論　文

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High Pressure Thermal Analysis of the Reaction between Magnesium-Nickel Alloys and Hydrogen

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A newly developed high pressure thermal analysis installation was used for the investigation of the hydrogen-sorbing characteristics of the Mg-Ni alloy. This apparatus made possible to measure DTA and TG curves simultaneously under hydrogen pressures up to 50 kgf cm^{-2}. Pressure-composition isotherms for the Mg_2Ni-H_2 system were obtained by isothermal measurements. The isobaric thermal cycling experiments revealed a shift of the initiation temperature for the desorption which corresponded to the activation process of powdered samples from "deactivated" state by having been exposed in air to "activated" state.

1. Introduction

Extensive investigations have been carried out on metal hydrides since these materials are proposed as hydrogen or heat storage media, and several ternary hydrides such as $LaNi_5H_6$ or $FeTiH_2$ have been developed and received great attention.[1,2] Although these hydrides have very attractive hydrogen sorption characteristics for many applications, none of them is able to meet all the requirements for a given specific application. The most serious problems are low hydrogen content and high cost of metallic materials. Magnesium hydride shows great advantages in both of these two factors, since it contains more than 7 weight percent hydrogen and is cheap. It, however, has some obvious disadvantages, too. It shows low hydrogen dissociation pressure (1 atm at 290°C), and needs to be heated over 300°C for the hydrogen desorption. The rate of the reaction between pure magnesium and hydrogen is too slow to be practically used. Nickel addition has been shown to improve the kinetics markedly.[3,4] The magnesium-nickel alloy is one of the most attractive materials for practical applications.

The thermodynamic properties and kinetics for the metallic material and hydrogen system have usually been investigated by the volumetric techniques as reported in a paper of Reilly and Wiswall.[5] In the present experiments, a new high pressure thermal analysis installation was used for the investigation of the hydrogen sorption characteristics of the Mg-Ni alloy. This apparatus can make DTA and TG measurements simultaneously under high pressures of hydrogen and give a number of important hydrogen sorbing characteristics at the same time in a short period.

On the Mg-Ni alloy and hydrogen system, an interesting information was obtained in the present experiments about its deactivation process when exposed in air and activation process by evacuating at high temperatures.

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2. Experimental

2.1 Apparatus

Figure 1 shows a schematic representation of the Rigaku high pressure TA (thermal analysis) installation designed for simultaneous measurements of DTA and TG under hydrogen pressures up to 50 kgf cm^{-2} in the range from ambient temperature to 600°C.

A differential microbalance was used in order to cancel the bouyancy effect. The maximum weighing capacity is 5 g and the sensitivity is 5 μg. The sample and reference holders are set in an electric furnace with molybdenum heating elements. All of these equipments are placed in a high pressure chamber whose inner volume is made of sintered

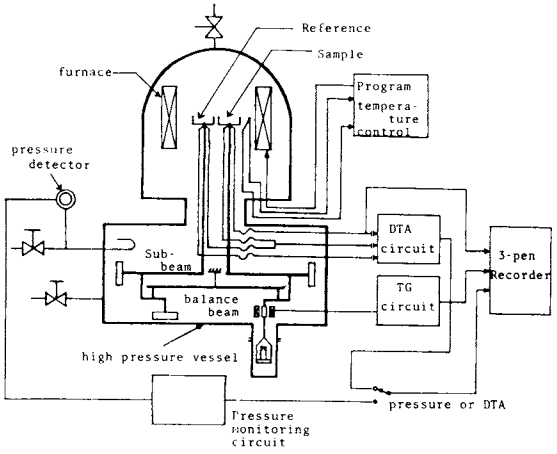

Fig. 1. Schematic of the high pressure thermal analysis installation.

stainless steel, 12 mm in outside diameter, and 20 mm in height, weighing about 10 g. The same type of holder is used for the reference cell with no specimen.

The temperature controlling unit permits operation at constant temperature and under thermal cycling between pre-set temperatures. The heating rate can be varied between 0.624 and 20°C min^{-1}, but the cooling rate is limited at low temperatures since no compulsory cooling system is provided except a water cooling jacket fitted on the inside wall of the chamber. Below 100°C, therefore, the cooling rate of 5°C min^{-1} is difficult to attain.

Measurements can be made at constant pressure or by pressure scanning. A strain gauge pressure transducer is used for pressure measurements up to 50 kg cm^{-2} with overall precision of 0.5%. Pressure scanning speed has to be controlled manually by two needle valves attached to the hydrogen lines to and from the chamber.

