INTERGRANULAR AND INTERPHASE BOUNDARIES IN MATERIALS

Investigation of micro-structural transition through disproportionation and recombination during hydrogenation and dehydrogenation in Mg/Cu super-laminates

Koji Tanaka · Nobuhiko Takeichi · Hideaki Tanaka · Nobuhiro Kuriyama · Tamotsu T. Ueda · Makoto Tsukahara · Hiroshi Miyamura · Shiomi Kikuchi

Abstract Micro/nano-structures and hydrogen storage properties of Mg/Cu super-laminates were investigated. Mg/Cu super-laminates showed reversible hydrogenation and dehydrogenation at 473 K. In order to clarify the process of hydrogenation and dehydrogenation at 473 K, we performed TEM observations of micro/nano-structures of the Mg/Cu super-laminates and Mg_2Cu powder prepared by conventional casting method. TEM observations revealed that the as-rolled Mg/Cu super-laminates had laminated structures in size of sub-micrometer thickness composed of Mg and Cu layers with dense lattice defects. The super-laminates after initial activation kept laminated structures and had uniformly distributed pores with a sub-micrometer diameter. On the other hand, the cast Mg_2Cu powder after initial activation had pores only beneath the surface oxide layers. It is considered that these micro/nano-structures of Mg/Cu super-laminates lead to lower dehydrogenation temperature and better kinetics, which would contribute to achieve high-performance hydrogen storage materials.

K. Tanaka (✉) · N. Takeichi · H. Tanaka · N. Kuriyama
National Institute of Advanced Industrial Science and
Technology (AIST), 1-8-31 Midorigaoka, Ikeda,
Osaka 563-8577, Japan
e-mail: koji.tanaka@aist.go.jp

T. T. Ueda · M. Tsukahara
IMRA Material R&D Co. Ltd., 5-50 Hachiken-cho, Kariya,
Aichi 448-0021, Japan

H. Miyamura · S. Kikuchi
The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone,
Shiga 522-0057, Japan

Introduction

Hydrogen storage materials have attracted more and more attention with the advance of R & D activities of fuel cell vehicles. Magnesium is expected as one of the hydrogen storage media, because it can store a large amount of hydrogen up to 7.6 mass%, as MgH_2 [1]. However, MgH_2 is too stable to release hydrogen smoothly; a practical decomposition rate is given at the temperatures above 673 K, which is too high for practical applications. A reduction of the grain size into nano-crystalline dimensions can significantly improve the reaction kinetics and diffusion properties of MgH_2 [2]. In addition, MgH_2 with certain amount of 3d-transition metals lead to even better performance and lower hydrogen desorption temperatures than magnesium [3].

Many Mg-based alloys and compounds have been investigated to improve their kinetics of hydrogenation and dehydrogenation at elevated temperature [4, 5]. However, it is difficult to cast Mg-containing alloys accurately with desirable composition by conventional melt-cast methods because of a high-vapor pressure of Mg, etc., and single-phase Mg-containing compounds cannot be obtained just by casting, due to the phase separation during solidification. Accordingly, many kinds of methods such as mechanical alloying, vapor phase process, combustion synthesis, etc., have been applied for Mg-based alloys and compounds. However, it is difficult to avoid oxidation of Mg in these methods because metal powders are used as a starting material, and therefore Mg-based alloys and compounds made by these methods do not show excellent properties.

Super-laminates have been attracting attention since co-authors Ueda et al. reported that Mg/Cu super-laminates showed reversible hydrogenation and dehydrogenation at

473 K, which was lower than reaction temperatures of conventional Mg-based materials [6]. The Mg/Cu super-laminate absorbs hydrogen at 473 K after initial activation at 573 K. It does not absorb hydrogen at 473 K without initial activation. It is considered that micro/nano-structures of Mg/Cu super-laminates lead to lower dehydrogenation temperature and better kinetics.

In this article, relations between micro/nano-structures of Mg/Cu super-laminates and kinetics of hydrogen absorption/desorption through disproportionation and recombination will be discussed.

