富山大学水素同位体機能研究センター研究報告14：55－64，1994.

論　文

水素吸蔵合金粉末の飛散防止用カプセルの適用性
（Ⅰ）水素の吸収・脱離特性に対するカプセルの影響

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A Porous Stainless Steel as Scatter-Proof Envelope of ZrNi-Alloy Powder
(Ⅰ) Effects of Envelope on Absorption/Desorption Characteristics

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(Received August 11, 1994; accepted November 28, 1994)

Abstract

Absorption and desorption characteristics of hydrogen were examined for a ZrNi-alloy capsule fabricated to prevent the scatter of fine powder. The ZrNi-alloy capsule was fabricated by compression molding of ZrNi-alloy pellet and stainless steel powder mixed with a given amount of magnesium powder. It was found that the fraction of 5% of magnesium was the best for absorption of hydrogen. In addition, it was revealed that the ZrNi-alloy capsule was not broken by hydride formation at the hydrogen concentration of $ZrNiH_{2.2}$. The characteristics of dissociation pressure on the ZrNi-alloy capsule were almost the same as those on bare ZrNi powder. From those results, it was concluded that the ZrNi-alloy capsule enveloped in the sintered stainless steel over-layers was feasible for preventing the scatter of fine powder of hydrogen storage materials.

1. Introduction

A hydrogen storage material is indispensable for establishing a hydrogen energy system. It is also important to develop a safe handling technique of a large amount of tritium for a thermonuclear fusion reactor[1-3]. There are, however, problems to be solved before its practical utilization to the above mentioned purposes. One problem is pulverization of the hydrogen storage material to powder during its activation process and/or absorption-desorption cycles. The pulverization of the material is of great importance to gain high absorption and/or desorption rates on the one hand and causes some disadvantages on the other hand; loss of thermal conductivity, inflammability against air exposure, and scatter of fine powder in a system.

Especially, scattering of the fine powder gives rise to a serious problem on the practical use of the materials for transport, storage and recovery of tritium, because a large amount of tritium absorbed by the scattered powder of the hydrogen storage material causes severe contamination of the tritium handling system of a thermonuclear fusion reactor. Some development should be inevitable on this point.

From this point of view, we have studied to develop scatter-proof envelope of a hydrogen storage material. One development on this point is to enclose the material in porous stainless steel sheets. In the present paper, we will describe hydrogen absorption/desorption characteristics of porous stainless steel capsules enclosing ZrNi-alloy powder. The ZrNi-alloy was selected as a model of hydrogen storage material in the present study, since it is one of the promising materials for tritium handling in the thermonuclear fusion device[3-4].

2. Experimental

2. 1. Fabrication of ZrNi-alloy capsule

Figure 1 shows a cross sectional view of the ZrNi-alloy capsule fabricated in the present study. The capsule consisted of a short piece of stainless steel tube, a ZrNi-alloy pellet and porous sheets of stainless steel. The latter two were prepared from respective powders by compression molding at room temperature and sintering at high temperature.

The fabrication procedures of the capsule are shown as a flow chart in Fig.2. Mixtures of Mg and ZrNi-alloy powders and of Mg and stainless steel(SS) powders were prepared first. The mixture of Mg and ZrNi-alloy was compressed to a disc of 10mm diameter and 1mm thickness at 750kg/cm^2 at room temperature in the atmosphere. The disc was set on the SS tube. Both the top and bottom of the tube were plugged with the mixture of Mg and SS powders and compressed at 1130kg/cm^2. This piece was heated at 1100°C for 20min in vacuum and then cooled to room temperature. In this processing, Mg simply acts as pore-former, because it dose not make alloys with the components of ZrNi-alloy and of SS by its nature and easily evaporates during the vacuum heating. Pore size and distribution in the sintered matrix could be controlled with varying mixing ratio between two kinds of powders.

The fraction of Mg mixed with SS powder was varied in the range from 0 to 30 vol% to examine effects of pore size on hydrogen absorption/desorption characteristics. The fraction of Mg mixed with ZrNi-alloy powder, on the other hand, was fixed to 10 vol%. The weight of ZrNi-alloy in each capsule was 0.4g.

