Relationship between initial hydrogen absorption properties and microstructures of Mg/Cu super-laminate composites with different accumulative roll bonding cycles

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Abstract. The relationship between initial hydrogen absorption properties and microstructures of Mg/Cu super-laminate composites (SLCs) with different accumulative roll bonding (ARB) cycles was investigated. Hydrogenation of Mg was dominant in Mg/Cu SLCs with 5 and 10 cycles of ARB, whereas that of Mg₂Cu was dominant in Mg/Cu SLCs with 20 and 30 cycles of ARB. The growth rate constants did not show a significant difference among Mg/Cu SLCs with different ARB cycles. It is considered that the average thickness of Mg + Cu layers in as-rolled Mg/Cu SLCs as a function of ARB cycles has a large influence on initial hydrogenation properties and microstructure formation processes.

1. Introduction

Mg is still considered as a good candidate for hydrogen storage materials because of its high hydrogen storage capacity of 7.6 mass% in the form of reversible MgH₂ [1, 2], low cost, light weight and high abundance. Nevertheless, its hydrogen absorption/desorption kinetics is sluggish even at elevated temperatures (> 573 K) associated with its strong thermodynamic stability of standard formation enthalpy -74 kJ (mol H₂)⁻¹ and this effectively places a limit on its utility [3]. To solve these drawbacks, many efforts have been made recently, such as appropriate alloying of Mg [4-6], adding catalysts [7-11] and manufacturing nano-crystalline powder [12, 13].

Since it was reported that accumulative roll bonding (ARB) is effective for the preparation and hydrogenation of Mg-Ni based hydrogen storage alloys [14], super-laminate composites (SLCs) prepared by this method have been investigated on the hydrogenation properties of Mg-Cu [15, 16], Mg-Pd [17-19], Mg-Al [20], and Mg-Ti-Ni [21] systems.

In the case of Mg-Cu system, for example, Mg/Cu SLCs exhibit reversible hydrogen absorption/desorption at 473 K after initial activation at 573 K under the hydrogen atmosphere of 3.3 MPa [15], although Mg₂Cu alloys prepared by conventional melting method require 573 K [22]. From our previous research [16], it is found that the large surface area and the short diffusion distance
because of fine structures of Mg/Cu SLCs after initial activation at 573 K improve the dynamics of hydrogen absorption/desorption, and therefore lower the reaction temperature to 473 K.

Hydrogen absorption starts about at 453 K during the heating process of initial activation of Mg/Cu SLCs (hydrogenation under the condition of 573 K, in H₂ atmosphere of 3.3 MPa and dehydrogenation under the condition of 573 K in vacuum). During this, hydrogenation of Mg and alloying of Mg with Cu followed by hydrogenation of Mg₂Cu occur competitively [23-25]. However, the formation mechanism of microstructures is not fully understood yet. For example, how much of Mg₂Cu can be formed in about ten minutes before temperature reaches 453 K during the heating process of initial activation.

It is reported that severe plastic deformation (SPD) such as high-pressure torsion (HPT) and equal-channel angular pressing (ECAP) can enhance atomic diffusion and promote solid-state reactions because of an increase in the density of lattice defects such as vacancies, dislocations and grain boundaries [26-31]. Therefore, it is important to know the effect of ARB. In this paper, we examined the relationship between initial hydrogen absorption properties and microstructures of Mg/Cu SLCs with different ARB cycles.

2. Experimental procedure
Commercial pure Mg (Takeuchi Metal Foil & Powder Co., LTD., 99.9 % of purity, 250 μm in thickness) and oxygen-free Cu (Fukuda Metal Foil & Powder Co., LTD, 99.98 % of purity, 10 μm in thickness) were used as starting materials. Mg foils were polished with #600 sandpaper in order to remove oxide layers and cold-rolled to 40 μm. These were cut into 20 mm x 40 mm in size and annealed at 673 K for 3.6 ks in Ar atmosphere of 0.1 MPa in order to remove internal stress and strain. Cu foils were cut into 20 mm x 40 mm in size and annealed at 873 K for 3.6 ks in Ar atmosphere of 0.1 MPa. Surfaces of Mg and Cu foils were cleaned with dilute hydrochloric and nitric acid, respectively. Twenty pairs of Mg and Cu foils were stacked in one. By combining Mg foil with Cu foil in different thickness, a stack with molar volume ratio Mg/Cu of 2 was prepared. Prior to ARB, this stack was wrapped up in a Cu plate with 1 mm in thickness and pressed under the condition of 735 MPa for 300 s in order to enhance adhesion and to prevent slip between Mg and Cu foils during ARB. The wrapped stack was roll-bonded at room temperature in air to get a Mg/Cu laminate using a conventional two high-roll mill until its length became about twice longer than the original one. Then the laminate was cut into half and piled. The piled laminate was wrapped up in a Cu plate again and then roll-bonded as described above. This procedure was repeated to fabricate a Mg/Cu super-laminate composite (SLC). Four types of specimens were prepared by changing the number of above procedure, which are 5, 10, 20 and 30 cycles of ARB.