Experiments

A commercial Cu sheet (99.99% purity, 10 μm in thickness) and Mg sheet (99.9% purity, rolled to 40 μm in thickness at our laboratory) was used as starting materials. The sheets, cut into pieces of 20 mm × 30 mm in size, were stacked alternately. By combining Cu sheet with Mg sheet in different thickness, a stack with molar volume ratio Mg/Cu of 2 was prepared. Mg/Cu super-laminates were prepared by a repetitive fold and roll method using a conventional two-high roll mill as described previously [7].

The Mg/Cu super-laminates absorb hydrogen at 473 K after initial activation at 573 K. They do not absorb it at 473 K without initial activation. We speculated that the reaction occurred at 473 K because of some phases and/or micro/nano-structures formed during the fold-and-roll process and/or the initial activation. In order to investigate the mechanism of hydrogen absorption and desorption at 473 K, we performed (1) comparison of hydrogenation properties between Mg super-laminates, Mg/Cu super-laminates and Mg_2Cu powder, (2) in-situ XRD analyses to observe phase transformations of the Mg/Cu super-laminates, (3) TEM observations of micro/nano-structures of the Mg/Cu super-laminates and Mg_2Cu powder prepared by a conventional casting method, and (4) thermogravimetry (TG) of the Mg/Cu super-laminates, the Mg_2Cu powder and MgH_2 powder during dehydrogenation.

TEM specimens were prepared by conventional mechanical grinding followed by ion thinning of JEOL EM-09100IS, and observed using JEOL JEM-3000F.

Results

The results of in-situ XRD analyses [8] suggest that the reaction mechanism is as follows: In the hydrogenation process for the super-laminates at 573 K, Mg_2Cu is formed at the interface between Mg and Cu layers through inter-diffusion and then the Mg_2Cu decomposes into MgH_2 and $MgCu_2$. In the dehydrogenation process at 573 K, the

MgH_2 releases hydrogen and returns to metallic Mg. The Mg reacts with $MgCu_2$, and Mg_2Cu is formed again. Through the sequence, Mg_2Cu phase absorbs and desorbs hydrogen reversibly in parallel with disproportionation and recombination of intermetallic phase at 473 K.

Hydrogen content values as a function of reaction time at 573 K are shown in Fig. 1. Mg super-laminates started to absorb hydrogen immediately after hydrogen was introduced; however, the reaction was very slow and did not finish before 48 h. It took about 30 h for uncrushed as-cast Mg_2Cu powder to start to absorb hydrogen, and the reaction was very slow although crushed as-cast Mg_2Cu powder started to absorb earlier than uncrushed as-cast Mg_2Cu powder and the reaction was relatively fast. Un-crushed initially activated Mg_2Cu powder started to absorb immediately; however, the reaction was still slow. On the other hand, as-rolled Mg/Cu super-laminates started to absorb hydrogen immediately, and the reaction was very fast although initially activated Mg/Cu super-laminates started to absorb immediately and the reaction was much faster.