2.2 Materials

Magnesium-nickel alloys were prepared by Furukawa Magnesium Co. by melting magnesium and nickel in predetermined proportions in graphite crucible heated with propane gas burner and pouring the melt into molds. The analytical results of impurities in the two of the alloys are listed in Table 1. The alloys were confirmed to be mixtures of Mg and Mg_2Ni phases by conventional X-ray powder diffraction technique.

Table 1. Analytycal results of Mg-Ni alloys

sample	component: weight fraction, %			
	Ni	Pb	Zn	Fe
Mg/10%Ni	9.8	0.011	0.04	0.012
Mg_2Ni	54.6	0.002	0.013	0.42

2.3 Procedures

The first activation or hydriding of the Mg-Ni alloys was not performed in the TA apparatus but in the usual high pressure microreactor of about 30 cm^3 inner volume.

The alloy was filed to a particle size of less than 0.5 mm thickness. The filed alloy, weighing about 10 g, was put in the microreactor. After degassing at 350°C for 2 hours, hydrogen was introduced into the reactor up to pressure of 50 kgf cm^{-2} and the alloy was hydrided at this pressure and temperature for about 10 hours. The hydrogen absorption proceeded gradually during this period.

Dehydriding was performed by degassing at 350°C for 2–4 hours. This hydriding-dehydriding treatment was repeated several times in order to get a completely activated sample. Finally the hydrided sample was taken out into air. They were brown or black fine powders. Their specific surface areas were measured by the conventional BET method as 1–4 m^2 g^{-1}. These hydrides in powdered form were weighed in a sample cell of the TA apparatus for various measurements described in the following.

3. Results and discussion

3.1 Pressure-composition isotherm measurements

P-C (pressure-composition) isotherms have been conveniently used to describe thermodynamic properties of a given metal-hydrogen system. Such *P-C* isotherms have been usually obtained by the volumetric technique.[5] This method, however, takes too much time and has a risk to get a fatal error by any leakage during run. In the present experiment, our TA apparatus was used for *P-C* isotherm measurements of the Mg_2Ni-H_2 system.

About 600 mg of the sample was completely activated by being subjected to several hydriding-dehydriding reaction cycles before *P-C* isotherms were measured. Measurements were made only at two levels of temperatures, 320 and 350°C, and the pressure scanning speed was 0.14 kgf cm^{-2} min^{-1}. The results are shown in Fig. 2.

The initiation of the reaction is abrupt as can be

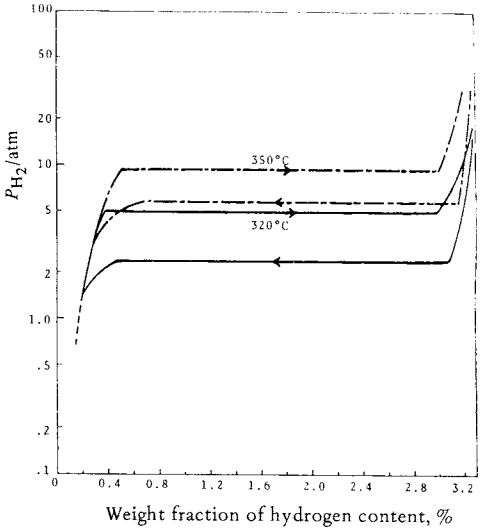

Fig. 2. *P-C* isotherms for the Mg_2Ni-H_2 systems at 320 and 350°C.

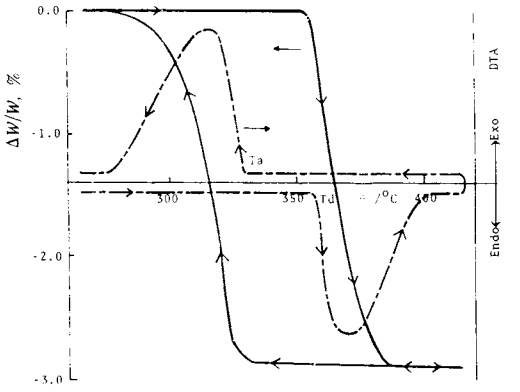

Fig. 3. Thermal analysis of the Mg_2Ni-H_2. (P_{H_2} = 6 kgf cm^{-2}, temperature scanning speed = 5°C min^{-1})

Table 2. Plateau pressures for the Mg_2Ni-H_2 system

Temperature	Desorption	Absorption
320°C	2.8 atm	5.0 atm (5.3)*
350°C	5.8 atm	9.5 atm (9.9)*

