Microencapsulation of Mg-Ni Hydrogen Storage Alloy

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Metal-hydrogen systems are currently used in a heat storage and other applications; however, some difficulties still exist in the actual process. It is well-known that hydrogen storage alloys, particularly powders, have very poor thermal conductivity (Suda et al., 1980) and disintegrate into a very fine powder easily with the repeated cycling of hydrogen charging and discharging. Compacting the storage materials into pellets is an effective method to avoid these problems. Ron et al. (1980) proposed porous metallic matrix hydrides (PMHs) with which powdered hydrides and aluminum were thoroughly mixed, compacted and then sintered under high hydrogen pressure. They showed that PMHs have larger strength and higher thermal conductivity. The thermal conductivity of fine powder bed increased by a factor of 10–50 (Bershadsky et al., 1989; Ron et al., 1992).

On the other hand, Ishikawa et al. (1985) proposed a copper microencapsulation method for hydrogen storage alloy, because the compact by the sintering treatment tended to disintegrate on repeated cycle and decreased the storage capacity. Figure 1 shows the ideal microstructure of a microencapsulated alloy. With this method, powder was coated in a thin layer of copper by a plating technique. They showed that the compacts obtained by this method have enough strength without the loss of storage capacity, although they have been compressed at room temperature. Ishikawa et al. (1986) studied the hydriding rate of the powder Cu-encapsulated at various pressures. The results showed that the powder bed absorbs hydrogen more quickly even if impure gas (such as CO, CO_2, CH_4, and N_2) exists. The reason was probably that the powder bed had higher effective thermal conductivity and unique membranous structure.

These published reports greatly contributed to improvement of hydrogen storage alloy for practical use. However, data on both thermal property and kinetics of the Cu-microencapsulated hydrogen storage alloy is needed for predicting temperature distribution in the heat storage unit where simultaneous hydrogen and heat transfer occurs. In this article, an experimental study of thermal conductivity, diffusivity and dehydrating rate of Mg-Ni hydrogen storage alloy is described, in which a main attempt was made to assess the effect of Cu-encapsulation on them.

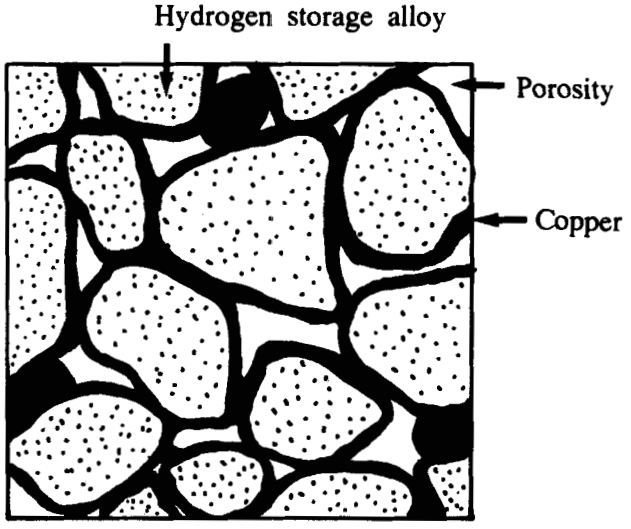

Figure 1. Ideal microstructure of an encapsulated hydrogen-storage alloy.

Materials and Method

Alloy of Mg_2Ni, one of representative hydrogen storage materials, was obtained from the Japanese Metals and Chemicals Ltd., Japan. The chemical analysis of the sample used was: 50.06% in Mg, 48.20% in Ni, 1.63% in O, and 0.11% in N. This sample contained an excess magnesium in comparison with the stoichiometrical composition of Mg_2Ni. The procedure of microencapsulation is: (1) The ingot of the sample was mechanically crushed; (2) pure hydrogen was charged and discharged repeatedly for the activation of alloy; (3) the fine powder of alloy, 20 micron in average diameter, was only used for an encapsulation. Figure 2 shows the size distribution of the powder used for the microencapsulation. For the strength of compact, it was important to control the size distribution; (4) the powder was immersed to an aqueous solu-

