

A variety of microstructures in Mg/Cu super-laminate composites caused by competitive reactions during hydrogenation

**K Tanaka¹, K Shibata², Y Nishida^{2, 3}, K Kurumatani^{2, 4}, R Kondo²,
S Kikuchi⁵ and H T Takeshita²**

¹National Institute of Advanced Industrial Science and Technology (AIST), Osaka, Japan

²Kansai University, Osaka, Japan

³Present address: LIXIL Corporation, Tokyo, Japan

⁴Present address: Fukunishi Foundry Co., Ltd., Osaka, Japan

⁵The University of Shiga Prefecture, Shiga, Japan

E-mail: koji.tanaka@aist.go.jp

Abstract. A variety of microstructures in Mg/Cu super-laminate composites (SLCs) caused by competitive reactions during hydrogenation has been shown experimentally. Two types of MgCu₂ structures, three-dimensional (3-D) network and layer, were observed after initial hydrogenation of Mg/Cu SLCs under the conditions of 573K, 86.4ks in H₂ of 3.3MPa. It was proposed that Mg/Cu SLCs could be hydrogenated by two kinds of processes. The one is alloying Mg with Cu to form Mg₂Cu followed by hydrogenation of Mg₂Cu, leading to the formation of 3-D network of MgCu₂. The other is hydrogenation of Mg followed by the reaction of MgH₂ to Cu, leading to the formation of layer MgCu₂. SEM observations revealed that there existed Mg₂Cu nano-crystals at the interface between Mg and Cu in as-rolled Mg/Cu SLCs, and layer MgCu₂ at the interface between MgH₂ and Cu in pellets of MgH₂ powder and Cu powder heated under the conditions of 673K, 86.4ks in H₂ of 8.0 MPa. The existence of Mg₂Cu nano-crystals enables alloying Mg with Cu at low temperatures (<473K).

1. Introduction

Mg is attractive as hydrogen storage materials owing to the advantages such as light weight, great abundance and high hydrogen storage capacity [1]. However, sluggish dehydrogenation rate and low equilibrium H₂ pressure at ambient temperatures is the issue to be solved for practical application of MgH₂. Thus, various Mg-based alloys and compounds have been investigated to improve the rate and to lower the temperature of hydrogen desorption [2-5].

The improvement of hydrogen absorption/desorption kinetics, its relations with microstructures, and the effect of initial structures of Mg/Cu super-laminate composites (SLCs) on hydrogen absorption/desorption properties have been reported in previous papers for Mg₂Cu-H₂ system [6-8]. Through these investigations, two types of processes have been proposed for hydrogenation of Mg/Cu SLCs: The one is alloying Mg with Cu to form Mg₂Cu followed by hydrogenation of Mg₂Cu, leading to the formation of three-dimensional (3-D) network of MgCu₂ coexisting with MgH₂. The other is hydrogenation of Mg followed by the reaction of MgH₂ to Cu, leading to the formation of layer MgCu₂ existing between MgH₂ layers and Cu layers. The dominant process depends on the initial structures of Mg/Cu SLCs [7]. However, alloying Mg with Cu at low temperatures (<473K) and the reaction of MgH₂ to Cu under H₂ atmosphere are not known in general. In this paper, we reveal these reactions are competitive in Mg/Cu SLCs during initial hydrogenation and therefore microstructures of Mg/Cu SLCs are diverse.

2. Experimental procedure

Commercial Mg (99.9 % purity, 40 μm in thickness) and Cu (99.99 % purity, 10 μm in thickness) metal foils were used as raw materials. The foils were cut into pieces of 20 mm x 30 mm in size. The Mg and the Cu foils were stacked in one alternately. By combining Mg foils with Cu foils in different thickness, a stack with molar ratio Mg/Cu of 2 was prepared.



Mg/Cu SLCs were prepared by a repetitive fold and roll method using a conventional two-high roll mill [9]. Two types of specimens were prepared by changing rolling reduction in cold-rolling. Each of them had a fine and a coarse microstructure, respectively.

Commercial MgH_2 (Alfa Aesar, 98 % purity, 25-150 μm in practical particle size, the main impurity of Mg) and Cu (Kojundo Chemical Laboratory Co., Ltd., 99.9 % purity, 45 μm in nominal particle size) powder were used as raw materials. MgH_2 powder and Cu powder were mixed in the molar ratio of 2 for 300 s by using agate mortar and pestle, and the mixed powder was cold-pressed at the pressure of 1.73 GPa to obtain pellets with 7 mm in diameter.

