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Ball Milling Effects during Fluorination of the Eutectic Alloy Mg-Mg₂Ni

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Summary

A hydrogen storage system composed of borohydride complex ions stabilized in an aqueous KOH or NaOH solution has been developed by applying catalytic hydrolysis to generate hydrogen under ambient pressure and temperature conditions.

In this work, ball milling and fluorination effects on the catalytic hydrolysis of the alkaline stabilized BH₄⁻ solution have been investigated for Mg, Mg₂Ni, Mg-23.5 mass % Ni eutectic alloy and their hydrides. Fluorination (F-treatment) after ball milling was found effective for enhancing hydrolysis kinetics for Mg₂Ni and its hydride, but not effective for Mg and MgH₂.

By the formation of MgF₂ at the extreme surface of Mg₂Ni during F-treatment, Mg₂Ni is disproportionated to Mg_{2-x}NiH₄ in balance with xMgF₂. We believe the Mg_{2-x}NiH₄ contributes to the catalytic hydrolysis to generate hydrogen at significantly higher rates than other Mg-based catalysts. Experimental work has been extended to evaluate the catalytic function of the Mg-Mg₂Ni eutectic alloy after ball milling and F-treatment in order to understand the roles of NiH₄⁻ in the Mg_{2-x}NiH₄. F-treated Mg-23.5 mass % Ni eutectic alloy after ball milling has exhibited a fairly high catalytic function, in between those of F-MgH₂ and F-Mg₂NiH₄. It was clearly shown in this work that MgH₂ works to hinder the catalytic functions of Mg-23.5Ni eutectic alloy in the hydrolysis of BH₄⁻ complex.

Roles of the NiH₄⁻ complex ion in Mg_{2-x}NiH₄ in hydrolysis have been investigated to date and should be subjected to further detailed studies.

Introduction

In our previous work on F-treatment [1], Mg and Mg₂Ni have been found to form MgF₂ that exhibits a close affinity with both molecular hydrogen in gas-solid reactions and protons in electrochemical reactions. F-treatment contributes significantly to reducing pressure and temperature levels during hydrogenation as the results of the removal of oxide layer and the formation of hydride at the extreme surface. In the eutectic alloy of Mg-Mg₂Ni, MgF₂ is formed along the grain boundaries between the Mg and Mg₂Ni phases. MgF₂ formed at the boundaries works to induce hydrogen dissociation at the surface of both Mg and Mg₂Ni phases to form hydride layers at the vicinity of the boundaries. Those works are reported elsewhere [2-6]. [Note: hereafter, “F-” will be used for F-treated and “U-” for untreated.]

From the earlier results, a combined procedure of ball milling with fluorination was expected to provide excellent hydriding/dehydriding properties and characteristics to the Mg-Mg₂Ni eutectic alloy. However, during this IEA project, it was found that both the ball milling and fluorination procedures are insufficient to improve the dehydriding kinetics of this material. We have concluded that the close bonding between Ni and H in the form of NiH₄⁻, as reported in a series of earlier works [7-12], must not be affected by those treatments to result in significant improvements in hydriding kinetics.

Meanwhile, Mg₂Ni and its fluorinated hydride were found to work as excellent catalysts in the hydrolysis of the alkaline stabilized BH₄⁻ complex ion as a hydrogen storage material [13-17]. By stoichiometric calculation of the hydrolysis reaction BH₄⁻ + 2H₂O → 4H₂ + BO₂⁻ (in an aqueous alkaline solution such as KOH and NaOH), hydrogen generated by the hydrolysis amounts to 17.1 mass % in [4H₂/(BH₄⁻ + 2H₂O)]. However, the actual H-capacity is largely dependent on the concentration and the solubility of BH₄⁻ in alkaline solution. In **Table 1**, H-capacity is listed as a function of BH₄⁻ concentration in aqueous KOH or the NaOH solution, where BH₄⁻ is supposed to be dissolved from NaBH₄.

