ni on the basis of the affinities of Cu and Ni with hydrogen, we consider that the α phase is possibly also formed in the case of Mg_2Cu. Other authors have reported that MgH_2 could be formed by a catalysing effect of Mg_2Cu at temperatures higher than 573 K [26, 27]. Judging from their results, we conclude that the α phase of Mg_2Cu can also be formed.

Assuming that the α phase of Mg_2Cu, *i.e.* Mg_2CuH_x ($x < 0.3$), is stabilized, we can understand the formation of MgH_2 as follows:

$$2Mg_2CuH_x + 2Mg \longrightarrow (2-x)Mg + 2Mg_2Cu + xMgH_2 \qquad (4)$$

In this case the Mg_2CuH_x phase on the left-hand side is easily changed into the Mg_2Cu phase on the right-hand side of reaction (4) with the formation of MgH_2 and this reaction can explain the result of the X-ray diffraction pattern in Fig. 4(d).

It is necessary to know the source of supply of the hydrogen which forms the hydrogen solution phase Mg_2CuH_x and then forms MgH_2. It is assumed that the hydrogen is supplied by the host compound hydride phase $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}H_3$ by interdiffusion of hydrogen as discussed in refs. 19–21. The composite material Mg_2Cu/Mg without the host compound, which is formed in the process of heat treatment, is not considered to form the MgH_2 phase after the hydriding treatment at temperatures below 373 K. This supports the assumption that the hydrogen is supplied by the hydride $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}H_3$.

The reaction or formation process of MgH_2 by hydrogen from the hydride compound in the composite materials is important for potential applications of Mg-based metal hydrides around room temperature. In the composite materials used in this work the reaction or forming speed is relatively slow. Hence we are now investigating the reaction process by adjusting the composition and controlling the conditions of heat treatment, as well as ensuring the formation of the MgH_2 phase within 10 hydriding and dehydriding cycles.

6. Conclusions

The hydriding properties and microstructures of the new composite material $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}$/Mg were investigated. It was found that the hydriding properties of the host compound are improved and the MgH_2 phase is formed even at temperatures below 373 K. We conclude that the formation of the Mg_2Cu phase and the diffusion of hydrogen supplied by the hydride phase of the host compound are essential for the formation of the MgH_2 phase.

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