Mg/Cu SLCs were hydrogenated under the conditions of 573 K, 86.4 ks in H_2 of 3.3 MPa with a Sieverts' type instrument, whereas pellets of MgH_2 powder and Cu powder were heated under the conditions of 673 K, 86.4 ks in H_2 of 8.0 MPa with a Sieverts' type instrument for acceleration. Constituent phases were analyzed by powder X-ray diffraction (XRD). Microstructures of Mg/Cu SLCs, and pellets of MgH_2 powder and Cu powder were observed with a scanning electron microscope (SEM). SEM specimens were prepared by conventional mechanical grinding and polishing followed by ion milling.

3. Results and discussion

Fig. 1 shows backscattered electron (BSE) SEM images of the cross-section of two types of as-rolled Mg/Cu SLCs and those of Mg/Cu SLCs after hydrogenation at 573 K for 86.4 ks in H_2 of 3.3 MPa, "Fine" ((a), (b)) and "Coarse" ((c), (d)). The microstructure of as-rolled "Fine" (fig. 1(a)) was much finer than that of as-rolled "Coarse" (fig. 1(c)). As-rolled "Fine" had the uniform microstructure due to its thinness of Cu layers. In addition, cracks were often observed, and gaps between Mg layers and Cu layers were seldom observed in as-rolled "Fine", whereas cracks were seldom observed and gaps were often observed in as-rolled "Coarse". The cracks were formed because of the severe deformation of accumulative rolling and the gaps were probably formed because of the insufficient contact of foils. It can be thought that an effective cold-rolling was not achieved in as-rolled "Coarse" and therefore the mixing of Mg and Cu was not well done in it, different from as-rolled "Fine".

Microstructures of hydrogenated "Fine" (fig. 1(b)) and "Coarse" (fig. 1(d)) are different from each other. The domain size and the total area of MgCu_2 layers are larger in "Coarse" than "Fine". It is clearly seen in fig. 1 (d) that there exist two types of MgCu_2 structures: the one is 3-D network of MgCu_2 coexisting with MgH_2 and the other is layer MgCu_2 existing between MgH_2 layers and Cu layers. It should be pointed out that pores often stay adjacent to the layer MgCu_2 . The layer MgCu_2 was relatively popular and the 3-D network of MgCu_2 was rare in hydrogenated "Coarse". The situation was reverse in hydrogenated "Fine". These results indicate that there exist two different hydrogenation mechanisms in Mg/Cu SLCs and the dominant mechanism depends on their initial structures.

Since Mg/Cu SLCs were heated from RT to 573 K in H_2 , hydrogenation of Mg and alloying Mg with Cu should be competitive. The hydrogenation mechanisms of Mg/Cu SLCs can be considered as follows. Mg metal can react with Cu metal and H_2 gas under the present conditions. When alloying Mg with Cu occurs prior to hydrogenation of Mg ($\text{A} \rightarrow \text{H}$ process),

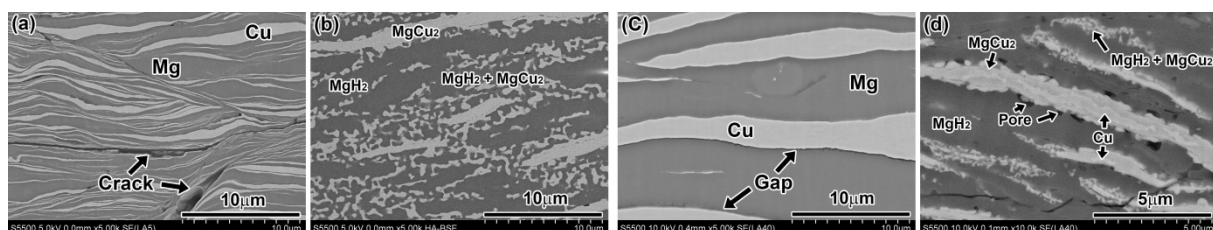
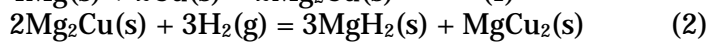
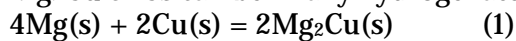
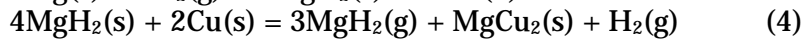
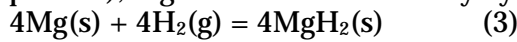


Fig. 1. BSE- SEM images of the cross-section of two types of as-rolled Mg/Cu SLCs ((a), (c)) and those of Mg/Cu SLCs after hydrogenation at 573 K for 86.4 ks in H_2 of 3.3 MPa ((b), (d)). "Fine" ((a), (b)) and "Coarse" ((c), (d)).