* numbers in parentheses are data by Reilly and Wiswall.[7]

seen from the DTA curve in Fig. 3. The heat transfer to and from the sample cell is not fast enough to catch up with the reaction kinetics. So, once the reaction is initiated, pressure scanning is manually stopped until the equilibrium is re-established. Actually the reaction proceeded to the opposite end of the plateau at one time. The characteristic isotherms in Fig. 2 were consequently obtained. A hysteresis of 3 to 4 kgf cm^{-2} was observed in this system. The solubility of hydrogen in the metallic phase and the hydrogen content of Mg_2Ni hydride were determined using our specially designed hydrogen gas analyser, in which the sample was degassed in a silica tube at 800°C for 10 hours and the hydrogen evolved was accumulated by a Toepler pump through a palladium membrane film. Then the amount of hydrogen was calculated by *PVT* (pressure-volume-temperature) relationship.

The hydrogen content of the Mg_2Ni hydride prepared at 350°C and 50 kgf cm^{-2} was determined as 3.32 wt%, while the theoretical content of the stoichiometric Mg_2NiH_4 is 3.63 wt%. This discrepancy might be attributed to the impurities in the alloy, listed in Table 1 or the inhomogeneity of the sample. The reversible hydrogen contents at the plateau pressures corresponding to the width of the plateaux are approximately 2.6% at 320°C and 2.5% at 350°C. The observed plateau pressures summarized in Table 2 are in fairly good agreement with the values reported by Reilly and Wiswall.[7]

3.2 Isobaric measurements

The present apparatus can also be utilized to examine the reaction by changing temperature at constant pressure. A typical result of the Mg_2Ni-H_2 system is shown in Fig. 3. The sample was well activated by several dehydriding-hydriding reaction cycles before measurements. Hydrogen pressure was kept at 6 kgf cm^{-2} and the temperature scanning speed was 5°C min^{-1}. The initiation temperature of desorption, denoted by T_d was 365°C and T_a, denoted for that of absorption, was 328°C. The weight percent of hydrogen desorbed was 2.9%.

In order to investigate the activation process of the metal-hydrogen system, more than one reaction cycle was repeatedly measured by temperature cycling between two predetermined levels. A typical diagram obtained is shown in Fig. 4 for the Mg_2Ni-H_2 system. Similar measurements have been performed for several hydrides of Mg-Ni alloys; Mg_2Ni (Mg/55%Ni), Mg/10%Ni, Mg/5%Ni, Mg/1%Ni, Mg.

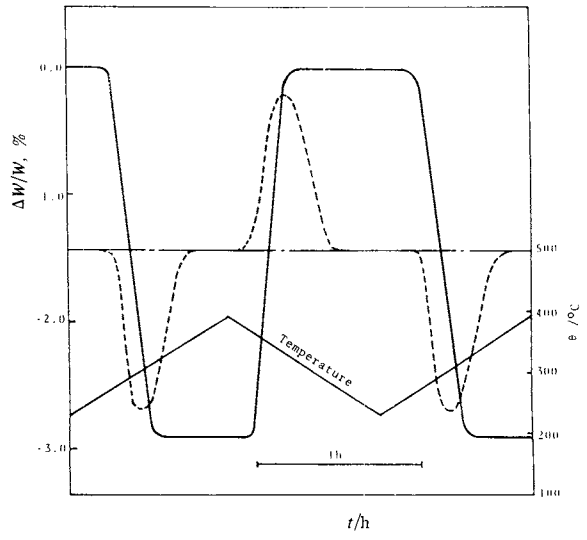

Fig. 4. Thermal cycling of the Mg_2Ni-H_2 system at a rate of 5°C min^{-1} under a hydrogen pressure of 5 kgf cm^{-2}.

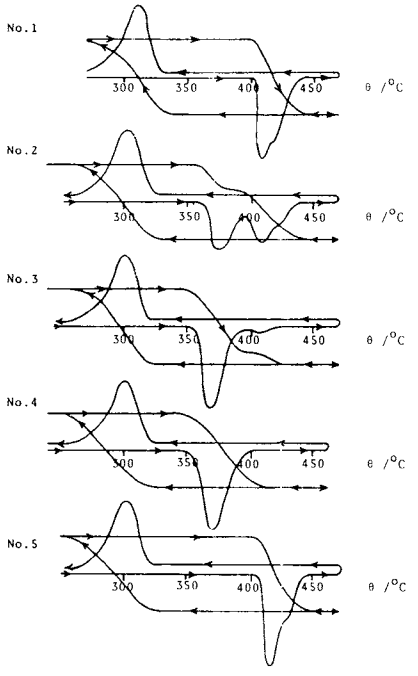

Fig. 5. TG and DTA diagrams of Mg/5%Ni hydride. (P_{H_2}=4 kgf cm^{-2}, temperature scanning speed=5°C min^{-1})

