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Metal Hydride Characteristics by Zr and Ti

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Abstract−Hydrogen absorption experiments were carried out using zirconium (Zr) and titanium (Ti) in the form of a metal sponge, strip and rod to investigate the metal hydride characteristics. The Zr and Ti sponges showed a high hydrogen absorption capacity despite a low reaction temperature. The H/M, which indicates the capacity of hydrogen absorption, was measured at 2.0 for the Zr/Ti sponge at 25 °C. In the case of the Zr/Ti strip and rod, however, the hydrogen absorption capacity was very low at 25 °C. The capacity of hydrogen absorption increased with an increase in the reaction temperature. When the Ti strip was not activated, the H/M ratio was measured at 0.58. When the Ti strip was once and twice activated at 800 °C for 1 hour, the H/M ratio increased to 1.6 and 1.83, respectively. The hydrogen absorption capacity decreased with the increment of concentration of helium in hydrogen due to a blanketing effect of metal surface by the helium. A pulverizing phenomenon during the metal hydriding was observed in both the Zr/Ti strip and the Zr/Ti rod. However, this pulverizing phenomenon was not observed in the Zr/Ti sponges because of their high surface area.

Key words: Hydrogen, Absorption, Metal Hydriding, Immobilization, Zirconium, Titanium

INTRODUCTION

There are a number of potential methods for storing hydrogen. A metal hydride form is one of the useful ways of hydrogen storage [Holtslander and Yaraskavitch, 1981]. Recently, many studies have been performed on hydrogen storage and delivery using hydrogen storage metals [Reilly and Weswall, 1976; Lee and White, 1984; Hwang and Gong, 1991; Kabutomori et al., 1998; Ishiyama et al., 2000]. Many metals react with hydrogen to form solid hydrides, but only transition metals have the required properties for hydrogen storage application. The metals used as a metal hydride include zirconium and titanium. The properties of these metal hydrides that make them suitable are very low dissociation pressures at a normal temperature, a high capacity for hydrogen, ease of preparation, and stability in air and water at a storage temperature [Holtslander and Miller, 1982]. The hydrides of zirconium, titanium, hafnium, and yttrium as well as erbium have been suggested as useful for hydrogen storage [Burger and Trevorrow, 1980]. The dissociation pressure of zirconium and titanium hydrides is less than 10^{-15} Pa at 25 °C and less than 5 kPa at 500 °C; however, at 1,000 °C these hydrides are completely dissociated, whereas the hydrides of yttrium and erbium are extremely stable with dissociation pressures less than 100 Pa, even at 1,000 °C. Zr and Ti hydrides are suitable for recoverable storage, whereas the hydrides of erbium and yttrium are more suited for the nonrecovery of hydrogen [Holtslander and Yaraskavitch, 1981]. Another advantage of metal hydrides is their large capacity for hydrogen. The density of hydrogen in some metal hydrides is similar to, or greater than, that of liquid hydrogen [Cox and Williamson, 1977].

Zr and Ti were selected for this study since hydrogen is bound strongly at a normal storage temperature, and the hydride is easily prepared and can be dissociated to recover hydrogen if required.

In the present study, hydrogen absorption experiments by Zr and Ti in the form of a metal sponge, strip and rod were carried out to investigate the characteristics of metal hydrides. The effects of the reaction temperature, the type of metal, activation conditions and the presence of helium in the hydrogen were investigated.

EXPERIMENTAL

This work was performed by using commercial Zr and Ti in the form of a metal sponge, strip, and rod. A 3/8 inch ID × 150 mm length of stainless steel tube was used as the reactor for the hydrogen absorption. The experimental apparatus for the hydrogen absorption is shown in Fig. 1. The experiments for the metal hydriding were carried out with the following four steps by using the GENIE PROGRAM developed by Lee et al. [Lee, 1998]: 1) the evacuation step for removing the rest gas in the system, 2) the volume meas-