Mg/Cu SLCs were hydrogenated under the conditions of 573 K, 86.4 ks in H₂ atmosphere of 3.3 MPa with a Sieverts’ type instrument to measure the initial hydrogen absorption properties. Constituent phases were identified by powder X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS). Microstructures of Mg/Cu SLCs were observed with a scanning electron microscope (SEM) and a scanning transmission electron microscope (STEM). SEM and STEM specimens were prepared by conventional mechanical grinding and polishing followed by ion milling.

The formation mechanism of microstructures in Mg/Cu SLCs during initial hydrogenation through competitive reactions was estimated by evaluating the growth rate constants of Mg₂Cu in Mg/Cu SLCs under 453 K with different ARB cycles. The measurement method of the growth rate constants of Mg₂Cu in Mg/Cu SLCs was reported in detail in Ref [30] and the experimental results of the growth rate constants of those with different cycles of ARB will be reported in detail elsewhere.

3. Results and discussions
Fig. 1 shows cross-sectional backscattered electron (BSE) SEM images of as-rolled Mg/Cu SLCs with different ARB cycles; (a) 5, (b) 10, (c) 20, (d) 30 cycles, respectively. Dark contrast is Mg and bright contrast is Cu. The microstructures of Mg/Cu SLCs became finer as the number of ARB cycles increased. For example, the average thickness of Mg and Cu layers in the case of 10 cycles of ARB
Fig. 1 (b)) was 443 and 162 nm, respectively, whereas that in the case of 30 cycles (fig. 1 (d)) was 123 and 64 nm, respectively. Fig. 1 (a) and (b) look similar, and fig. 1 (c) and (d) look similar. It seems that there are some differences between these two groups.

Fig. 2 shows the initial hydrogenation properties of as-rolled Mg/Cu SLCs with different ARB cycles under the conditions of 573 K, 86.4 ks (24 h) in H₂ atmosphere of 3.3 MPa; (a) 5, (b) 10, (c) 20, (d) 30 cycles, respectively.

Fig. 2. Initial hydrogenation properties of as-rolled Mg/Cu SLCs with different ARB cycles under the conditions of 573 K, 86.4 ks (24 h) in H₂ atmosphere of 3.3 MPa; (a) 5, (b) 10, (c) 20, (d) 30 cycles, respectively.
Fig. 3 shows cross-sectional BSE-SEM images of Mg/Cu SLCs after initial hydrogenation under the conditions of 573 K, 86.4 ks (24 h) in H₂ atmosphere of 3.3 MPa with different ARB cycles; (a) 5, (b) 10, (c) 20, (d) 30 cycles, respectively. The size and the total area of MgH₂ layers were (a) > (b) > (c) > (d). Hydrogenation reaction of Mg₂Cu is as below.

\[ 2\text{Mg}_2\text{Cu} + 3\text{H}_2 = 3\text{MgH}_2 + \text{MgCu}_2 \]

When Mg₂Cu absorbs hydrogen, it disproportionate to MgH₂ and MgCu₂ and show network structures of MgH₂ + MgCu₂ [15, 23, 25]. The size and the total area of network structures of MgH₂ + MgCu₂ were (d) > (c) > (b) > (a).