Figure 2 shows TEM images of uncrushed as-cast Mg_2Cu powder (a), uncrushed Mg_2Cu powder during initial activation (b), and uncrushed initially activated Mg_2Cu powder (c). The interesting points of them are summarized as follows: In uncrushed as-cast Mg_2Cu powder, (1) The surface was covered with oxides and hydroxides. (2) The grain size of Mg_2Cu was very large (over few tens micrometer). (3) $MgCu_2$ existed as inclusion. (4) Lattice defects were sparse. In uncrushed Mg_2Cu powder during initial activation, (1) Spongiform structures composed of MgH_2 and $MgCu_2$ were formed. (2) The grain size of MgH_2 was about 10 nm and that of $MgCu_2$ was about few hundreds nm. In uncrushed initially activated Mg_2Cu
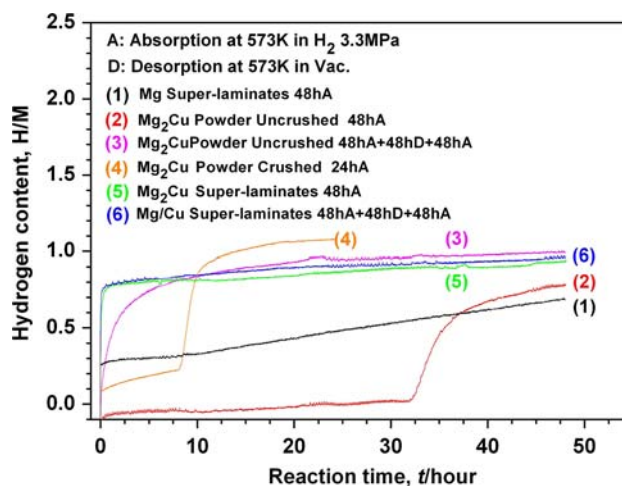
Fig. 1 Hydrogen content values as a function of reaction time at 573 K in Mg super-laminates, $MgCu_2$ powder, and Mg/Cu super-laminates
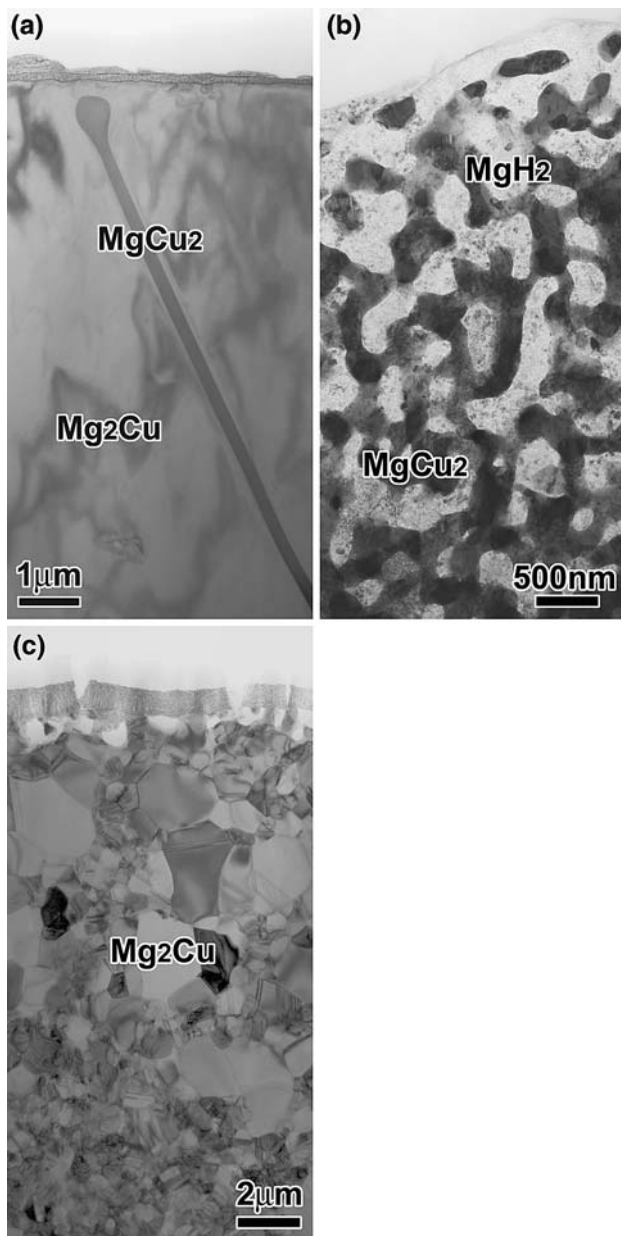
Fig. 2 TEM images of uncrushed as-cast Mg_2Cu powder (**a**), uncrushed Mg_2Cu powder during the initial activation (**b**), and uncrushed initially activated Mg_2Cu powder (**c**)

powder, (1) Cracks appeared in the surface oxides and hydroxides. (2) The pores with a sub-micrometer diameter distributed only along the interface between surface oxides and Mg_2Cu. (3) The grain size of Mg_2Cu became smaller. That of surface area was around 1 micrometer and that of inner area was sub-micrometer. (4) Lattice defects were sparse in the surface area. Lattice defects and strains were introduced in the inner area.