The sintered SS surface of sample capsule was observed prior to absorption/desorption measurements with a conventional scanning electron microscope (SEM) equipped with a characteristic X-ray detector.

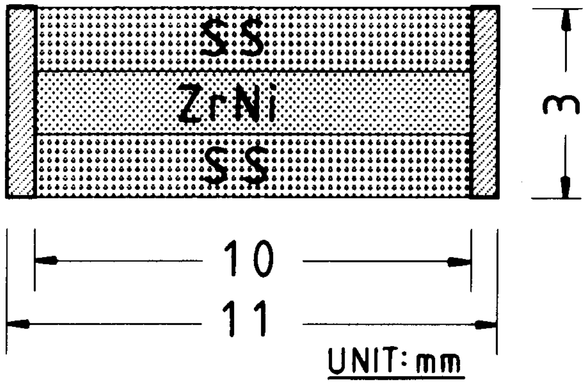

Fig. 1. A cross sectional view of a ZrNi-alloy capsule. Symbols of SS and ZrNi describe the sintered SS over-layers and the compressed ZrNi-alloy pellet, respectively.

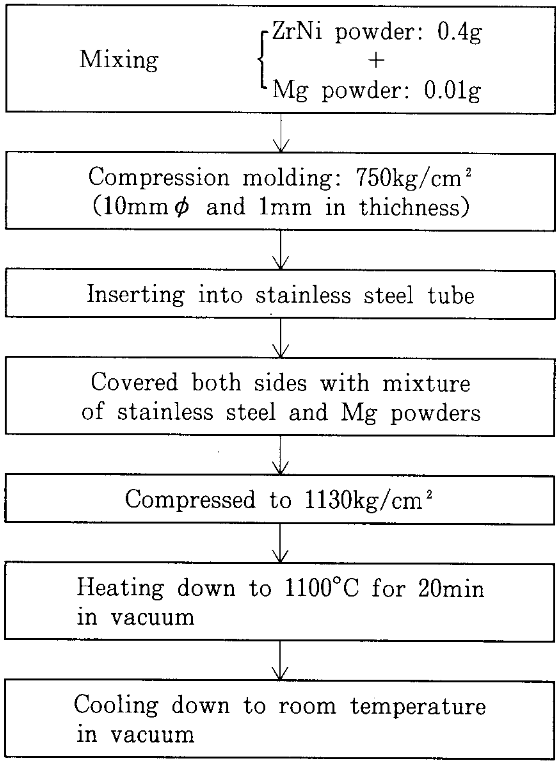

Fig. 2. A flow chart of preparation procedures of a ZrNi-alloy capsule.

2. 2. Apparatus for absorption/desorption experiments

Figure 3 shows a schematic diagram of the experimental apparatus for absorption-desorption measurements. It consists of a hydrogen supply and an absorption measuring unit connected to a high vacuum system with a vacuum gauge and a quadrupole mass spectrometer. It can be evacuated with a sputter ion pump backed with an oil-sealed rotary pump. The residual pressure at the measuring unit was routinely below 10^{-6} Torr. The pressure change of hydrogen in each run was measured by using two capacitance manometers (MKS Baratron TYPE 390HA: 1 and 1000 Torr Head) attached to the measuring part.

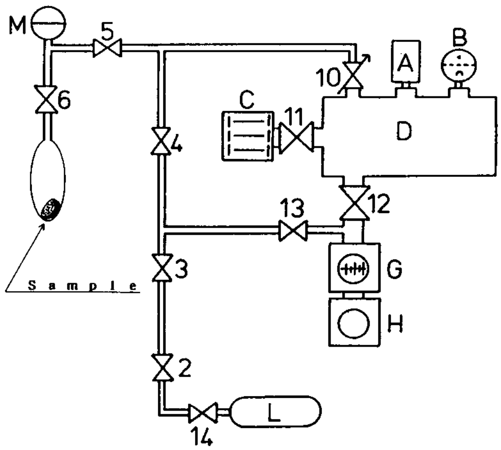

Fig. 3. A schematic diagram of the experimental apparatus: A, Mass spectrometer; B, B-A gauge; C, Sputter ion pump; D, Vacuum chamber; G, Turbo molecular pump; H, Rotary pump; L, Hydrogen cylinder; M, Capacitance manometer.