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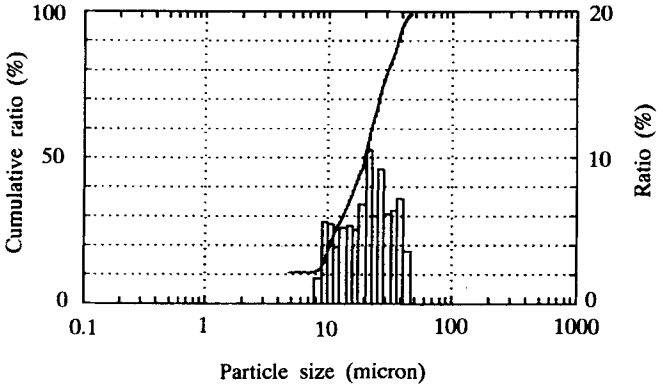

Figure 2. Powder size distribution of the sample used.

tion of HCHO, NaOH and Cu^{2+}–ethylene–diamine–tetraacetic acid (EDTA) complex at 298 K. According to this immersion, a thin copper membrane was formed around each particle by chemical reaction:

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + H_2 + 2H_2O + 2HCO^{2-} \quad (1)$$

The membrane had open pores microscopically due to the generation of hydrogen gas. The concentration of aqueous solution determined the mass of copper coated. In this study, the mass of copper amounted to 10.0 mass % and the mean thickness of copper membrane was theoretically 0.1 micron. The powder was compressed to a cylindrical shape, 10 mm in diameter and 1 mm in thickness, by using a uniaxial single-acting press. The compressing condition was 980.7 MPa in pressure and 298 K in temperature. The compact obtained had 19.6% in porosity, as a result. Another sample was also prepared without this encapsulation treatment, to study the effect of copper coating.

The thermal diffusivity of samples was measured by the laser flash method. The experimental apparatus used (Figure 3) was detailed elsewhere (Akiyama et al., 1992). The measurement procedure of the laser flash method was as follows: A pulse laser beam was flashed on the top surface of a disk-shaped sample. Temperature response at the back face was recorded by digital transient memory. Thermal diffusivity D was generally given by the equation:

$$D = 0.1388 Al^2/t_{1/2} \quad (2)$$

Here, A is a correction factor for radiation loss, l is a thickness of the sample, and $t_{1/2}$ is a specific time at which the back face temperature reached half of its maximum value. A value of A is determined by the ratio of heat leak due to radiation to heat conduction within the sample. If the apparatus is thermally-insulated without heat loss, the value of A equals one. A preliminary test was conducted to estimate a value of A for the encapsulated materials. A laser was flashed during 400 ms to the sample held at 773 K. Temperature at back face rose slightly, reached maximum value and then kept almost constant. Figure 4 shows temperature response at back face of the sample. Temperature rise was less than 5 K. It is well-known that temperature falls down shortly after reaching a maximum temperature when the sample is held at very

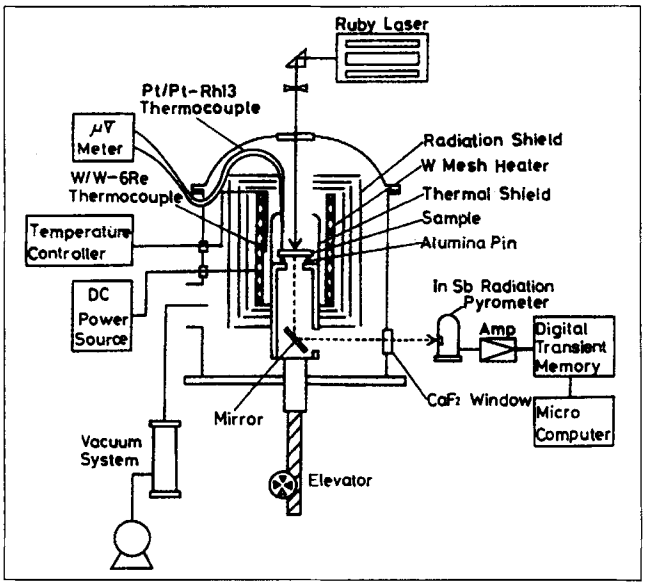

Figure 3. Experimental apparatus for the laser flash method.

high temperature. This is the reason that the effect of heat radiation is larger at higher temperature. Judging from the response shown in Figure 4, it was concluded that the influence of radiation loss was negligible at 773 K. Since all measurements of thermal diffusivity were done less than 773 K in this study, the value of A was set to one.