Table 3 shows the experimental procedure and the results for the Mg/5%Ni-H_2 system. Hysterisis width denotes the width between desorption and absorption TG curves at the half value of the dissociation weight loss. The initial dissociation weight loss is 4.7%, which is considerably lower than the theoretical value of 7.3%. It was very difficult to hydride the Mg-Ni alloys completely when Ni contents are less than 10%, and Mg metal is usually detected in the hydrides by X-ray powder diffraction. The results in Table 3 are also put into the form of diagrams in Fig. 5, where scales for the TG and DTA curves are arbitrary. The change of

Table 3. Experimental procedure and the results of TA for the Mg/5%Ni-H_2 system.

run number	P_{H_2} / kgf cm^{-2}	T_d / °C	T_a / °C	Dissociation weight loss, wt %	Hysterisis width/°C
Degassing at room temperature ⟶ H_2 pressure to 4 kgf cm^{-2}					
No. 1	4	404	322	4.7	96
No. 2	4	365 395 (D)	322	4.3	
No. 3	4	355 400 (D)	318	4.4	
No. 4	4	353	320	4.5	64
Degassing at room temperature ⟶ introducing air into the chamber for 10 min ⟶ degassing ⟶ H_2 pressure to 4 kgf cm^{-2}					
No. 5	4	405	320	4.0	99
No. 6	4	395 405 (D)	320	4.1	

(D) denotes doublet.

its sorption characteristics, however, is more obvious in this figure.

The starting Mg/5%Ni hydride sample had been kept in air before being introduced into the TA apparatus, which means the sample was in a "deactivated" state. The first run for the deactivated sample is characterized by a high T_d and a large hysterisis width. In the second run, DTA curve for desorption has two peaks. The higher temperature peak corresponding to the desorption of deactivated hydride still remains at the same position but decreases in height. A new peak appeared at a position approximately 50°C lower than the initial peak. This peak can be ascribed to the desorption of activated hydride. In the fourth run the hydride is completely activated and the hysterisis width decreased to 64°C from the initial value of 96°C. And then, finally the sample was hydrided and cooled down to the room temperature. All of the hydrogen in the chamber was replaced by air and the hydrided sample was exposed in air for 10 min. After that the chamber was evacuated and the fifth run was performed in the same way as the first run. Its desorption characteristics returned to that of the initial deactivated state. The 10 minute exposure in air was found to be enough to deactivate the hydride. The desorption peak of deactivated hydride was always observed as doublet as can be seen in Fig. 5, although no explanation could be given yet for this. It should also be noted that no conspicuous change was observed in the absorption features through this cycling runs.

Similar experiments have been made for other Mg-Ni alloys and the results are summarized in Table 4. The shift of desorption peaks were observed in common, which corresponded to the process from "deactivated" state to "activated" state. It is an interesting result that T_d for deactivated state are approximately constant independent of the nickel content or the degree of activation. And partly activated sample behaved as a mixture of completely deactivated portion and completely activated portion. T_d for deactivated state is around 355°C, as far as the runs at 4 kgf cm^{-2} are concerned. These values are approximately, 390 and 370°C, respectively for the runs at 12 kgf cm^{-2}. In order to complete the shift, several reaction cycles needed in this experiments.

Table 4. Initiation temperatures for desorption and absorption in the systems of Mg-Ni alloys and hydrogen.

pressure / alloys	~4 kgf cm^{-2}	~12 kgf cm^{-2}
Mg	443 (343) No reaction	438 ⟶ 407 (382) 376
Mg/1%Ni	410 (D)⟶356 (328) 315	395 (376) 371
Mg/5%Ni	405 (D)⟶353 (328) 320	418 (D)⟶388 (376) 370
Mg/10%Ni	408 (D)⟶360 (340) 337	404 (D)⟶390 (376) 366

The top and bottom numbers denote the initiation temperatures of desorption and of absorption, respectively. The middle number in a parenthesis denotes the equilibrium temperature calculated by the experimental equation of Stampfer, Holley and Suttle.[8] The equilibrium temperatures are not the same since pressures slipped off the predetermined value to some extent in some runs. The arrow indicates the shift of initiation temperature with reaction cycling.

However, a long time annealing at 400°C in hydrogen atmosphere was found to be enough to activate the sample. Furthermore the sample which was deactivated by exposing in air for 10 minutes was able to be reactivated by only one cycle as shown in Table 3.