Figure 3 shows TEM images of as-rolled Mg/Cu super-laminates (a), Mg/Cu super-laminates during initial

activation (b), and initially activated Mg/Cu super-laminates (c). The interesting points of Mg/Cu super-laminates are summarized as follows: In as-rolled Mg/Cu super-laminates, (1) Laminated structures in size of sub-micrometer thickness composed of Mg and Cu layers were formed. (2) Lattice defects were dense. (3) The Mg layers had a (0001) preferred-orientation. In Mg/Cu super-laminates during initial activation, (1) Laminated structures were kept. (2) Spongi-form structures composed of MgH_2 and $MgCu_2$ were formed. (3) The grain size of MgH_2 was about 10 nm and that of $MgCu_2$ was about few hundreds nm. In initially activated Mg/Cu super-laminates, (1) Laminated structures were kept. (2) The pores with a sub-micrometer diameter distributed uniformly between Mg_2Cu layers.

Kissinger plot [9] derived from TG measurements is shown in Fig. 4. Activation energy for hydrogen desorption was 217.0 ± 1.4 kJ/mol in initially activated Mg/Cu super-laminates, 139 ± 36.5 kJ/mol in uncrushed initially activated Mg_2Cu powder and 151.9 ± 10.6 kJ/mol in MgH_2 powder. Activation energy for different samples seems almost the same values, which means dominating factors in hydrogen desorption process expected to be the same. However, pre-exponential factor values were high in order of initially activated Mg/Cu super-laminates ($5.94 \times 10^{14} \text{ s}^{-1}$), uncrushed initially activated Mg_2Cu powder ($2.07 \times 10^{11} \text{ s}^{-1}$), and MgH_2 ($1.43 \times 10^9 \text{ s}^{-1}$), which means hydrogen desorption rate is also in this order.

Discussion

Uncrushed as-cast Mg_2Cu powder starts to absorb hydrogen late after hydrogen is introduced because surface oxides and hydroxides disturb the diffusion of hydrogen to Mg_2Cu. It absorbs hydrogen very slowly because large grain size and parse lattice defects cause the slow diffusion of hydrogen. Uncrushed initially activated Mg_2Cu powder starts to absorb immediately because surface oxides and hydroxides are broken and grain size is small. However, the reaction is still slow because pores exist only along the interface between surface oxides and Mg_2Cu, therefore surface area is still small. On the other hand, as-rolled Mg/Cu super-laminates start to absorb hydrogen immediately and the reaction is very fast because small grain size and dense lattice defects cause the fast diffusion of hydrogen. They absorb hydrogen very quickly. Initially activated Mg/Cu super-laminates absorb much faster because pores exist uniformly between Mg_2Cu layers, therefore surface area is larger than as-rolled Mg/Cu super-laminates. Mg super-laminates started to absorb hydrogen immediately; however, the reaction was very slow and did not finish before 48 h. Mg/Cu super-laminates (a composition of MgH_2 and