The measurement of thermal diffusivity was carried out in a vacuum of 5×10^{-5} Pa to avoid the oxidation of sample. The back surface of the sample was coated by spraying carbon powder with high emissivity to improve the temperature response. The compact was heated up at the rate of 0.05 K/s from 298 K to 773 K. After that, the sample was gradually cooled down. Thermal conductivity k was calculated by the equation:

$$k = \rho C_p D \quad (3)$$

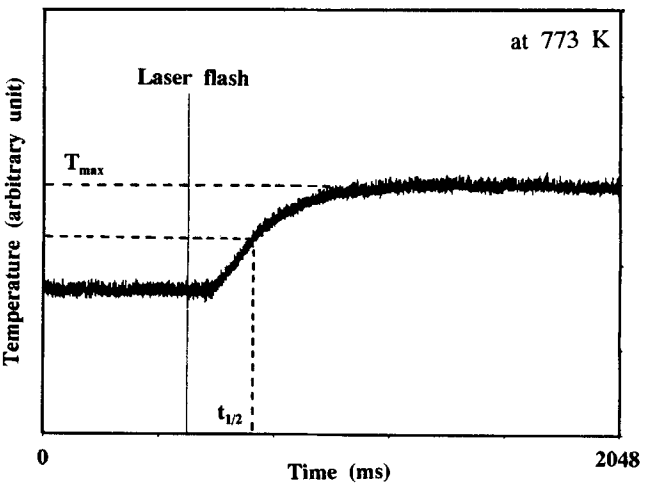

Figure 4. Example of temperature response at the back face in the laser flash method.

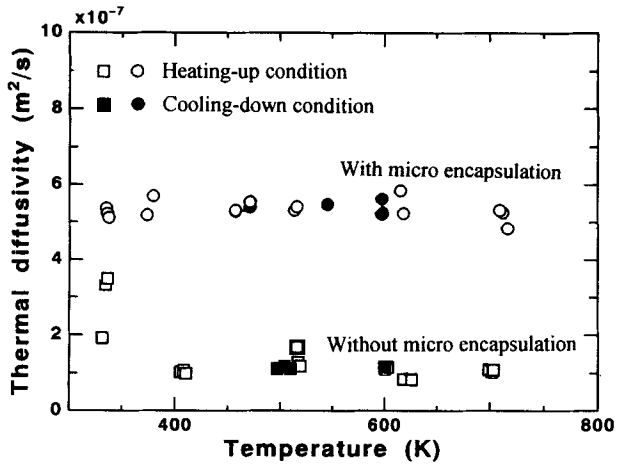

Figure 5. Thermal diffusivities of Mg-Ni alloy with and without the treatment of copper encapsulation.

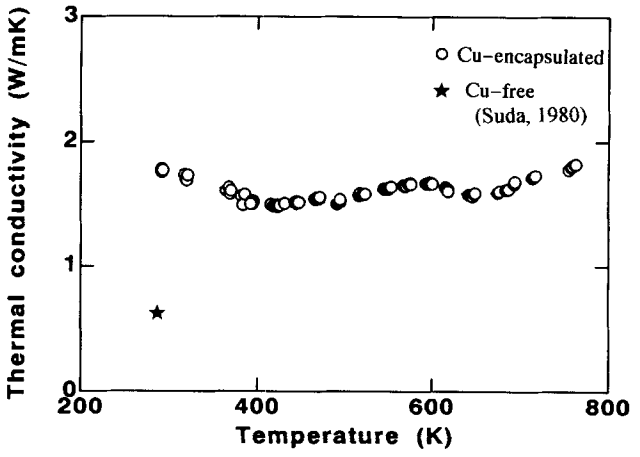

Figure 6. Temperature dependence of thermal conductivity of Mg-Ni compact from 278 to 773 K.

The apparent density of all samples encapsulated was measured using mercury based on Archimedes method. Obtained data was 2.60×10^3 kg/m^3 in mean value and was with relative errors less than 1.5%. The specific heat of samples was obtained by a calorimeter. Relative errors of data were less than 2%, and the mean value was 883 J/K·kg.