3. Results and discussion

3. 1. SEM observation

Photograph 1 illustrates an example of SEM micrographs of the sintered SS over-layers of four kinds of capsules. The mixing fraction of Mg powder was 10, 5, 3 and 0 vol%. It is seen from the photographs that the size of SS particles is distributed in the range from 10 to 30 μm. It is also apparent that the SS particles were thoroughly sintered at 1100°C. It appears that the size of a small opening in the sintered SS over-layers decreases with the decrease in mixing fraction of Mg. The magnesium added was not detected on the surface of the sintered SS over-layers.

Photograph 2 shows the surface of a bare ZrNi-alloy pellet, which was prepared with similar procedures and conditions to those for fabricating the ZrNi-alloy capsule. The particle size of ZrNi-alloy is below about 150 μm. Even a trace amount of magnesium was not observed on the surface of the bare ZrNi-alloy pellet. It is seen from the photograph that the outline of the ZrNi-alloy particle has not been almost changed by heat treatment. The size of opening is around 50-100 μm. This size is large enough for hydrogen to diffuse into the inside of ZrNi-alloy pellet.

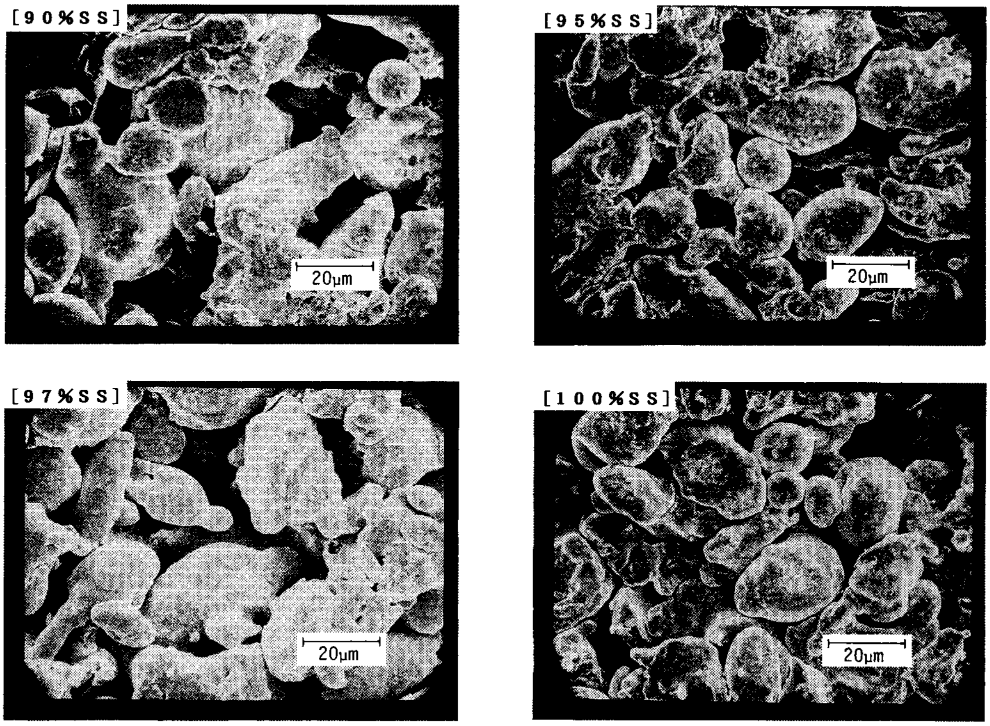

Photo. 1. Scanning electron micrographs of the surface of ZrNi-alloy capsule.

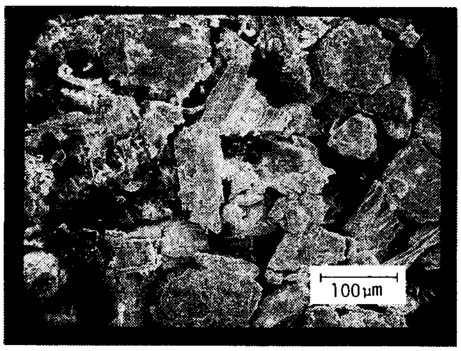

Photo. 2. An example of a scanning electron micrograph of the bare ZrNi-alloy pellet.