Fig. 3 TEM images of as-rolled Mg/Cu super-laminates (**a**), Mg/Cu super-laminates during initial activation (**b**), and initially activated Mg/Cu super-laminates (**c**)
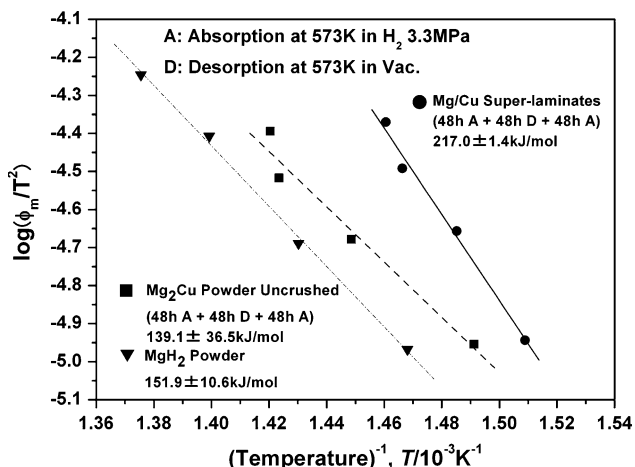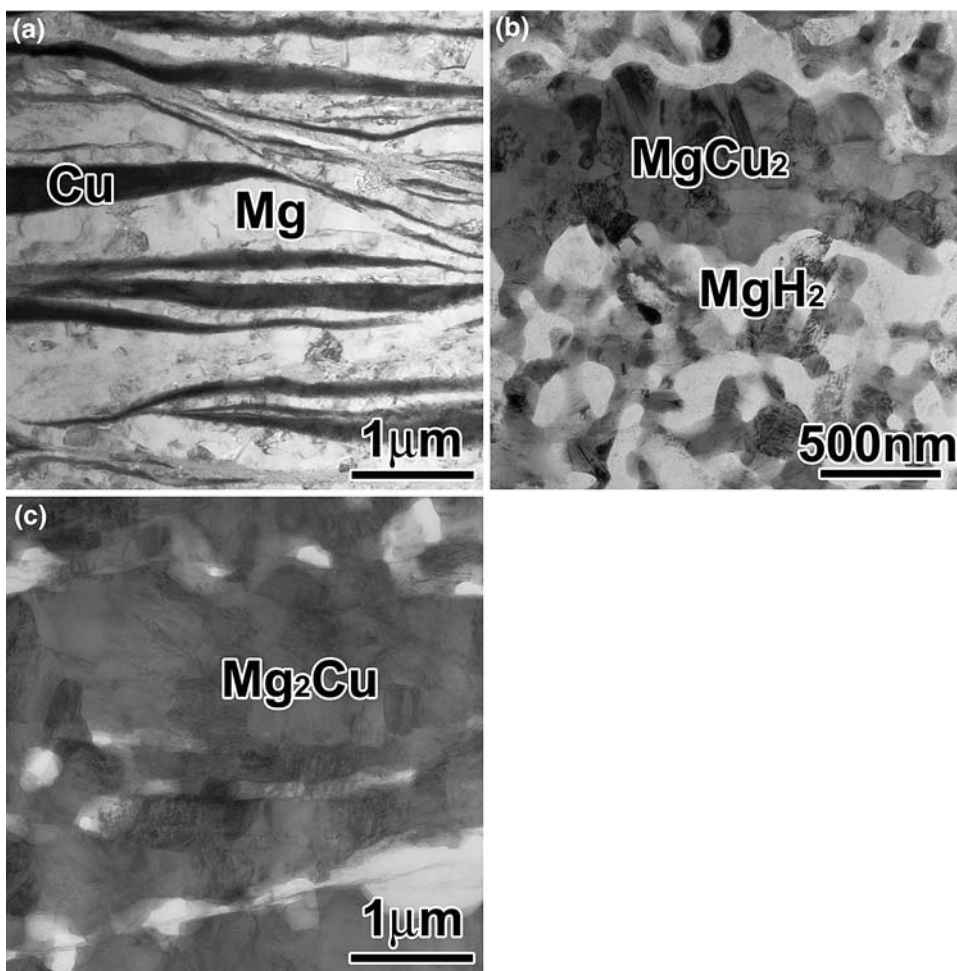
Fig. 4 Kissinger plot derived from thermogravimetry measurements of uncrushed Mg₂Cu powder, Mg/Cu super-laminates and MgH₂

Conclusions

A repetitive fold and roll method and initial activation introduce micro/nano-structures in Mg/Cu super-laminates. It is considered that these micro/nano-structures such as porous and fine grain size of Mg/Cu super-laminates lead to lower dehydrogenation temperature and better kinetics of hydrogen absorption/desorption, which would contribute to achieve high-performance hydrogen storage materials.

MgCu₂ at hydrogenation condition) desorb hydrogen faster than MgH₂ powder, which indicates that MgCu₂ behave as catalysts.

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