Table 1. Average thickness of Mg and Cu before initial hydrogenation, and approximate values of area fractions of MgH₂ and MgH₂ + MgCu₂ after initial hydrogenation in Mg/Cu SLCs with 10, 20 and 30 cycles of ARB.

| Samples          | Thickness of Mg and Cu | Approximate values of area fractions |
|------------------|------------------------|-------------------------------------|
|                  | Mg (nm) | Cu (nm) | MgH₂ (Hydrogenated Mg) | MgH₂ + MgCu₂ (Hydrogenated Mg₂Cu) |
| 10 cycles of ARB | 443     | 162     | 0.4                    | 0.1                                 |
| 20 cycles of ARB | 173     | 65      | 0.3                    | 0.4                                 |
| 30 cycles of ARB | 123     | 64      | 0.2                    | 0.6                                 |

The average thickness of Mg and Cu before initial hydrogenation, and the approximate values of area fractions of MgH₂ (hydrogenated Mg) and MgH₂ + MgCu₂ (hydrogenated Mg₂Cu) were estimated from fig. 1 and 3, and summarized in table 1. It is seen that hydrogenation of Mg was dominant in Mg/Cu SLCs with less 10 ARB cycles, and that of Mg₂Cu was dominant in Mg/Cu SLCs with over 20 ARB cycles. This result can explain very well the features of fig. 2, since the hydrogen absorption/desorption kinetics of Mg is sluggish even at elevated temperatures (> 573 K) [3] and Mg₂Cu can absorb hydrogen fairly rapidly at 573 K [22]. From these results, it is expected that
something happened in Mg/Cu SLCs between 10 cycles and 20 cycles of ARB, and showed different initial hydrogenation properties.

Fig. 4 shows schematic models of microstructures in Mg/Cu SLCs formed during (a) the heating process and (b) the hydrogenation process of initial hydrogenation. Since Mg/Cu SLCs were heated from room temperature to 573 K in H₂ atmosphere during initial hydrogenation, hydrogenation of Mg and alloying of Mg with Cu followed by hydrogenation of Mg₂Cu are competitive. From the experiments of Mg-Cu diffusion couples [32, 33], it is expected that core-shell like structures shown in fig. 4 (a) can be formed during the heating process [15, 25]. Constituent phase of the core-shell like structures are Cu, MgCu₂, Mg₂Cu, and Mg in the order from the core to the shell. A Mg shell becomes MgH₂ and a Mg₂Cu shell disproportionates to MgH₂ + MgCu₂ to form network structures after hydrogenation as shown in fig. 4 (b). It is considered that the difference of the amount of Mg₂Cu formed before hydrogenation causes the big differences of microstructures in Mg/Cu SLCs after hydrogenation. Therefore, it is expected that the growth rate constants of Mg₂Cu change depending on the number of ARB cycles.

Figure 4. Schematic models of microstructures in Mg/Cu SLCs formed during (a) heating and (b) hydrogenation process of initial hydrogenation [15, 25].

Since MgCu₂ is not formed under 473 K [34, 35] and hydrogen absorption of Mg/Cu SLCs with 20 cycles of ARB starts at about 453 K, the growth rate constants of Mg₂Cu in Mg/Cu SLCs with different ARB were measured under 453 K. The measurements were performed following the method written in ref. [30] and the details of results will be reported elsewhere. Table 2 summarizes the growth rate constants of Mg₂Cu in Mg-Cu diffusion couples and Mg/Cu SLCs with 10, 20 and 30 cycles of ARB. The growth rate constants of Mg/Cu SLCs with 5 cycles of ARB could not be measured because Mg₂Cu did not grow enough owing to the insufficient contact between Mg and Cu foils.

Table 2. Growth rate constants of Mg₂Cu in Mg-Cu diffusion couples, and Mg/Cu SLCs with 10, 20 and 30 cycles of ARB.

| Samples                        | Growth constant k / m² s⁻¹ |
|--------------------------------|---------------------------|
|                                | 373 K                     | 413 K                     | 453 K                     |
| Mg-Cu diffusion couples [32]   | 2.0 x 10⁻²⁵                | 2.7 x 10⁻²³                | 1.5 x 10⁻²¹                |
| 10 cycles of ARB               | 1.2 x 10⁻²¹                | 1.7 x 10⁻²⁰                | 4.1 x 10⁻¹⁹                |
| 20 cycles of ARB               | 2.2 x 10⁻²¹                | 9.5 x 10⁻²⁰                | 7.7 x 10⁻¹⁹                |
| 30 cycles of ARB               | 1.7 x 10⁻²¹                | 4.6 x 10⁻²⁰                | 7.6 x 10⁻¹⁹                |

The growth rate constants of Mg₂Cu in Mg/Cu SLCs is approximately ten to the second - forth order larger than that of Mg-Cu diffusion couples below 453 K. It indicates that Mg₂Cu can grow at low temperature with sufficient rate in Mg/Cu SLCs. It can be said that the growth rate constants were
increased by ARB. However, there was no big difference among Mg/Cu SLCs with different ARB cycles contrary to our expectation.