Mg/Cu SLCs can be finally hydrogenated by the following two steps,



On the other hand, when hydrogenation of Mg occurs prior to alloying Mg with Cu (H → A process), Mg/Cu SLCs can be finally hydrogenated by the following two steps.



These two hydrogenation processes are illustrated in fig. 2 simply.

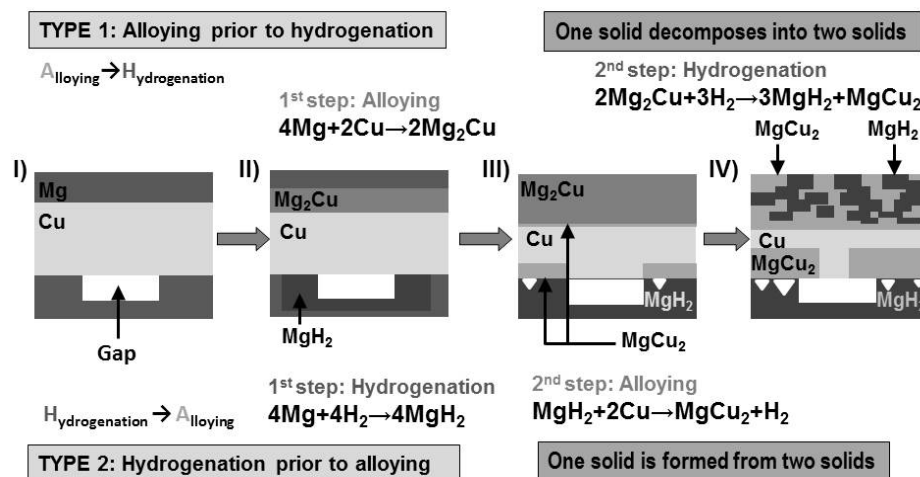


Fig. 2. Schematic models of the microstructure formation mechanism by competitive reactions in Mg/Cu SLCs.

As-rolled “Fine” had a large area of interface between Mg layers and Cu layers, and a short diffusion length for alloying Mg with Cu, due to its fine and uniform structure. Therefore, alloying Mg with Cu followed by hydrogenation of Mg_2Cu should have mainly occurred in as-rolled “Fine” according to the equations (1) and (2). On the other hand, since the mixing of Mg and Cu was not well done in as-rolled “Coarse”, hydrogenation of Mg prior to alloying Mg with Cu significantly should have occurred in as-rolled “Coarse” according to the equations (3) and (4).

Fig. 3 shows SEM images of the cross-section of as-rolled “Fine”. Fig. 3(a) is a secondary electron (SE) image and fig. 3(b) a BSE image of the same area. It is seen that there exist Mg_2Cu nano-crystals at the interface between Mg and Cu in as-rolled “Fine”. Therefore, it is expected that alloying Mg with Cu during heating from RT to 573 K is possible.

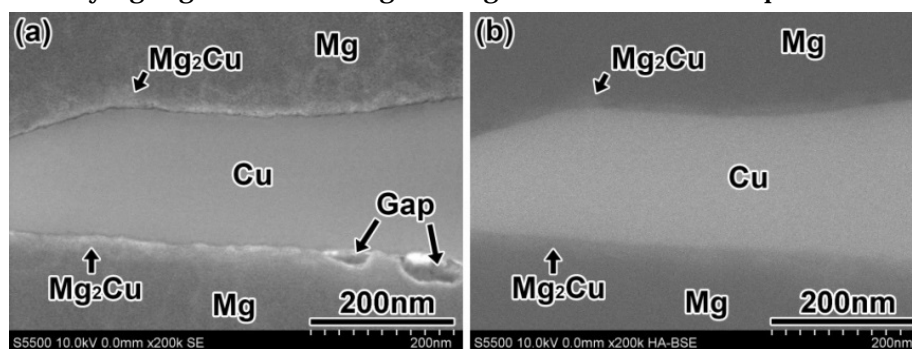


Fig. 3. SEM images of the cross-section of as-rolled “Fine”: (a) SE image, (b) BSE image.

