Effect of Cu or Ti Substitution in MgNi on Crystal Structure and Hydrogen Absorption-Desorption Properties

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Our previous study showed the noble MgNi intermetallic compound with a CuTi-type crystal structure could be synthesized from amorphous MgNi precursor under more than 5 GPa by high pressure synthesis and could be hydrogenated into novel hydride with a CsCl-type crystal structure at 355 K under 2 MPa of hydrogen. In this study, hydrogen absorption-desorption properties of the MgNi compound with CuTi-type structure were investigated. It was found that the MgNi with CuTi-type structure absorbed and desorbed hydrogen reversibly at 473 K. Effects of substitution of Ni by Cu or Ti in the MgNi compounds were also investigated. Ternary $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.2, 0.5$) and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ compounds were synthesized from amorphous precursors by high pressure synthesis. The $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.2, 0.5$) and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ have CsCl-type crystal structure. The lattice parameter of $\text{MgNi}_{1-x}\text{Cu}_x$ increased with increasing of Cu content. $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.2, 0.5$) and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ could be hydrogenated under hydrogen pressure of 2 MPa and the crystal structure of these hydrides were CsCl-type structure. The hydrogen desorption temperature of these hydrides decreased with increasing of amount of Cu or Ti substitution of Ni. The substitution of Ni by Ti in MgNi improved the hydrogen absorption capacity from 1.65 to 2.06 mass%. [doi:10.2320/matertrans.M2009064]

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1. Introduction

High-pressure synthesis is known to be an effective method to explore novel compounds. In the field of developments of hydrogen storage media, many new hydrides have been reported with this technique. High-pressure synthesis can be mainly classified into two groups according to by means of pressure transmitting media, one method is autoclave with gaseous media, the other is anvil-type apparatus with solid media. For example, CsMgH_3 ,¹⁾ LaMg_2H_7 ,²⁾ and CeMg_2H_7 ²⁾ were synthesized under a high pressure of about 10 MPa by using the autoclave apparatus. On the other hand, Mg_3MnH_7 ,³⁾ and $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ ⁴⁾ and so on, were reported with high pressure up to GPa order using anvil-type apparatus. We reported that $\text{Mg}_2\text{Ni}_3\text{H}_{3.4}$,^{5,6)} Mg_3MnH_y ,⁷⁾ MgY_2H_8 ,⁷⁻¹⁰⁾ Mg_3REH_9 (RE = La, Ce, Pr),^{10,11)} MgTM_2H_y (TM = Zr, Nb, Hf),¹²⁾ $\text{Mg}_{6.2}\text{NbH}_y$,¹²⁾ Mg_xTaH_y ,¹²⁾ Mg_3MoH_y ,¹³⁾ Mg_4NbH_y ,¹³⁾ MgNi_2H_y ,^{14,15)} Mg_2LiH_y ,¹⁶⁾ MgCu ,¹⁷⁾ $\text{Mg}_{54}\text{Cu}_{17}$ ¹⁷⁾ and MgNi_2 of high pressure phase¹⁸⁾ were obtained by this apparatus.

Mg-based alloys and their hydrides have been extensively studied because of their promising hydrogen storage capacity as hydrogen storage media. Among Mg-based materials, Mg–Ni system has been most widely studied since Reilly firstly reported Mg_2NiH_4 as hydrogen storage alloy.¹⁹⁾ However, a major shortcoming of the Mg-based hydrides is that those need high operating temperatures, especially for dehydrogenation. There are two intermetallic compounds as equilibrium phases in the Mg–Ni binary system, that is, Mg_2Ni and MgNi_2 .²⁰⁾ MgNi_2 , which have known not to react with hydrogen,¹⁹⁾ was also hydrogenated by high pressure hydrogen up to 2 GPa.^{14,15)} To improve their hydrogenation and dehydrogenation properties, it is important to explore new Mg-based hydrides or intermetallic compounds. Orimo *et al.* have reported the hydriding properties of amorphous MgNi and its nano-scaled structure.²¹⁾ The amorphous MgNi

was hydrogenated by mechanical grinding under hydrogen atmosphere of 1 MPa and the hydrogen content was 2.2 mass%.²¹⁾

On the other hand, we reported that MgNi with CuTi-type structure was synthesized from amorphous MgNi precursor by high-pressure synthesis.²²⁾ The crystalline MgNi of high pressure phase with CuTi-type crystal structure was hydrogenated into novel hydride with CsCl-type structure in metal sub-lattice at 355 K under hydrogen pressure of 2 MPa and the hydride was decomposed into Mg_2Ni and MgNi_2 up to 623 K under an Ar atmosphere.²²⁾

Recently, it was revealed that the MgNi hydride desorbed hydrogen returned to the CuTi-type structure crystal at the lower temperature of 473 K. So there is a possibility that the MgNi absorbs and desorbs hydrogen reversibly.

The purpose of the present work is to investigate reversible hydrogen absorption-desorption properties of MgNi, and to study the effect of Cu or Ti addition to MgNi on their crystal structure and hydrogen absorption-desorption properties.