Table 1 - Experimental H-contents of BH₄⁻ in NaOH solution

NaBH ₄ : H ₂ O	NaBH ₄ /(NaBH ₄ +xH ₂ O)	H-contents (mass %)
1 : 2	51.4	10.8
1 : 3	41.3	8.70
1 : 4	34.5	7.30
1 : 5	29.7	6.25
1 : 6	26.0	5.48
1 : 7	23.2	4.88
1 : 8	20.9	4.40

Such materials as NaBH₄ have been studied as hydrogen storage materials (18-27). Recently a series of research efforts on NaAlH₄ has been undertaken with regard to the gas-solid phase application for high capacity hydrogen storage (28-34).

This work is intended to develop an hydrogen storage system by applying the gas-liquid phase for catalytic hydrolysis. In this work, F-Mg F-Mg₂Ni, and F-Mg-23.5 mass%Ni eutectic alloy after ball milling were experimentally evaluated as catalysts for generating hydrogen by hydrolysis from the NaOH stabilized BH₄⁻ complex ion solution. This work has been performed to develop a new hydrogen storage system based on BH₄⁻-complex that has been known to compose high H-capacity hydrides such as KBH₄ and NaBH₄.

Experimental results and discussions

All samples were prepared by a conventional ball milling procedure under ambient temperature for 90 min in order to reduce the average particle size below 25 μm before F-treatment.

F-treatment by F-1 method (1,35) was introduced for Mg simply to remove the surface oxide and produce the MgF₂ layer that was expected to enhance hydride formation at the extreme surface. Mg₂Ni, Mg₂NiH₄ and Mg-23.5Ni eutectic alloys were fluorinated for preparing the disproportionated Mg_{2-x}NiH₄ and xMgF₂. An F-Mg-23.5%Ni sample was prepared by the F-10 method in which 3g of Mg-23.5Ni was ball milled with 10 ml of F-1 solution at 2,700 rpm for 90 min and 0.5g of treated sample was applied with 20ml of testing solution. X-ray diffraction patterns of the fluorinated and partially hydrided Mg-23.5Ni particles are shown in **Figure 1**.

Catalytic functions of Mg, Mg₂Ni and Mg-23.5Ni and their F-treated samples, which were partially hydrided at the extreme surface, were evaluated by measuring hydrogen gas generated during catalytic hydrolysis of a BH₄⁻-containing NaOH solution (20 ml of 10g NaBH₄ per liter of 10 wt% NaOH solution). All catalysts were applied after arranging to have the same specific surface area. Hydrogen gas collected in a conventional glass P-V apparatus and was measured at room temperature. Individual experimental data are plotted as a function of elapsed time.