In order to confirm the reaction of MgH_2 to Cu to form MgCu_2 in H_2 , microstructures of pellets of MgH_2 powder and Cu powder before and after heating in H_2 were examined with a

SEM. Fig. 4 shows BSE- SEM images of an as-pressed pellet of MgH_2 powder and Cu powder (a) and one heated under the conditions of 673 K, 86.4 ks in H_2 of 8.0 MPa (b). It is seen from fig. 4 (a) that MgH_2 particles and Cu particles contact tightly to each other, although gaps due to their original shapes were observed. On the other hand, it is seen from fig. 4 (b) that layer MgCu_2 was formed between MgH_2 particles and Cu particles, together with large gaps. These structural features are the same as those of the layer MgCu_2 observed in hydrogenated “Coarse”, fig. 1 (d). It is proved that the not-well-known reaction (4) can occur under H_2 atmosphere. Fig. 3 and 4 support our hypothesis.

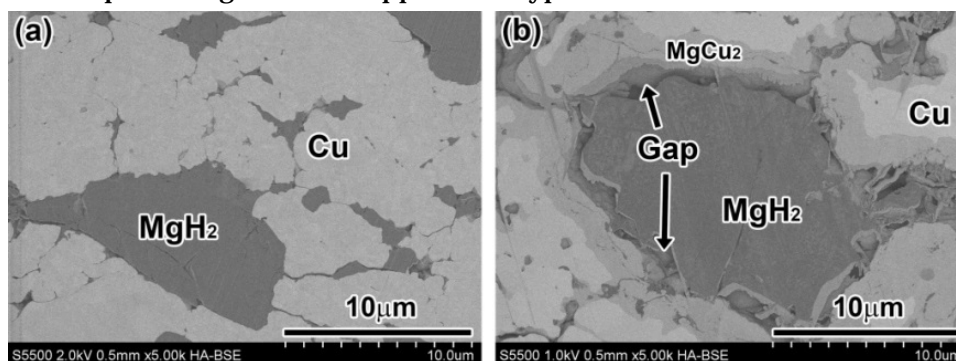


Fig. 4. BSE- SEM images of an as-pressed pellet of MgH_2 powder and Cu powder (a) and one heated under the conditions of 673 K, 86.4 ks in H_2 of 8.0 MPa (b).

4. Conclusions

The present study can be summarized as follows:

- (1) Two types of process are competitive for hydrogenation of Mg/Cu SLCs: the one is alloying expressed by the equation of $4\text{Mg(s)} + 2\text{Cu(s)} = 2\text{Mg}_2\text{Cu(s)}$, followed by hydrogenation, $2\text{Mg}_2\text{Cu(s)} + 3\text{H}_2\text{(g)} = 3\text{MgH}_2\text{(s)} + \text{MgCu}_2\text{(s)}$ (A \rightarrow H process), and the other is hydrogenation, $4\text{Mg(s)} + 4\text{H}_2\text{(g)} = 4\text{MgH}_2\text{(s)}$, followed by alloying, $4\text{MgH}_2\text{(s)} + 2\text{Cu(s)} = 3\text{MgH}_2\text{(g)} + \text{MgCu}_2\text{(s)} + \text{H}_2\text{(g)}$ (H \rightarrow A process).
- (2) The former process forms 3-D network of MgCu_2 coexisting with MgH_2 , and the latter layer MgCu_2 existing between MgH_2 layers and Cu layers.
- (3) The existence of Mg_2Cu nano-crystals formed during repetitive cold-rolling enables alloying Mg with Cu at low temperatures ($<473\text{K}$), therefore hydrogenation of Mg and alloying Mg with Cu can be competitive during initial hydrogenation.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 23560794.

References

- [1] Stampfer, Jr. J F, Holley, Jr. C E and Suttle F 1960 *J. Am. Chem Soc.* **82** 3504
- [2] Orimo S, Fujii H and Ikeda K 1997 *Acta Mater.* **45** 331
- [3] Liang G, Huot J, Boily S and Schulz R 2000 *J. Alloy. Compd.* **305** 239
- [4] Reilly J J and Wiswall R H 1967 *Inorg. Chem.* **6** 2220
- [5] Reilly J J and Wiswall R H 1968 *Inorg. Chem.* **7** 2254
- [6] Tanaka K, Takeichi N, Tanaka H, Kuriyama N, Ueda T T, Tsukahara M, Miyamura H and Kikuchi S 2008 *J. Mater. Sci.* **43** 3812
- [7] Tanaka K, Takeshita H T, Kurumatani K, Miyamura H and Kikuchi S 2013 *J. Alloy. Compd.* **580** S222
- [8] Tanaka K, Takeshita H T, Shin H, Kurumatani K, Kiyobayashi T, Takeichi N, Miyamura H and Kikuchi S 2014 *Mater. Trans.* **55** 1122
- [9] Ueda T T, Tsukahara M, Kamiya Y and Kikuchi S 2005 *J. Alloy. Compd.* **386** 253