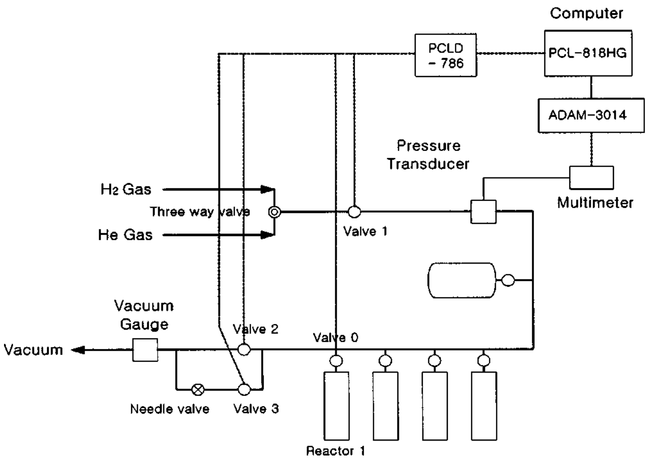

Fig. 1. Experimental apparatus for hydrogen absorption.

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urement step for measuring the free volume of the reactor, 3) the activation step for removing the surface oxide, and 4) the hydrogen absorption step. The metal surface was cleaned by heating (Zr: 1,000 °C, Ti: 800 °C) in a vacuum for 1 hour to dissolve the surface oxide and then cooling to the desired reaction temperature.

The hydrogen absorption capacity was calculated by using the following equation.

$$\frac{P_iV_m}{T_m}=\frac{P_eV_m}{T_m}+\int_0^L\frac{P_e dV}{T}+\frac{P_eV_r}{T_r}+n_{ads}R$$

$$=\frac{P_eV_m}{T_m}+\int_0^L\frac{P_eA\,dx}{T(x)}+\frac{P_eV_r}{T_r}+n_{ads}R.....$$

$$=\frac{P_eV_m}{T_m}+\frac{P_eV_c}{T_{LM}}+\frac{P_eV_r}{T_r}+n_{ads}R \qquad (1)$$

where T_{LM} is the logarithmic mean temperature at x=0, T_0 and x=L, T_L.

RESULTS AND DISCUSSION

Metal hydrides are formed by the direct combination of the metal and hydrogen and the reaction is exothermic as follows:

$$M+\frac{x}{2}H_2 \leftrightarrow MHx + Q\ cal \qquad (2)$$

where M and x represent the metal and the appropriate stoichiometry for the reaction of the metal, respectively.

Fig. 2 shows the effect of the reaction temperature on the formation of a metal hydride using Zr and Ti sponges. From the experimental results, it was found that the reaction rate was very fast and the reaction was completed within less than 5 minutes. The reaction temperature specified is the initial temperature when the hydrogen was first introduced to the reactor vessel containing the metal. The reaction was exothermic, and the temperature was raised quickly with time. The Zr and Ti sponges showed a high hydrogen absorption capacity at a relatively low reaction temperature. The H/M ratio, which indicates the capacity of hydrogen absorption, was measured at 2.0 for the Zr sponge at reaction temperature of 25 °C. The H/M ratio was also measured at 2.0 for the Zr and Ti sponges at reaction temperatures of 200 °C and 500 °C. Therefore, the capacity of hydrogen absorption by Zr and Ti sponges was not dependent on the reaction temperature. However, as shown in Fig. 3 and Fig. 4, in the case of the strip and rod types of Zr and Ti rod, the hydrogen absorption capacities were very low at 25 °C. However, the capacities of hydrogen absorption increased with an increase in the reaction temperature, and the H/M ratio was measured at 1.71 for the Ti strip, 0.61 for the Ti rod and at 0.99 for the Zr rod at 500 °C. The rate of the reaction for the strip and rod types of Zr and Ti was slow compared with that of the sponge, especially at a low experimental temperature of 25 °C. Because of the bulk form of the rod, the diffusion of hydrogen into the metal appeared to be the rate-controlling step in the reaction, and hence a higher temperature was