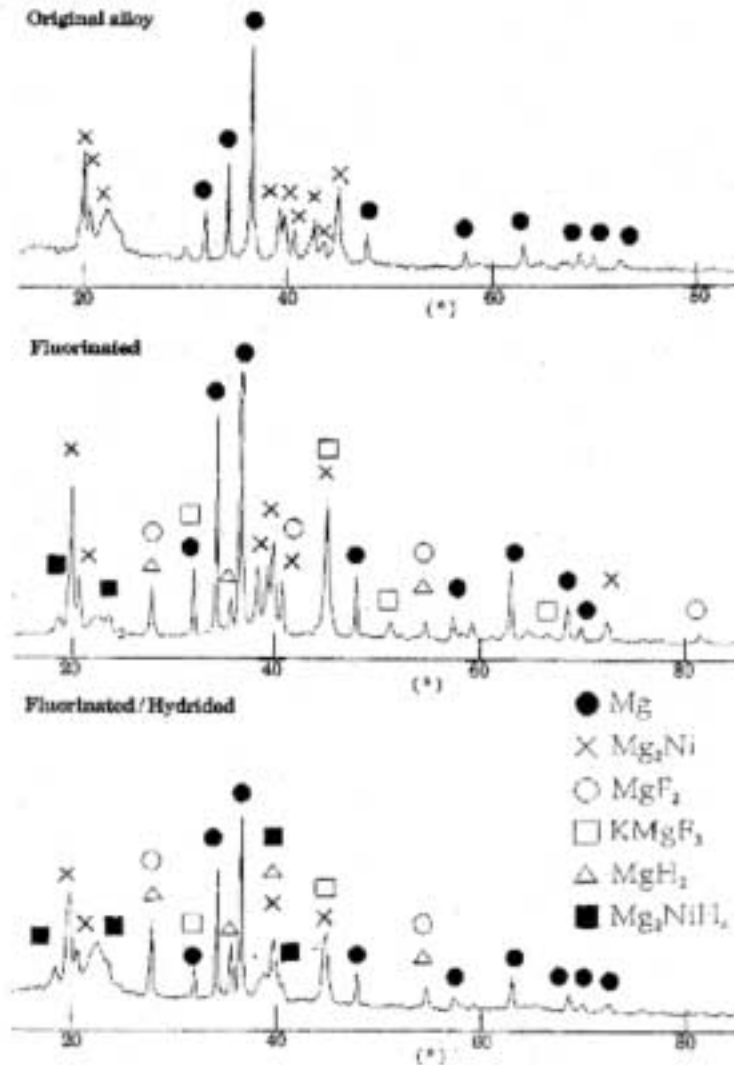


Figure 1 - XRD patterns of the ball milled/fluorinated Mg-23.5 mass% Ni eutectic alloy before and after hydrogenation at 75°C and 1.0 MPa (5 H/D cycles)

Experimental data for U -Mg, U -MgH₂ and U -Mg₂Ni are shown in **Figure 2** and for U -Mg₂NiH₄ and F -Mg₂Ni in **Figure 3**. U -Mg₂NiH₄ and F -Mg₂NiH₄ are shown in **Figure 4**, and the temperature dependency of F -Mg₂NiH₄ on the rates of hydrolysis is illustrated in **Figure 5**. Hydrolysis by F -Mg-23.5Ni eutectic alloy after ball milling is shown in **Figure 6**.

The effect of ball milling on U -Mg₂Ni was investigated for comparison with F -Mg₂NiH₄. The results are shown in **Figure 7** and **Figure 8**. For lower temperatures (10-20°C, Figure 7) ball milling gives better catalytic performance than F -Mg₂NiH₄, but ball milling is similar to F -Mg₂NiH₄ at higher temperature ranges (30-50°C, Figure 8). The reduced amounts of hydrogen generated were considered to be a result of oxide formation during ball milling.

All F-treated samples were composed of MgF₂ and/or Mg_{2-x}NiH₄ at the extreme surface. From the materials balance viewpoint, it is considered possible that MgF₂ formed during F-treatment might result in the disproportionation of F -Mg₂Ni and F -Mg₂NiH₄ to Mg_{2-x}NiH₄ (x is dependent on the amount of xMgF₂ formed) at the extreme surface. F -Mg-23.5Ni might also result in the formation of MgH₂, xMgF₂, and Mg_{2-x}NiH₄.