2. Experimental Procedures

The starting materials were Mg (99.9 mass%), Ti (99.9 mass%), Ni (99.9 mass%) and Cu (99.9 mass%) powders. Amorphous MgNi, $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.2, 0.5$) and $\text{MgNi}_{1-x}\text{Ti}_x$ ($x = 0.1$) were used as precursors, which were prepared by mechanical alloying for 80 h with rotation speed of 300 rpm from Ni, Ti, Cu and Mg_2Ni powders. Mg_2Ni was prepared by sintering at 803 K for 5 h under Ar-3 mol% H_2 atmosphere from mixture of Mg and Ni powders. Then, amorphous precursor was pressed into pellet. The pellet was put into a BN container. The container was then put into a graphite tube heater, and placed into a pressure media made from pyrophyllite. All the manipulations of sample preparations were conducted in a glove box filled with an Ar gas. The sample was placed into the anvil-type apparatus and then high-pressure synthesis was carried out with it. Samples were heated at 523–623 K for 2 h under 6 GPa and then quenched

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into ambient temperature and pressure. Phase identification was carried out by X-ray diffractometry (XRD). Then, lattice parameters were refined by CELL²³⁾ program. Thermal stability of the samples was measured by differential scanning calorimeter (DSC) under an Ar atmosphere. Hydrogenation of the samples was also performed by DSC under hydrogen pressure of 2 MPa. The thermal gas desorption properties were examined by thermal desorption mass spectroscopy (TDMS) combined with thermogravimetry (TG) and differential thermal analysis (DTA). The pressure composition isotherms (PCT curves) were measured by using Sieverts-type apparatus.

3. Results and Discussion

Figure 1 shows XRD patterns of MgNi prepared at 623 K for 2 h under 6 GPa, and the sample after hydrogenation of MgNi and after dehydrogenation of the MgNi hydride. MgNi hydride with CsCl-type structure in metal sub-lattice desorbed hydrogen and returned to MgNi compound with CuTi-type crystal structure by heating up to 473 K although a small amount of Mg₂Ni was observed. The results of X-ray diffraction confirmed that the crystal structure of MgNi desorbed hydrogen was same as that before absorption of hydrogen. To investigate hydrogen absorption-desorption properties of MgNi compound, PCT curves were measured. Figure 2 shows PCT curves of MgNi compound synthesized by high-pressure at 423–473 K. The low-pressure hydrogen uptake of MgNi with CuTi-type structure occurred under pressure of hydrogen less than 0.2 MPa and further hydrogen

Fig. 1 XRD patterns of high-pressure synthesized MgNi samples as synthesized, after hydrogenation and after dehydrogenation.

Fig. 2 PCT curves of MgNi synthesized by high-pressure at 423–473 K.

absorption took place under pressure of hydrogen more than 3 MPa. The MgNi absorbed 2.75 mass% ($H/M = 1.13$) of hydrogen at 448 K at hydrogen pressure of 10 MPa, but amount of desorbed hydrogen was smaller than that of absorbed at a temperature below 448 K. However MgNi desorbed almost hydrogen at 473 K. Thus, it could be said that the MgNi absorbed and desorbed hydrogen reversibly at 473 K.

Figure 3 shows XRD patterns of $MgNi_{1-x}Cu_x$ ($x = 0.0, 0.2, 0.5$) prepared from amorphous precursors at 623 K or 573 K for 2 h under 6 GPa. $MgNi_{0.8}Cu_{0.2}$ and $MgNi_{0.5}Cu_{0.5}$ were synthesized as single phases at 573 K while MgNi was synthesized as a single phase at 623 K. The crystal structure of $MgNi_{1-x}Cu_x$ ($x = 0.2, 0.5$) was CsCl-type structure which differed from that of MgNi of CuTi-type and the lattice parameter of the samples increases with increasing of Cu content. Figure 4 shows DSC curves of the $MgNi_{1-x}Cu_x$ ($x = 0.0, 0.2, 0.5$). Two exothermic peaks were observed for MgNi and $MgNi_{0.8}Cu_{0.2}$. The exothermic peak of MgNi of low temperature corresponds to the decomposition of MgNi of high-pressure phase into Mg₂Ni and amorphous phases.²²⁾ $MgNi_{0.8}Cu_{0.2}$ may also decompose into Mg₂Ni phase and amorphous phase during first exothermic reaction. The decomposition temperature of $MgNi_{1-x}Cu_x$ ($x = 0.0, 0.2, 0.5$) decreased with increasing of Cu content. This result is similar to behavior of reported amorphous $MgNi_{1-x}Cu_x$.²⁴⁾ Orimo *et al.* reported that the crystallization temperature into Mg₂Ni and MgNi₂ of amorphous $MgNi_{1-x}Cu_x$ linearly decrease with increasing of Cu content.²⁴⁾

To investigate hydrogenation properties of the $MgNi_{1-x}Cu_x$ ($x = 0.0, 0.2, 0.5$), DSC measurement was

Fig. 3 XRD patterns of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$) prepared at 623 K or 573 K for 2 h under 6 GPa.

