

Thermodynamic Evaluation for Formation of MgCu₂ from MgH₂ and Cu

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Abstract

We proposed that there are competitive two kinds of pathways in the hydrogenation of Mg/Cu super-laminate composites; the one is that alloying (formation of MgCu₂ from Mg and Cu) occurs in advance and Mg₂Cu is hydrogenated to form MgH₂ and MgCu₂, and the other is that Mg is hydrogenated and then MgH₂ and Cu reacts to form MgCu₂ together with H₂ gas, according to a hypothesis that the reaction of MgH₂+2Cu → MgCu₂+H₂ occurs. In order to confirm that the hypothesis is true, we investigated the conditions such as pressure and temperature at which the above-mentioned reaction proceeds. Well-mixed MgH₂ and Cu powder was compacted to form pellet at 1.73GPa and then heated at various hydrogen pressures and temperatures. Experimental results at 673K indicated that the above-mentioned reaction occurs at pressures higher than 6.5MPa, approximately lower limit for the hydrogenation of Mg₂Cu, whereas Mg₂Cu is formed at 3.3MPa.

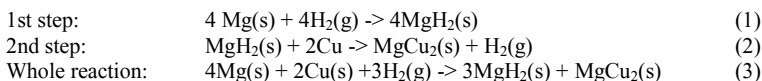
Introduction

Since it was reported that accumulative rolling is effective for preparation of Mg-Ni based hydrogen storage alloys[1], the hydrogenation properties of super laminate composites (SLCs) prepared by accumulative rolling have been investigated for Mg-Ti-Ni, Mg-Al, Mg-Cu and Mg-Pd systems[2-7]. In the case of Mg-Cu system[5], the SLCs exhibit extremely faster hydrogen absorption than Mg₂Cu alloy prepared by conventional melting method: Reversible hydrogen absorption and desorption is observed even at 473K for the SLC, although it is usually tried at about 573K or higher for conventional alloy[8].

In order to clarify the mechanism, microscopic observation using TEM has been performed for the SLCs in various hydrogenation states[7, 9] and many pores, which were not observed in the alloy prepared by melting, homogeneously distributed in Mg₂Cu layers formed during initial activation treatment although the effects introduced by cold rolling, such as introduction of many dislocations, would be eliminated due to heating at 573K in the treatment. In our recent study[10], we observed the metallographic structures of the SLCs prepared by the treatment in H₂ atmosphere of 3.3MPa and at the temperatures which firstly increased from room temperature to 573K and was secondly kept at constant (573K) for 86.4ks. One of the structures obtained is shown as a backscattering electron image in Fig. 1. Two different microstructures are

observed for $\text{MgH}_2 + \text{MgCu}_2$; the one is in the form of net-like and the other is in layered form. In addition, some gaps are observed in the layered $\text{MgH}_2 + \text{MgCu}_2$ structure. These strongly imply the Mg/Cu SLC was hydrogenated in two different ways.

We have been proposed the possible two hydrogenation processes as follows. The one is that the alloying of Mg and Cu to form Mg_2Cu firstly occurs and then Mg_2Cu is hydrogenated to decompose to MgH_2 and MgCu_2 (A→H process). In the case of hydrogenation by this process, net-like $\text{MgH}_2 + \text{MgCu}_2$ structure is obtained[7, 9]. The other is that the hydrogenation of Mg firstly occurs and then the alloying of MgH_2 and Cu to form MgCu_2 occurs accompanied by H_2 emission (H→A process). The latter two step reaction is described as follows.



From refs. [8] and [11], the standard hydride formation enthalpy and entropy of eq. (2) was calculated to be $+57.7 \text{ kJ}\cdot\text{mol}^{-1}$ and $+112 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. By using these data, the Gibbs energy of the reaction corresponding to eq. (2) is $+10.2 \text{ kJ}\cdot\text{mol}^{-1}$ under the conditions of 573K and 3.3MPa. This indicates that the reaction can proceed to the opposite direction, which is inconsistent with our hypothesis and observed fact. As far as we know, there is no information available to solve this discrepancy.

In the present study, the reactions of MgH_2 with Cu in H_2 atmosphere of various pressures were examined in order to certify our hypothesis, H→A process. In addition, the information obtained through this study will contribute to understanding for the hydrogenation properties of MgCu_2 with C15 Laves type structure which is representative among hydrogen storage alloys.

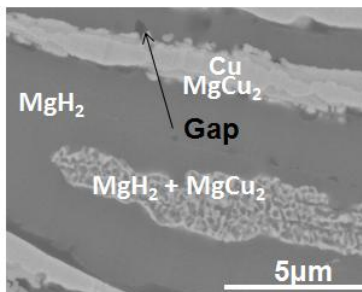


Fig. 1 Backscattered electron image of Mg/Cu super-laminate composite after hydrogenation at 573K and 3.3MPa for 86.4ks.