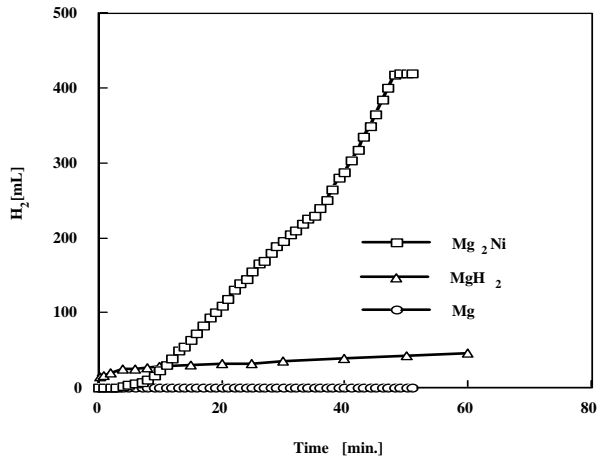


Figure 2 - Hydrolysis rate of Untreated Mg, MgH₂, and Mg₂Ni

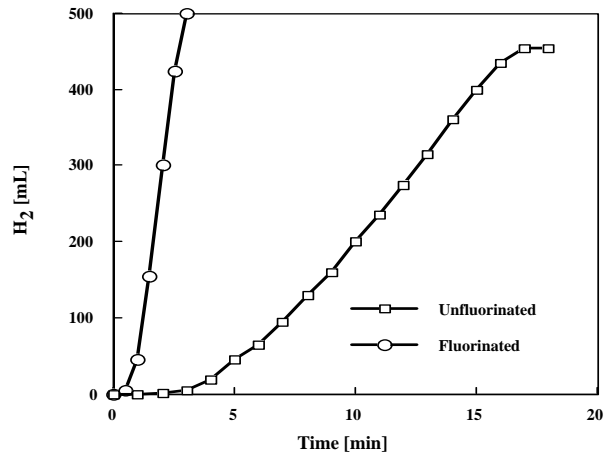


Figure 3 - Rates of H-generation by F-treated and untreated Mg₂Ni

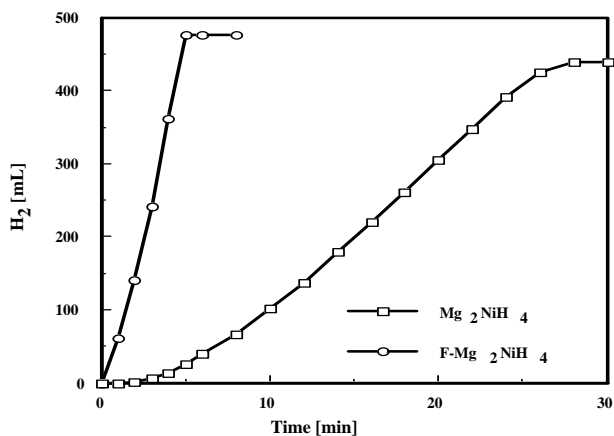


Figure 4 - Rates of H-generation by Mg₂NiH₄ before and after F-treatment

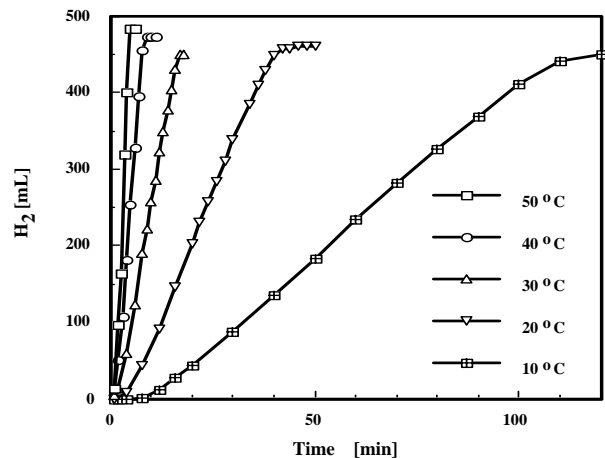


Figure 5 - Temperature dependency of F-treated Mg₂NiH₄ on H-generation rates

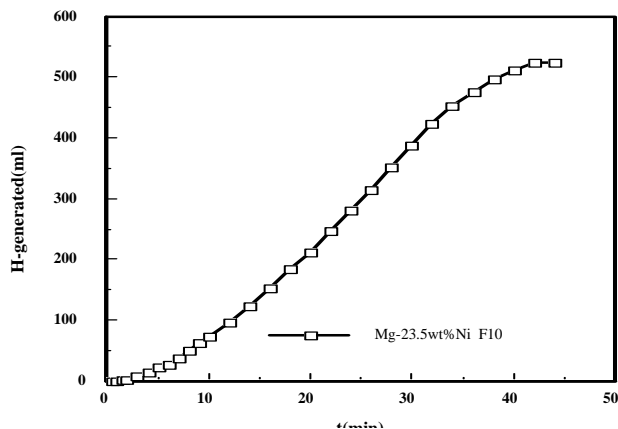


Figure 6 - Rates of H-generation by F-Mg-23.5 mass% Ni after ball milling (24 °C)