Results and Discussion

First, the thermal diffusivity of two compacts was measured to make sure an effect of Cu-microencapsulation. One was with Cu and another was without Cu. Sample temperature was momentarily fixed at desired temperatures between 298 and 773 K to flash laser several times. Values of $t_{1/2}$ were acquired through a transient memory, and were averaged. They showed high reproducibility with relative errors less than 1%. Mean value for the Cu-encapsulated compact was roughly 200 ms (Figure 4), which was appreciably smaller than 500–1,400 ms for Cu-free one. Figure 5 shows thermal diffusivity for the two compacts with and without Cu-microencapsulation treatment, which was obtained by Eq. 2. The circle presents data for the Cu-encapsulated compact, and square, the Cu-free one. The open mark indicates data measured under the heating condition, and the closed mark indicates the cooling one. The results show that the thermal diffusivity of Cu-encapsulated one was about seven times larger than of the Cu-free one. This verifies that the copper-coating played a major role to improve the thermal diffusivity of the compact, due to high thermal conductivity of copper (400 W/m·K). Additionally, the diffusivity was almost constant in the temperature range for measurements and was not appreciably influenced by temperature history of the compact.

Secondly, the thermal conductivity of compact was determined for three samples encapsulated. The temperature interval for flashing was set to be more narrow, about 25 K. Obtained mean value of $t_{1/2}$ showed high reproducibility with relative errors less than 1% among three samples used. Figure 6 illustrates the thermal conductivity of compacts between 298 and 773 K. A value of thermal conductivity ranged between 1.4 and 1.9 W/m·K, and its mean value was 1.6 W/m·K between 298 and 773 K.

Finally, the dehydriding rate of powder was examined to confirm whether the microencapsulation influences the dehydriding rate. For this purpose, the experimental apparatus for thermo-gravimetry (TG) – differential thermal analysis (DTA) was employed. The powder used was approximately 150 mg in mass, and was heated by an infrared heater using tungsten. The sample weight of 150 mg was small enough for keeping an isothermal condition. The reaction tube was filled by hydrogen gas at 0.1 MPa. Powder temperature was increased to 673 K at a heating rate of 0.333 K/s. The change of weight loss with time was monitored by the thermogravimetry for Cu-encapsulated and Cu-free powders. The reason for weight loss was that the sample evolved hydrogen according to the following equations: $Mg_2NiH_4 \rightarrow Mg_2Ni + 2H_2$ (at 523 K); $MgH_2 \rightarrow Mg + H_2$ (at 563 K). Figures in parentheses indicate decomposition temperature at 0.1 MPa. Figure 7 shows the changes of weight loss with temperature. Dehydriding curves were not smooth due to the coupled reactions. It is noteworthy that the two curves of weight loss were almost identical under this condition. This validated that the dehydriding rate for the Cu-encapsulated powder was the

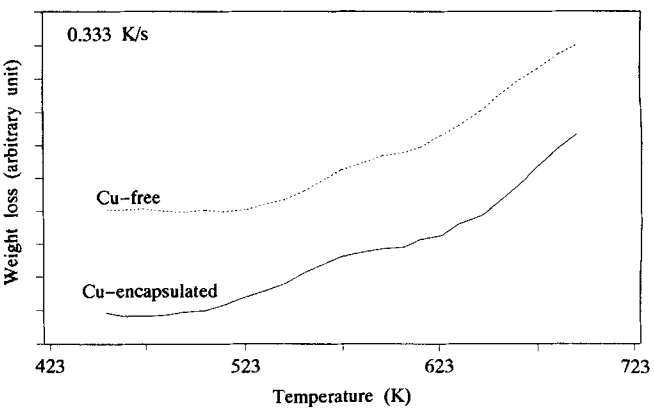

Figure 7. Comparison of dehydrating curves between the Cu-encapsulated and Cu-free powders.

same as the intrinsic dehydriding one under the isothermal condition. In other words, hydrogen diffusion through the copper membrane did not control the dehydriding rate. The total ratio of weight losses was the same between both the powders, 2.9 mass %.

It was, therefore, concluded that the Cu-microencapsulation on Mg-Ni hydride alloy improved thermal diffusivity and conductivity without losing the dehydriding property. The data of thermal conductivity obtained, 1.6 W/m·K, can be available for predicting temperature distribution within the compact.

Notation

C_p = specific heat, J/kg·K
D = thermal diffusivity, m^2/s
l = thickness, m
$t_{1/2}$ = time at which the back temperature reached half of its maximum value, s
k = thermal conductivity, W/m·K

Greek letter

ρ = apparent density, kg/m^3

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