Experimental Details

The formation of MgCu_2 from MgH_2 and Cu can be proceeded by dehydrogenation of MgH_2 followed by the reaction of the Mg metal with Cu, besides by that based on eq. (2). Therefore, the reaction experiments must be conducted in H_2 atmosphere of the pressure which is higher than the equilibrium one of MgH_2 formation. The criterion of H_2 pressure at each temperature in the experiments was determined by using the data reported by Stampfer, Jr. et al. [12] in the present study.

Powdery 98% MgH_2 (Alfa Aesar, 25-150 mm in practical particle size) and 99.9 % Cu (Kojundo Chemical Laboratory Co., Ltd., 45 mm in nominal particle size) was chosen as starting materials. Because the X-ray diffraction (XRD) profile of the starting MgH_2 powder

indicated the existence of small amount of Mg metal, which seems to be a major component of 2 % impurity, hydrogenation treatment was conducted for the MgH₂ powder under the conditions of $T=673$ K, $p_{H_2}=7.0$ MPa and $t=172.8$ ks (2 days), in order to convert the residual Mg metal into MgH₂.

The rehydrogenated MgH₂ powder was mixed with Cu powder in the molar ratio of 2:1 for 0.3 ks (5 minutes) by using agate mortar and pestle and cold-pressed at 1.73 GPa to obtain pellets with 7 mm in diameter. The reaction was conducted with a conventional Sieverts' type instrument in order to detect pressure increase expected from eq. (2). The reaction temperatures and H₂ pressures were 573 K and 3.3 MPa, 673 K and 3.3 MPa, 673 K and 6.5 MPa, and 673 K and 8.0 MPa, respectively, and reaction time was 86.4 ks (1 day) for all the samples. Metallographic structures and constituent phases were observed by scanning electron microscopy (SEM) and XRD for the samples after the reactions.

Results And Discussion

XRD profiles of the samples after the reaction under the above-mentioned conditions are shown in Fig. 2, together with as cold-pressed sample. Although MgH₂ and Cu metal were observed but Mg metal not in the profile of the as-pressed sample, SEM observation indicated the existence of very small amount of unreacted Mg inside MgH₂ particles. Fortunately the surface area of each MgH₂ particle was completely converted into MgH₂ as far as we observed, indicating that the MgCu₂ formation due to the reaction of unreacted Mg metal with Cu negligibly occurs. In the case of the sample heated at 573K and 3.3MPa, only MgH₂ and Cu metal were detected as well as the as-pressed sample. Then, in the case of the sample heated at 673 K and 3.3 MPa, Mg₂Cu and MgCu₂ phases were observed besides MgH₂ and Cu metal, whereas, in the case of the samples heated at 673 K and 6.5 MPa and 8.0 MPa, only MgCu₂ phase was observed besides the starting constituents.

In order to confirm the form of MgCu₂ appeared, microstructures were examined by using SEM. Fig. 3 shows the backscattering electron image of as-pressed sample and the one heated at 673 K and 8.0 MPa. For as-pressed one, MgH₂ and Cu powders adhere tightly to each other, although gaps due to their original shapes were observed. In the case of the sample heated at 673 K and 8.0 MPa, MgCu₂ phase in the layered form was observed between MgH₂ and Cu particles, together with gaps. These structural features are the same as those of the layered

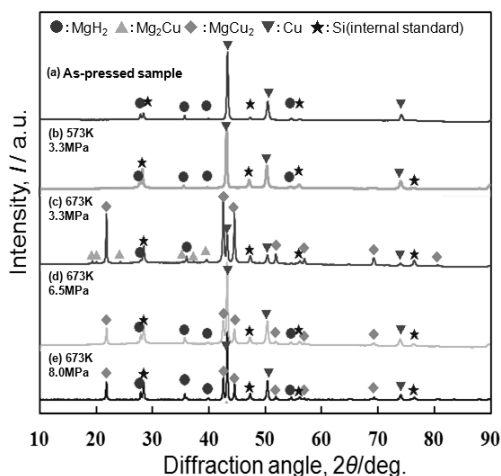


Fig. 2 XRD profiles of (a) as-pressed MgH₂+Cu mixture and samples after heating at (b) 573K and 3.3MPa H₂, (c) 673K and 3.3MPa H₂, (d) 673K and 6.5MPa H₂ and (e) 673K and 8.0MPa H₂

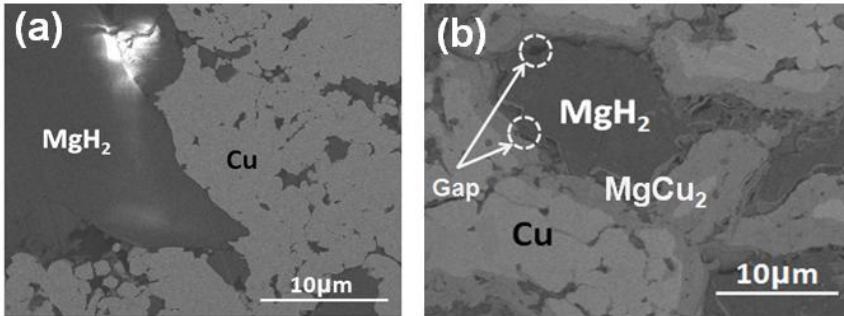
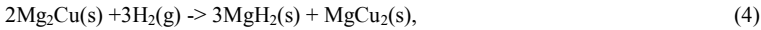


Fig. 3 Backscattered electron images of (a) as-pressed $\text{MgH}_2 + \text{Cu}$ mixture and (b) the mixture heated at 673K under 8.0MPa hydrogen atmosphere.