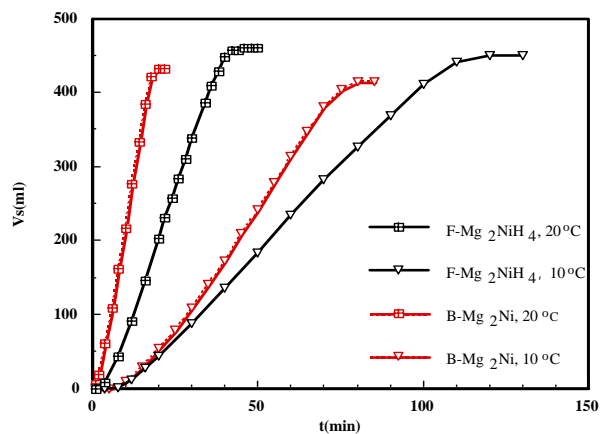


Figure 7 - Catalytic effects of F-treated Mg₂NiH₄ and ball-milled Mg₂Ni on H-generation

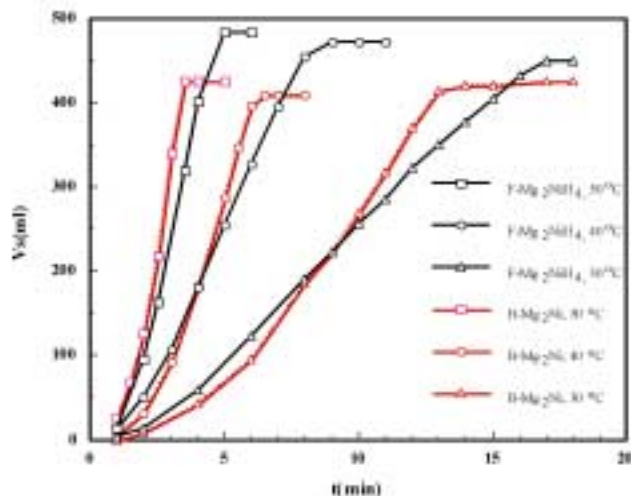


Figure 8 – Catalytic effects of F-treatment on Mg_2NiH_4 and ball milling on Mg_2Ni

MgH_2 was found to not be effective as a catalyst, as clearly shown in experimental results (Figure 2). $Mg_{2-x}NiH_4$ was considered to exhibit catalytic function, where the excess NiH_4^- in $Mg_{2-x}NiH_4$ contributed to the hydrolysis. On the other hand, MgH_2 formed in $F-Mg-23.5\%Ni$ after ball milling was considered to be the reason for a catalytic effect lower than that of $F-Mg_2Ni$. We considered that the effect is caused by MgH_2 -coverage along with the grain boundary between Mg and Mg_2Ni phases exposed by ball milling. This is reasonably seen from Figure 3 for $F-Mg_2Ni$ and Figure 6 for $F-Mg-23.5Ni$. Hydriding/dehydriding cycles before F-treatment was found to not be effective for enhancing catalytic function of Mg_2NiH_4 . Comparisons of the rates of hydrogen generation suggested the following relative ratings :

$$U-Mg < F-MgH_2 < U-Mg_2Ni < F-Mg-23.5Ni < F-Mg_2NiH_4 < F-Mg_2Ni.$$

Conclusions

For the catalytic hydrolysis of the BH_4^- complex ion stabilized in aqueous NaOH solutions, Mg and Mg-Ni alloys have been developed as catalysts by applying ball milling and fluorination techniques. Mg and MgH_2 did not work as catalysts even after ball milling and F-treatment. Hydriding/dehydriding cycles before F-treatment were found to have little influence on the rates of hydrolysis. Ball milling without F-treatment on Mg-23.5 %Ni did not exhibit significant improvement on the rates of hydrolysis.

The best catalyst obtained in this work was $F-Mg_2Ni$, which resulted in the generation of hydrogen at high rates during the hydrolysis of 10wt% NaOH stabilized BH_4^- complex solution. The authors attributed the effect to the excess NiH_4^- complex ions in $Mg_{2-x}NiH_4$ that appeared at the extreme surface by the disproportionation of Mg_2Ni during F-treatment.

However, the disproportionation of Mg_2Ni during F-treatment has not been studied in enough detail to define the roles of $Mg_{2-x}NiH_4$ at the extreme surface. The authors will continue to investigate the roles of disproportionation during F-treatment by performing a series of instrumental analyses such as XPS, AUGER, SIMS, and XRD.

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