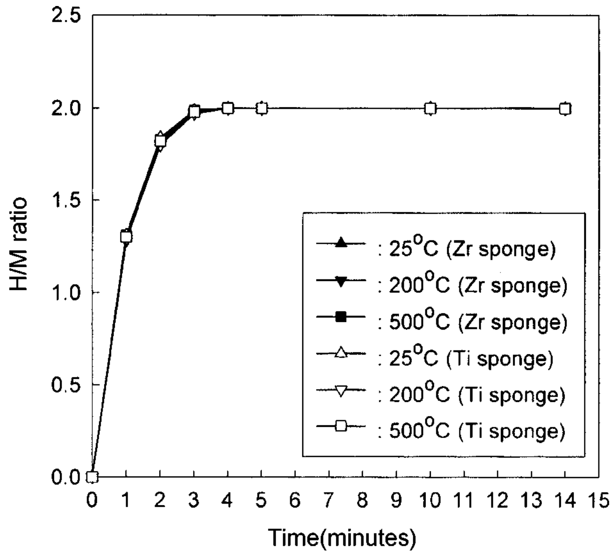

Fig. 2. Effect of the reaction temperature on the formation of metal hydride using Zr and Ti sponges.

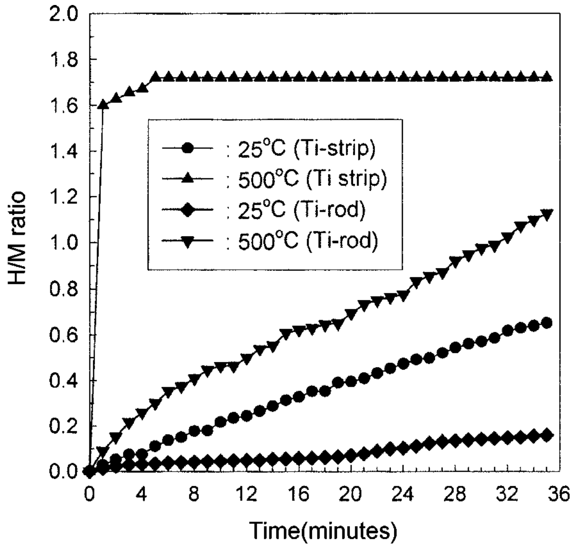

Fig. 3. Hydriding reactions of Ti-strip and Ti rod at various reaction temperatures.

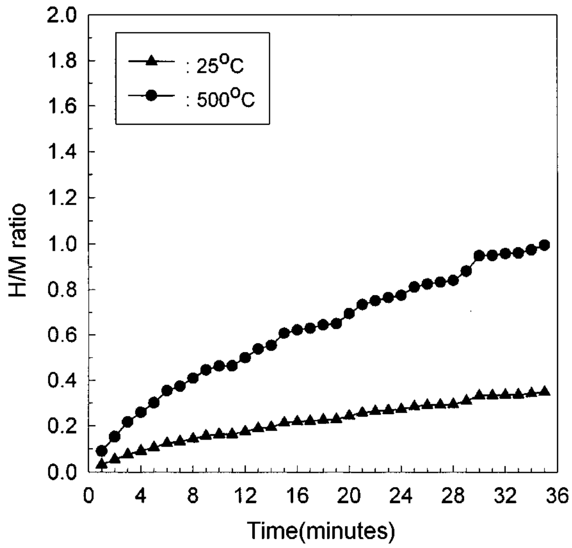

Fig. 4. Hydriding reactions of Zr rod at various reaction temperatures.

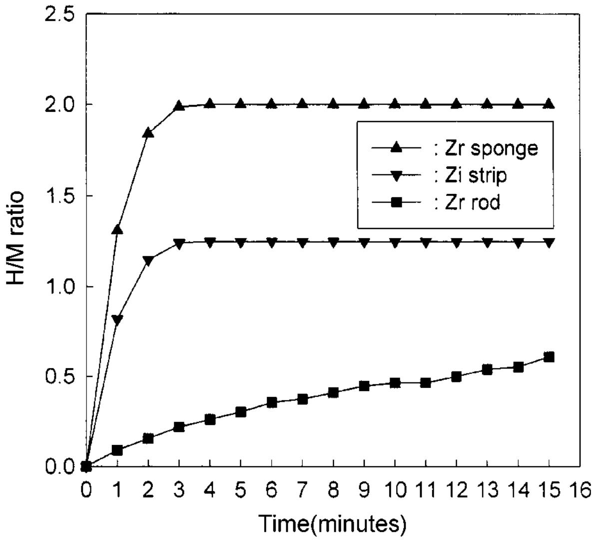

Fig. 5. Effect of metal type on the formation of metal hydride using Zr at 500 °C.