$\text{MgH}_2 + \text{MgCu}_2$ structures observed in hydrogenated SLCs, as easily found from the comparison of Fig. 3 (b) with Fig. 1.

Fig. 4 shows the van't Hoff plots for the eq. (1), eq. (2) and the hydrogenation of Mg_2Cu expressed as the following equation,



where the corresponding standard hydride formation enthalpy and entropy is taken from ref. 12, ref. 11 and ref. 8, respectively. Our present experimental conditions are also shown as dots in this figure for comparison. Before starting discussion, it is worth to note that, since the starting material is in the most hydrogenated state under the conventional conditions and the reaction in each sample did not complete, the products obtained, which indicates which step the dehydrogenation proceeds to among the three dehydrogenation steps, should be focused on. The line corresponding to eq. (2) is located between eq. (1) and eq. (4), which means that the stability of hydrogenated state from the thermodynamic standpoint would decrease in the order of Mg, MgCu_2 and Mg_2Cu . However, this is strange, because the line corresponding to the following equation obtained from eq. (2) and eq. (4),

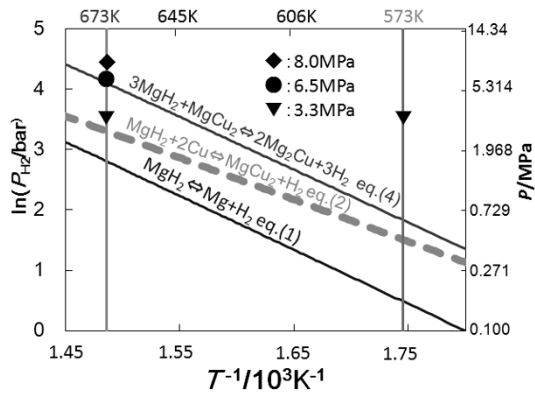


Fig. 4 Van't Hoff plots of $\text{MgCu}_2\text{-H}_2$, $\text{Mg}_2\text{Cu-H}_2$ and Mg-H_2 systems.

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is located between these two lines, meaning that MgH_2+Cu would always be more stable than $\text{MgH}_2+\text{MgCu}_2$ as the hydrogenated state of Mg_2Cu , which disagrees with many previous reports [7-10]. In fact, although the dots indicating (673 K, 3.3 MPa), (673 K, 6.5 MPa) and (673K, 8.0 MPa) are over both the lines for eq. (1) and eq. (2), which means that no change would occur for these samples, intermetallic compounds are obtained. In order to solve the discrepancy, the line corresponding to eq. (2) should be located over the one for eq. (4). If so, the dots indicating (673 K, 6.5 MPa) and (673 K, 8.0 MPa) are over the lines corresponding to eq. (1) and eq. (4) and below the line for eq. (2), which indicates that the dehydrogenation from the state of MgH_2+Cu stops by only the reaction for eq. (2) and only MgCu_2 can be observed as intermetallic compound, and the dot indicating (673 K, 3.3 MPa) is over the line corresponding to eq. (1) and below eq. (4) and eq. (2), which means that the dehydrogenation can proceed by the two reactions for eq. (2) and (4) and both MgCu_2 and Mg_2Cu can be observed.

From the above-mentioned results and discussion, it can be concluded that the metallographic structure shown in Fig. 3 is due to the reaction corresponding to eq. (2). It is worth to note that, in the dehydrogenation according to this equation, two solid phases react to form one solid phase, which is the same manner as in peritectoid reaction in cooling. On the other hands, in the present study, insignificant reaction of MgH_2 with Cu was observed at 573K and 3.3MPa, although the reaction was observed for SLCs under the same conditions. Since SLCs show much faster hydrogenation than the samples prepared by conventional methods, it can be considered that the reaction of the samples used in the study is too slow to show the existence of MgCu_2 , which might be supported by the facts that small amount of MgCu_2 was formed even at 673K, as found in Figs.2 and 3. If it is right, it means that accumulative rolling can contribute to acceleration of not only hydrogenation but also alloying.

Conclusions

The present study can be summarized as follows:

- (1) Layered $\text{MgH}_2+\text{MgCu}_2$ form observed in hydrogenated Mg/Cu super laminate composites is prepared by the reaction of the hydrogenation of Mg followed by alloying Cu with MgH_2 to produce MgCu_2 and H_2 .
- (2) The hydrogenation of MgCu_2 at 673K requires higher H_2 pressure than 8.0MPa and the state of MgH_2+Cu is much less stable than previously reported.
- (3) It can be proposed that accumulative rolling contributes to acceleration of not only hydrogenation but also alloying of Mg/Cu super laminate composites.

Acknowledgments

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