3. 2. Absorption behavior of hydrogen

Prior to an absorption run, each capsule sample was degassed at 600°C for 1 hour in the measuring part shown in Fig. 3 as a standard activation process. After cooling down to room temperature, the sample was exposed to hydrogen at a given pressre. Figure 4 shows examples of hydrogen absorption curves observed for a bare ZrNi-alloy pellet. The amount of a hydrogen charge in each absorption run was 7.5×10^{-2} cm^3(STP), which is equivalent to 2.5×10^{-3} of [H]/[ZrNi] ratio. Thus the reaction observed is the absorption of hydrogen, and is not the hydride formation[4].

It is clearly seen from the figure that the absorption rate increases with repeating absorption run and shows almost a constant rate at the 5th run. The increase in the absorption rate is considered due to surface decontamination with hydrogen. The reverse order between the 5th and the 6th run should be due to surface contamination by residual gases such as H_2O, CO and CO_2 after activation process. The small surface area of the sample would be responsible for the relatively ease surface contamination in those cases.

Figure 5 shows absorption curves over the ZrNi-alloy capsules and the bare ZrNi-alloy pellet. Each absorption curve is the result of the first absorption run. Numerical percentages written in the figure describe the volume fraction of SS powder contained in the mixture of Mg and SS powders at the fabrication process.

It is seen that the presence of the sintered SS over-layers caused to decrease

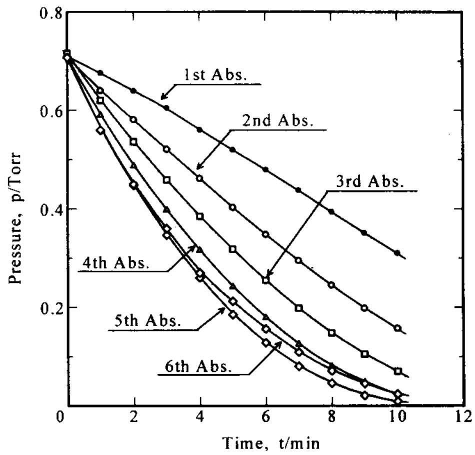

Fig. 4. Change in the hydrogen absorption behavior for the bare ZrNi-alloy pellet.

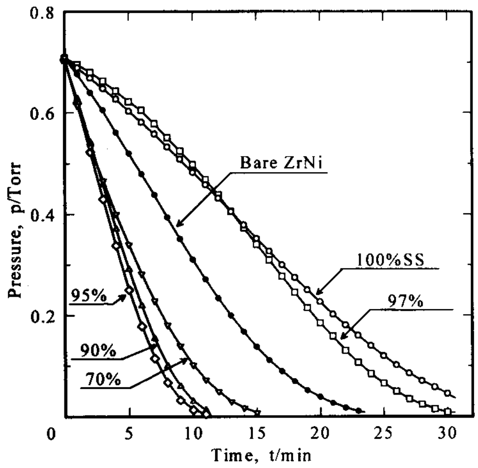

Fig. 5. Effect of magnesium contents on the absorption rate of hydrogen.

in the absorption rate as expected. However, this is true only for 100 and 97%-SS capsules. Contrarily, the absorption rates for the other ZrNi-alloy capsules are considerably greater than that for the bare ZrNi-alloy pellet.

There are ways of reasoning for their higher absorption rates. One is the effect of magnesium residue. We could not, however, detect a trace amount of magnesium on the surface of the sintered SS over-layers after the activation. This indicates that the magnesium in the sintered SS over-layers was vaporized by heating at 1100°C. It could be plausible, however, that the magnesium powder in the ZrNi-alloy pellet was not thoroughly vaporized. The residual magnesium would play a role to prevent the deactivation after the heat treatment. Further investigations on effects of magnesium are required.

