High-Pressure Synthesis of Novel Hydrides in Mg-RE-H Systems (RE= Y, La, Ce, Pr)

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Metal hydrides will become important energy carriers in mobile vehicles, therefore the mass of the system needs to be reduced. The automobile industry has set more than 5% weight percent of hydrogen as a target for efficient hydrogen storage. A very promising approach is to use magnesium. Mg-based alloys are well known to exhibit a high hydrogen capacity. But there are some problems of their high reaction temperature and low kinetics. To reduce the problems, a number of studies exploring new Mg-based alloys and hydrides have been conducted with conventional metallurgy technique such as melting, sintering and ball milling.

As another approach, high-pressure synthesis has been to explore novel Mg-based hydrides. The present authors reported new hydrides such as Mg2Ni3H3.4 and (Ca, Mg)2NiHδ and Mg2LaH7 by using a cubic-anvil-type apparatus. Since rare earth elements (RE) have large compressibility of the atomic radii (e.g. the radius of La is reduced more than 12% under 5 GPa), there seems to be possibility to obtain noel hydrides in the Mg-RE-H systems. RE hydrides have also high molcces of hydrogen. Therefore, the purpose of this study is to explore new hydrides of the Mg-RE systems (RE= Y, La, Ce, Pr) using the cubic anvil-type apparatus and clarify the crystal structures, thermal stabilities and hydrogen contents of newly found hydrides.

The raw materials were MgH2, YH3, LaH3, CeH3 and PrH3 powders. Powder mixtures were pressed into a pellet and put into GPa pressure apparatus. Samples were prepared at 800˚C for 2h under 2-5GPa.

In Mg-Y-H system, MgY2Hx with a FCC-type structure has been prepared at 800˚C under more than 3GPa as shown in Fig. 1. Fusion extraction analysis showed 3.7mass% of the hydrogen amount in MgY2Hx, corresponding to x=7.8. The lattice constant of MgY2H~7.8 was found to be 0.51657(2)nm. This value is smaller than that of LaH3 (0.5602nm) showing same FCC structure.

For MgH2 –x mol%LaH3, the new hydride was obtained in the range of 25<x<33 (Fig. 2). The hydrogen content of the new hydride with x=25 was found to be 4.1mass% by means of fusion extraction analysis, corresponding to Mg3LaH9. The crystal structure of the hydrides with x=25, Mg3LaH9 was a primitive tetragonal structure with lattice constants of a=0.8172 and c=0.5015. The thermal stability of new hydrides with x=25-33 was investigated by DSC as shown in Fig. 3. For example, the x=25 showed an endothermic peak at around 620K. Since the onset appears to decrease with increasing x in the rage of 25<x<33, the new hydride has a compositional range as suggested in Fig. 2.

Mg-Ce-H and Mg-Pr-H systems were also explored. Mg3CeH9 and Mg3PrH9 with a primitive tetragonal structure were synthesized under 5GPa. The hydrogen content of these hydrides were 3.7 and 3.9mass%, respectively.

Fig. 1 X-ray diffraction patterns of MgH2-67mol%YH3 prepared at 800˚C for 2h under 2-5GPa
Fig. 2 X-ray diffraction patterns of MgH2-x mol%LaH3 prepared at 800˚C for 2h under 5GPa
Fig. 3 The DSC curves of of MgH2-x mol%LaH3 prepared at 800˚C for 2h under 5GPa