As mentioned above, it is reported that SPD such as high-pressure torsion (HPT) and equal-channel angular pressing (ECAP) can enhance atomic diffusion and promote solid-state reactions because of an increase in the density of lattice defects such as vacancies, dislocations and grain boundaries [26-31]. It is reasonable to consider the introduction of a high density of vacancies and dislocation, and the grain refinement during ARB process.

Fig. 5 shows cross-sectional bright field STEM images of as-rolled Mg/Cu SLCs with 5 and 10 cycles of ARB. Mg$_2$Cu was formed during ARB process [30]. The grain size of Mg was 590 nm in Mg/Cu SLCs with 5 cycles of ARB (fig. 5 (a)) and 180 nm with 20 cycles of ARB (fig. 5 (c)). Since the grain size of annealed Mg is about 15 um, it can be said that Mg showed dynamic recrystallization even in Mg/Cu SLCs with 5 cycles of ARB. The average grain size of Mg in the case of 5 cycles of

**Figure 5.** Bright field STEM cross-sectional images of Mg/Cu SLCs with different ARB cycles; (a) and (b) 5, and (c) and (d) 20 cycles of ARB, respectively.

![As-rolled and After heating process](image)

**Figure 6.** Schematic models representing change of microstructures in Mg/Cu SLCs during heating process.
ARB was larger than that of 30 cycles of ARB. However, that is because of inhomogeneity. The grain size of most grains in Mg/Cu SLCs with 5 cycles of ARB was almost as same as 20 cycles of ARB, although large grains in Mg/Cu SLCs with 5 cycles of ARB (lower area in fig. 5(a)) made the average grain size larger. The dislocation density of Mg was high in both specimens. As seen in fig. 5 (b) (5 cycles of ARB) and (d) (20 cycles of ARB), the same things can be said about Cu. That is the reason why the growth rate constants were almost same among Mg/Cu SLCs with 10, 20 and 30 cycles of ARB.

Fig. 6 shows schematic models representing a change of microstructures in Mg/Cu SLCs during the heating process. The upper row is a thick layer structure case and the lower row is a thin layer structure case. If the growth rate constants are the same, Mg$_2$Cu can grow the same length during the heating process. As can be seen in fig. 6, Mg is still remained in thick layer structure case, whereas Mg$_2$Cu is dominant in the thin layer structure case. Therefore, it can be concluded that this is the reason why the hydrogenation of Mg was dominant in the case of 5 and 10 cycles of ARB, and the hydrogenation of Mg$_2$Cu was dominant in the case of 20 and 30 cycles of ARB. This change of dominant hydrogen absorption phase seems to occur at the critical average thickness of Mg + Cu layers. From table 1, the critical average thickness of Mg + Cu layers can be estimated about 200 nm.

4. Conclusion

The growth rate constants of Mg$_2$Cu did not show a significant difference among Mg/Cu SLCs with over 10 cycles of ARB. However, the average thickness of Mg + Cu layers in as-rolled Mg/Cu SCLs became thinner as the cycle number of ARB increased.

The average thickness of Mg + Cu layers is the key factor which regulates the volume fraction of Mg$_2$Cu formed during the heating process of initial hydrogenation since the growth rate constants of Mg$_2$Cu is relatively constant in Mg/Cu SLCs with over 10 cycles of ARB.

Hydrogenation of Mg is dominant in Mg/Cu SLCs with over the critical average thickness and hydrogenation of Mg$_2$Cu is dominant in Mg/Cu SLCs with under the critical average thickness. The critical thickness is about 200 nm which is reached by ARB more than 10 cycles.

The volume fraction of Mg$_2$Cu formed during the heating process of initial hydrogenation determines initial hydrogen absorption properties and microstructures of Mg/Cu SLCs after initial hydrogenation.

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