Mg is one of the promising candidates among hydrogen storage materials because of its abundance, inexpensiveness, light weight, and hydrogen absorption capacity of 7.6 mass% to form MgH₂. However, the standard formation enthalpy of MgH₂ is -76 kJ/(mol H₂)⁻¹ and too low to achieve hydrogen desorption under moderate conditions. Another problem is the sluggish reaction of Mg with H₂ gas. Thus, various Mg-based alloys and compounds have been investigated to improve the rate and to lower the temperature of hydrogen absorption/desorption.

Super-laminate composites (SLCs) have been attracting attention since Ueda et al. reported that Mg/Cu SLCs showed reversible hydrogen absorption/desorption at 473K [1]. The improvement of hydrogen absorption/desorption kinetics, its relations with micro/nano-structures, and the effect of initial structures of Mg/Cu SLCs on hydrogen absorption/desorption properties have been reported in previous papers for Mg₂Cu-H₂ system [2, 3]. However, the structure-property relationship of Mg/Cu SLCs is not fully understood yet. In this paper, we examined the formation mechanism of micro/nano-structures through competitive reactions during initial hydrogenation in Mg/Cu SLCs.

As shown in fig. 1, three types of MgCu₂ forms, (a) an open 3D-network, (b) a sheathing 3D-network and (c) a layer, were observed after hydrogenation of Mg/Cu SLCs at 573K and 3.3MPa of H₂ for 86.4ks. It is known that Mg₂Cu shows a disproportionation reaction to MgH₂ and MgCu₂ during hydrogenation like fig. 1(a). We propose that Mg/Cu SLCs could be hydrogenated by other two types of processes [3]. The one is simultaneous hydrogenation of Mg and alloying Mg with Cu to Mg₂Cu followed by hydrogenation of Mg₂Cu, leading to the formation of sheathing MgCu₂ 3D-network. The other is hydrogenation of Mg followed by a reaction of MgH₂ with Cu, leading to the formation of MgCu₂ layer.

In order to elucidate the formation mechanism, Mg/Cu SLCs, pellets of MgH₂ and Mg₂Cu, and those of MgH₂ and Cu powder as references were prepared, and micro/nano-structures of them were examined with SEM. Mg/Cu SLCs were hydrogenated at 573 K and 3.3 MPa of H₂ for 86.4 ks, whereas two kinds of pellets were heated at various temperatures and hydrogen pressures for 86.4 ks.

The formation of sheathing MgCu₂ 3D-network and layered MgCu₂ is confirmed by SEM observations of a pellet of MgH₂ and Mg₂Cu powder and those of MgH₂ and Cu powder, respectively.

References

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Fig. 1: Fig. 1 Back Scattered Electron Images of Mg/Cu SLCs after hydrogenation under the conditions of 573 K, 86.4 ks and 3.3 MPa of H₂. (a) Hydrogenation of Mg is late after alloying Mg with Cu. (b) Hydrogenation of Mg and alloying Mg with Cu starts at the almost same time. (c) Hydrogenation of Mg is early before alloying Mg with Cu.