Figure 6 shows the pressure dependence of the hydrogen absorption for the 95%-SS capsule. The experiments were carried out by adding in sequence a given amount of hydrogen from low to higher pressure side after the experiment shown in Fig. 5. In the case of the initial pressure of 0.708 Torr, the plots of logarithmic pressure against time showed a linear relation. This indicates that the absorption rate of hydrogen obeys the first order kinetics which is usually observed for this kind of materials[1,5-6]. In this case, the absorption rate constant was evaluated as 2.9×10^{-3} s^{-1}. Almost the same value was obtained from the initial part of other experiments shown in this figure except the lowest pressure one. Namely, it is concluded that the sintered SS over-layers do not give rise to change in absorption kinetics with hydrogen pressure.

On the other hand, the plots deviated downward for the initial hydrogen pressure above 0.708 Torr. The higher the initial pressure was, the faster the deviation arose. It appears to be due to the heat generation by hydrogen absorption[7]. Absorption of hydrogen by ZrNi-alloy is an exothermic reaction. In fact, temperature rise around 10°C was detected by a thermocouple attached to the outside of the quartz tube in the cases of P_o=71.2 and 535 Torr. It is reported by

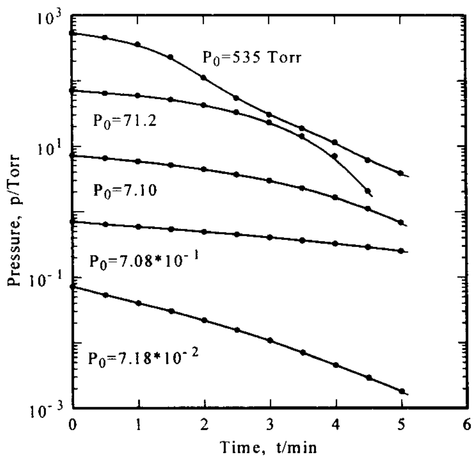

Fig. 6. Pressure dependence of the hydrogen absorption on 95%-SS capsule.

Watanabe et al.[4] that the heat of hydride formation for ZrNi-alloy was 25 kcal/mol (H_2) for monohydride and 19 kcal/mol(H_2) for trihydride of ZrNi.

After a series of such experiments, the concentration of hydrogen was evaluated as $ZrNiH_{2.2}$. Even at this stage, no significant change in appearance of the ZrNi-alloy capsule was observed, although the bare ZrNi-alloy pellet was entirely pulverized to fine powder at a such concentration of hydrogen. The hydrogen having been absorbed in the ZrNi-alloy capsule amounted to 65cm^3(STP), which corresponds to 168 Ci(1Ci = 37GBq) of tritium gas. This indicates that the capsule developed in the present study is promising for use as a scatter-proof container to load tritium gas of 200 Ci into one capsule.

3. 3. Temperature dependence of dissociation pressure

Figure 7 shows the temperature dependence of an equilibrium dissociation pressure. The measurements described by closed circles were performed by raising temperature stepwise from room temperature to 300°C after the measurements mentioned in Fig. 6. A linear relation was obtained below 150°C, but above this temperature a slight downward deviation from the line was observed. That is, although the amount of hydrogen released at 150°C is only about 2% of the initially absorbed amount, the release fraction at higher temperatures is considerably larger than that at lower temperatures. Therefore, the concentration of hydrogen in the ZrNi-alloy decreases acceleratingly with temperature rise. As a result, the linear relation will be lost. This sample, however, gave the hydrogen pressure of 694 Torr at 300°C in the present experimental conditions. This indicates that over 50% of the initially loaded hydrogen can be easily released from the ZrNi-alloy capsule.

With respect to the linear part below 150°C, the slope of the line gave the heat of trihydride($ZrNiH_3$) formation of ZrNi. That was evaluated as 17.8 kcal/mol(H_2), which is closed to the value of 18.6 kcal /mol(D_2) reported for $ZrNiD_{2.3}$[4]. The temperature dependence for $ZrNiD_{2.3}$ is

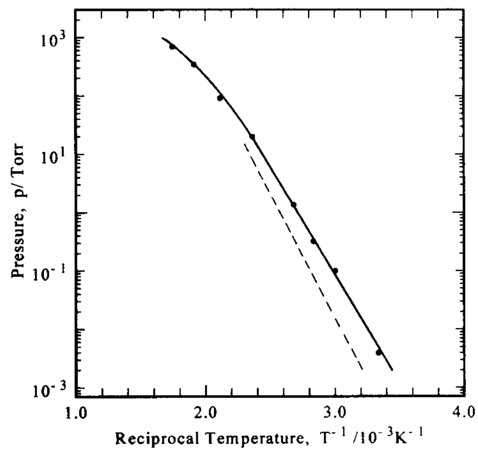

Fig. 7. Temperature dependence of the equilibrium dissociation pressure for 95%-SS capsule. The broken line shows the data for $ZrNiD_{2.3}$.

shown by a broken line in Fig. 7. Namely, it is revealed that the thermodynamic characteristic of ZrNi-hydride was not changed by the modification using the sintered SS over-layers.