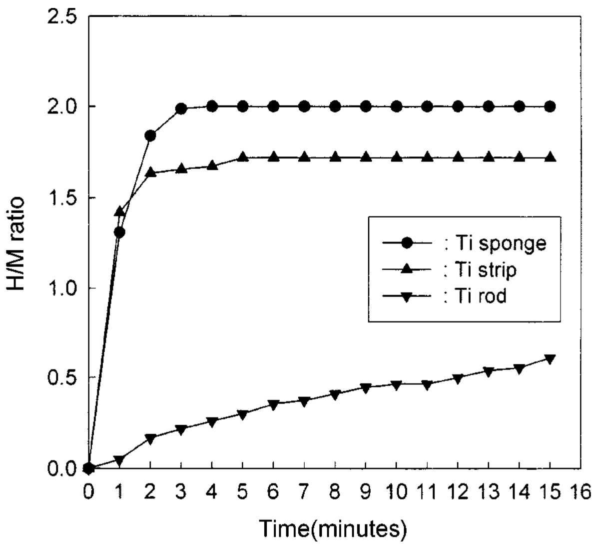

Fig. 6. Effect of metal type on the formation of metal hydride using Ti at 500 °C.

required [Holtslander and Miller, 1982].

Fig. 5 and Fig. 6 show the effect of the metal type on the formation of a metal hydride from Zr and Ti at a reaction temperature of 500 °C, respectively. As shown in experimental results, the sponge type of Zr and Ti had a higher capacity of hydrogen absorption than the strip and rod type of Zr and Ti. From these experimental results, it was found that the rate and capacity of hydride formation reaction is dependent on the surface area available for the reaction. According to BET analysis results, the sponge type materials (5.86×10^{-2} m^2/g) had a higher surface area than strip (2.4×10^{-2} m^2/g) and rod (1.1×10^{-2} m^2/g) types materials.

Fig. 7 shows the photograph for the pulverization phenomenon of Zr and Ti before and after metal hydriding. As shown in Fig. 7, a pulverizing phenomenon during metal hydriding was observed in both the Zr/Ti strip and the Zr/Ti rod. However, this pulverizing phenomenon was not observed in the Zr/Ti sponge. These results

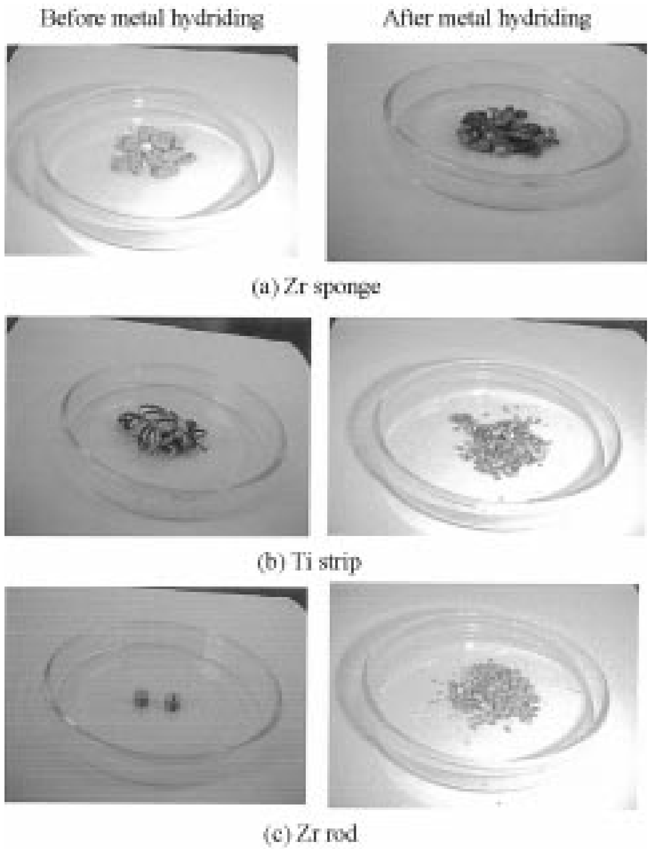

Fig. 7. Pulverizing phenomena of Zr and Ti before and after metal hydriding.