Fig. 4 DSC curves of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$) synthesized by high-pressure under an Ar atmosphere.

performed under 2 MPa of hydrogen atmosphere. Figure 5 shows DSC curves of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$) under hydrogen pressure of 2 MPa. An exothermic peak was observed for each sample. Our previous study showed that the exothermic reaction was a hydrogenation reaction.²²⁾ The hydrogenation temperature and total peak area of exothermic curve of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$) decreased with increasing of Cu content. Figure 6 shows XRD patterns of $\text{MgNi}_{0.8}\text{Cu}_{0.2}$ before and after DSC measurement. The metal sub-lattice of $\text{MgNi}_{0.8}\text{Cu}_{0.2}$ sample after hydrogenation

Fig. 5 DSC curves of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$) synthesized by high-pressure under hydrogen pressure of 2 MPa.

Fig. 6 XRD patterns of $\text{MgNi}_{0.8}\text{Cu}_{0.2}$ before and after DSC measurement under hydrogen pressure of 2 MPa.

maintained CsCl-type structure and the lattice parameter of which expanded by 3.3%. The behavior of $\text{MgNi}_{0.5}\text{Cu}_{0.5}$ was similar to that of $\text{MgNi}_{0.8}\text{Cu}_{0.2}$.

Figure 7 shows TDMS and TG profiles of hydrogenated $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$). The hydrogen content of these hydrides were measured by TG. The hydrogen desorption temperature of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$) decreased with increasing of Cu content and the hydrogen content of these samples decreased with increasing of Cu content too.

Fig. 7 TDMS and TG profiles of hydrogenated $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$).

Fig. 8 XRD patterns of $\text{MgNi}_{1-x}\text{Ti}_x$ ($x = 0.0, 0.1, 0.2$) prepared at 623 K or 523 K for 2 h under 6 GPa.

Figure 8 shows XRD patterns of $\text{MgNi}_{1-x}\text{Ti}_x$ ($x = 0.0, 0.1, 0.2$) prepared from amorphous precursors at 623 K or 523 K for 2 h under 6 GPa. The $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ was obtained as a single phase of CsCl-type structure. However, the sample

Fig. 9 DSC curves of MgNi and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ synthesized by high-pressure under an Ar atmosphere.

Fig. 10 DSC curves of MgNi and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ synthesized by high-pressure under hydrogen pressure of 2 MPa.

prepared from amorphous $\text{MgNi}_{0.8}\text{Ti}_{0.2}$ was consisted of Mg_2Ni , Mg_3TiNi_2 phase besides CsCl-type phase.

Figure 9 shows DSC curves of MgNi and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$. The decomposition of MgNi was two-step reaction at a temperature of up to 773 K. On the other hand, $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ decomposed into Mg_2Ni type phase and MgNi_2 type phase with one-step reaction with onset temperature of 677 K. So it could be said that the decomposition temperature of high-pressure phase increased with Ti substitution.

Figure 10 shows DSC curves of MgNi and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ under hydrogen pressure of 2 MPa. The onset temperature of hydrogenation of $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ is higher than that of MgNi . Figure 11 shows the XRD patterns of $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ before and after DSC measurement. After hydrogenation, the $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ maintained CsCl-type structure and the lattice parameter of which expanded by 4.8%.

Figure 12 shows TDMS and TG profiles of hydrogenated MgNi and hydrogenated $\text{MgNi}_{0.9}\text{Ti}_{0.1}$. The substitution of Ni by Ti in MgNi decreased onset temperature of hydrogen desorption and improved hydrogen desorption amount from 1.65 mass% ($\text{H}/\text{M} = 0.68$) to 2.06 mass% ($\text{H}/\text{M} = 0.84$).

4. Conclusion

High-pressure synthesized MgNi with CuTi-type crystal structure absorbed and desorbed hydrogen reversibly at 473 K although it was not reported whether amorphous MgNi

Fig. 11 XRD patterns of $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ before and after DSC measurement under 2 MPa hydrogen.

Fig. 12 TDMS and TG profiles of hydrogenated MgNi and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$.

absorbed and desorbed hydrogen reversibly. The MgNi with CuTi-type crystal structure absorbed 2.75 mass% ($\text{H}/\text{M} = 1.13$) of hydrogen at 448 K at hydrogen pressure of 10 MPa. The crystal structure of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.2, 0.5$) and $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ were CsCl-type structure. These compounds

were hydrogenated under hydrogen pressure of 2 MPa and the crystal structures of these hydrides were CsCl-type structures in metal sub-lattice. The decomposition temperature, hydrogenation temperature and hydrogen desorption temperature of $\text{MgNi}_{1-x}\text{Cu}_x$ ($x = 0.0, 0.2, 0.5$) decreased with increasing of Cu content. The decomposition temperature and hydrogenation temperature of $\text{MgNi}_{0.9}\text{Ti}_{0.1}$ was higher than that of MgNi . The substitution of Ni by Ti in MgNi decreased hydrogen desorption temperature and improved the hydrogen desorption capacity from 1.65 to 2.06 mass%.

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