Figure 8 shows the result of examination on the effect of the sintered SS over-layers on the thermal response. Sample used in this run was a 95%-SS capsule, which contained the hydride of $ZrNiH_{2.2}$. The capsule introduced into the quartz tube was heated at a temperature ramp of 5°C/min from room temperature to 307°C, and simultaneously the hydrogen pressure was followed successively. It is seen from the figure that the observed pressure is slightly low in the range from 200 to 280°C than the equilibrium pressure evaluated from Fig. 7.

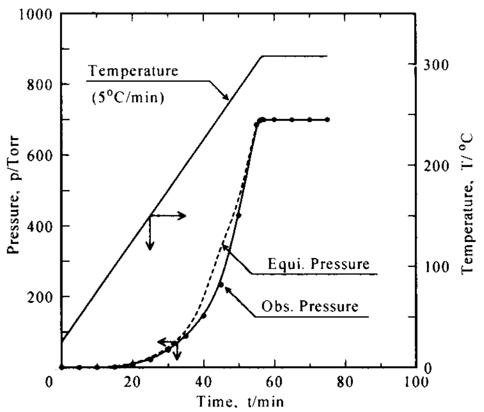

Fig. 8. Variation of hydrogen pressure followed the successive temperature rising.

Several factors will be considered for such pressure difference. The increase in the hydrogen pressure should become remarkably lower than that expected from Fig. 7, if the heat from an electric furnace is not thoroughly transmitted to the sintered SS over-layers and the hydride. It appears, however, that the sintered SS over-layers does not play a role of higher thermal barrier because the pressure difference was scarcely observed up to around 200 °C. Above this temperature, on the other hand, the pressure difference was slightly observed. With temperature rise, an increasingly large amount of hydrogen is released from the hydride confined in the 95%-SS capsule. The release of hydrogen is an endothermic reaction as mentioned above. For this reason, the temperature rise of the hydride will be slowed down by the hydrogen release. This indicates that the observed hydrogen pressure should be lower than the expected hydrogen pressure. In addition, such behavior will be more significant by the low thermal conductivities of quartz and ZrNi-hydride itself.

4. Conclusions

To prevent the scatter of fine powder of a hydrogen storage material, we examined the effect of an envelope made of porous stainless steel. The ZrNi-alloy powder was employed as a model of the hydrogen storage materials. A ZrNi-alloy pellet was enclosed by a stainless steel tube and plugs of porous SS over-layer made from SS powder. Both of the bare ZrNi-alloy pellet and the sintered SS over-layer were prepared from mixture of Mg and ZrNi-alloy powders and of Mg and SS powders, respectively. The ZrNi-alloy capsules fabricated in this manner were used for examinations of the absorption/desorption characteristics for hydrogen.

It was seen that the sintered SS over-layer added 5 vol% magnesium powder to the SS powder was most suitable for a ZrNi-alloy capsule and the hydrogen absorption obeyed the first order kinetics irrespective to exposure pressure of hydrogen. The capsule did not broken even at the hydrogen concentration of $ZrNiH_{2.2}$. In addition on the absorption behavior, the temperature dependence of equilibrium dissociation pressure for $ZrNiH_{2.2}$ was examined by a desorption method. As a result, it was revealed that the envelope of the sintered SS over-layers did not show any significant impediment on the equilibrium dissociation pressure of the hydride, and that it also did not act as a higher thermal barrier of ZrNi-alloy capsule.

It was concluded that the ZrNi-alloy capsule enveloped in the sintered SS over-layers would be much valuable for establishing safe handling techniques as storage-supply-recovery of a large amount of tritium as well as hydrogen.

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