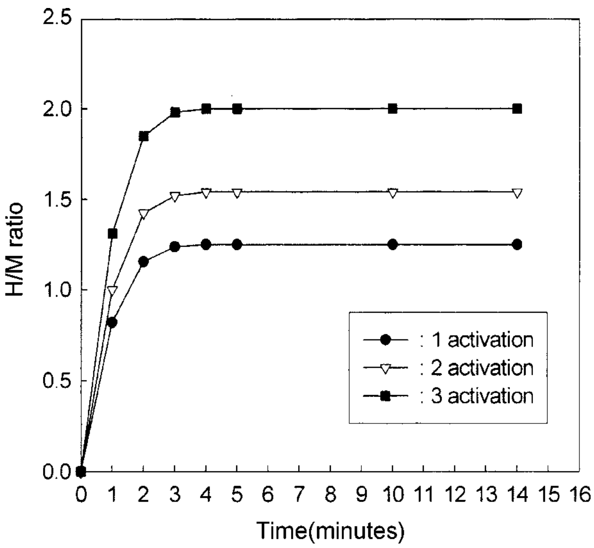

Fig. 8. Effect of activation on the formation of metal hydride using Zr strip at 500 °C.

reconfirm that the sponge type materials have a much higher surface area than the strip or rod type materials.

Fig. 8 shows the effect of activation on the formation of metal hydride from a Zr strip at a reaction temperature of 500 °C. When the Zr strip was activated once at 1,000 °C for 1 hour, the H/M ratio was measured at 1.25. However, the capacity of hydrogen absorp-

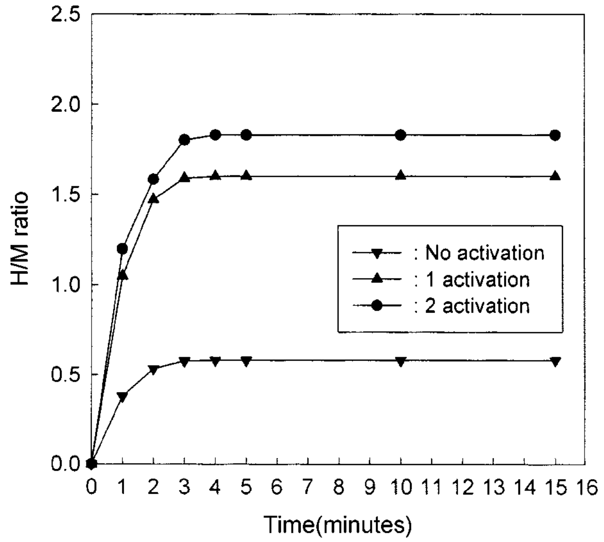

Fig. 9. Effect of activation on the formation of metal hydride using Ti strip at 500 °C.

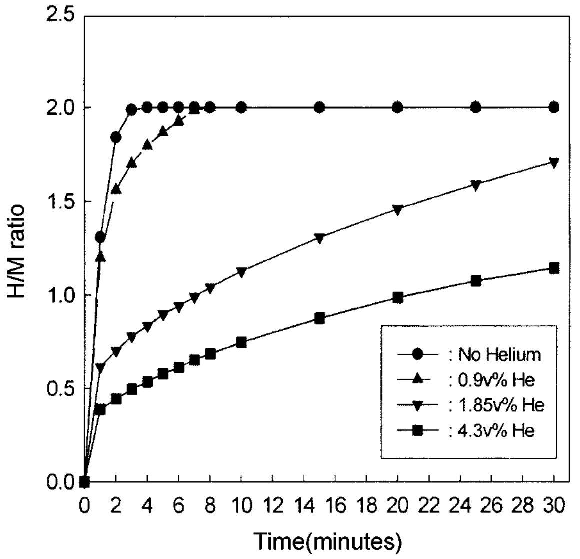

Fig. 11. Effect of helium on the formation of metal hydride using Ti sponge at 400 °C.

tion increased with the frequency of activation, and in the case of three times of activation, the Zr strip had a high capacity of hydrogen absorption, and the H/M ratio was also measured at 2.0. Fig. 9 shows the effect of activation on the formation of metal hydride from a Ti strip at a reaction temperature of 500 °C. When the Ti strip was not activated, the hydrogen absorption capacity was low, and the H/M ratio was measured at 0.58. But, when the Ti strip was activated once or twice at 800 °C for 1 hour, the H/M ratio increased to 1.6 and 1.83, respectively. From these results, it would seem that the activation step for removing the surface oxide is very important, and the metal surface must be clean for a high hydrogen absorption capacity.