The deactivation of powdered solid is generally considered to be caused by the absorption of various gas molecules (atoms) on the surface of solid. The present results also seems to support this absorption theory. The activation process may be thought as removal of absorbed molecules (or atoms) from the surface by being desorbed or by diffusing into the bulk. Oxygen and nitrogen are major constituents of absorbed gases in this case. Unfortunately no additional experiment has been done to distinguish the effects of these two molecules. Nevertheless, nitrogen is expected to be desorbed from the surface while oxygen penetrates into the bulk, since in our other experiment on the hydriding reaction, some powdered sample

which has been subjected to over 200 reaction cycles was found to be contaminated by the oxide phase but not by the nitride from x-ray examination.

It is quite reasonable that these activation processes, such as the desorption of absorbed molecules (atoms) and the diffusion into the bulk are controlled by the degree of annealing.

The Mg-Ni alloys are mixtures of Mg and Mg_2Ni, and the Ni solubility in Mg is negligibly small. Hydriding reactions of Mg and Mg_2Ni are described as follows,

$$Mg(s) + H_2(g) = MgH_2(s)$$
$$Mg_2Ni(s) + 2H_2(g) = Mg_2NiH_4(s)$$

where hydrides are represented as stoichiometric compounds which are not actual cases. It is well established that coexistence of Mg_2Ni accelerates the reaction rate of Mg itself, although it does not affect the equilibrium pressure of MgH_2.[3,4] The fact that T_d and T_a are essentially the same irrespective of the Ni content can be resonably understood, since change of the Ni content simply means change of the mixing ratio of Mg and Mg_2Ni (or MgH_2 and Mg_2NiH_4) phases and is not likely to have much effects on the sorption characteristics of Mg phase except the kinetics.

Kinetics of the reaction, however, was doubtlessly getting sluggish with decrease of the Ni content, and the hydriding reaction did not occur in the Mg-H_2 system any more at a hydrogen pressure of 4 kgf cm^{-2}.

In Table 5 are summarized thermal cycling experiments of the Mg_2Ni-H_2 system. The shift of T_d by activation was also clearly observed, and the hysterisis width was shortened as shown in Fig. 6, too.

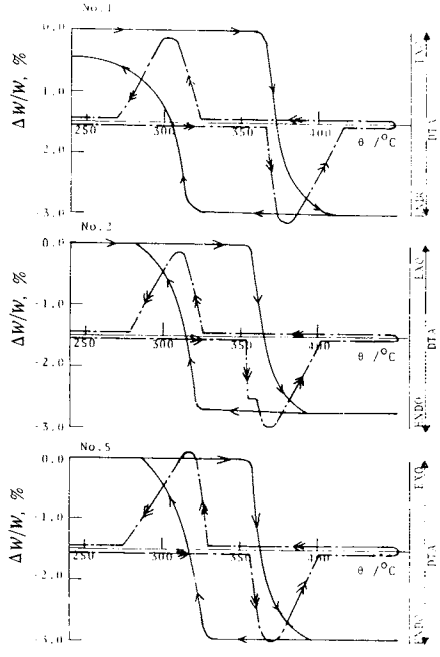

Fig. 6. TG and DTA diagrams of the Mg_2Ni-H_2 system.
(P_{H_2} = 6 kgf cm^{-2}, temperature scanning speed = 5°C min^{-1})

Table 5. Experimental procedure and the results of TA for the Mg_2Ni-H_2 system.

run number	P_{H_2} / kgf cm^{-2}	T_d / °C	T_a / °C	Dissociation weight loss, %	Hysterisis width/°C
Degassing at room temperature ⟶ H_2 pressure to 6 kgf cm^{-2}					
No. 1	6	366	323	3.09	69
No. 2	6	354	325	2.75	52
No. 3	6	356	327	2.84	48
No. 4	6	356	328	2.89	48
No. 5	6	356	329	2.95	45
Degassing at room temperature ⟶ introducing air into the chamber for 10 min ⟶ degassing ⟶ H_2 pressure to 6 kgf cm^{-2}					
No. 6	6	367	320	2.77	75
No. 7	6	356	322	2.76	54
No. 8	6	356	323	2.76	52

As far as our experiments are concerned, the T_d shift by the activation is characteristics of magnesium and its alloys. Similar isobaric experiments have been carried out for the $LaNi_5$-H_2, FeTi-H_2, $Ti_{0.7}Zr_{0.3}Cr_{0.8}Mn_{1.2}$-$H_2$ systems but no T_d shift was observed. The results obtained in the present experiments seem quite suggestive to the effect of absorbents on the hydrogen sorbing reactions.

Further experiments need to be made, however, in order to get a verified relationship between the absorption theory and the present experimental results.

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