The major difference in the chemistry with tritium compared with hydrogen or deuterium is the effect of helium from the tritium decay. This helium is known to inhibit the hydriding reaction. To investigate this effect, Ti sponge was hydrided with hydrogen containing 0.9 v%, 1.85 v% and 4.3 v% helium, respectively. Fig. 10 and Fig. 11 show the effect of helium on the metal hydriding reaction using Ti sponge at 25 °C and 400 °C, respectively. As shown in the experimental results, the hydrogen absorption capacity decreased with the increment of concentration of helium in hydrogen. This effect is thought to be due to a blanketing effect of metal surface by the helium, preventing access to the surface by hydrogen. When the helium concentration was 0.9 v%, 1.85 v% and 4.3 v%, the H/M ratio at the reaction temperature of 25 °C decreased to 1.61, 0.82 and 0.22, respectively. However, as shown in Fig. 11, when the reaction temperatue was 400 °C, the effect of helium for the hydrogen absorption decreased, and there is an initial rapid absorption of hydrogen followed by a much slower rate of reaction. These results are thought to be due to higher diffusion rate of hydrogen than that of helium with the increment of reaction temperature.

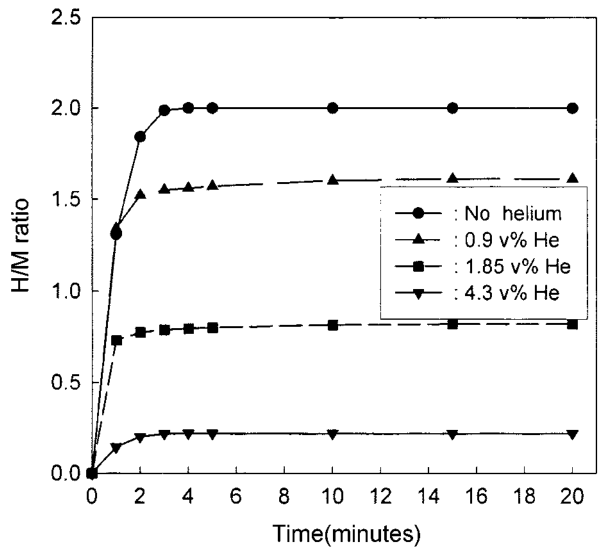

Fig. 10. Effect of helium on the formation of metal hydride using Ti sponge at 25 °C.

CONCLUSIONS

The sponge type of Zr and Ti showed a high hydrogen absorption capacity at a relatively low reaction temperature. The H/M ratio was measured at 2.0 for both the Zr sponge and Ti sponge at a reaction temperature of 25 °C. The reaction rate was very fast and the reaction was completed in less than 5 minutes. However, in the case of the strip and rod types of Zr and Ti, the hydrogen absorption capacities were very low at a reaction temperature of 25 °C. The sponge type of Zr and Ti with a higher surface area reacted more quickly than the strip or rod type of Zr and Ti. When the Ti strip was not activated, the H/M ratio was measured at 0.58. However, when the Ti strip was activated once or twice at 800 °C for 1 hour, the H/M ratio increased to 1.6 and 1.83, respectively. The capacity of hydrogen absorption increased with the frequency of activation. It was, therefore, established that the activation step for removing the surface oxide was very important, and the metal surface had to be clean for a high hydrogen absorption capacity. The hydrogen absorption capacity decreased with the increment of concentration of helium in hydrogen. This effect is thought to be due to a blanketing effect of metal surface by the helium, preventing access to the surface by hydrogen.

ACKNOWLEDGEMENT

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NOMENCLATURE

P : pressure [atm]
V : volume [ml]
T : temperature [°K]
T_{LM} : the logarithmic mean temperature at x=0, T_0 and x=L, T_L
n_{ads} : hydrogen absorption capacity [mole]
R : gas constant [22400/273]

Subscripts
i : initial state
e : equilibrium state
m : manifold
c : connection part from solenoid valve to reactor
r : reactor

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