High Pressure Synthesis of Novel $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ Hydrides ($x = 0-0.2$)

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In our previous papers, we have reported the hydrogenation of MgNi_2 with C36-type structure under GPa-order hydrogen pressure. In this paper, the effect of Cu substitution in MgNi_2 was studied on the crystal structures, thermal stabilities and hydrogen contents of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ hydrides ($x = 0-0.2$). The hydrides were obtained by high pressure synthesis using cubic-anvil-type apparatus at 973 K for 8 h under 5 GPa. The hydrides were found to have primitive orthorhombic ($Pmmm$, $x = 0.0-0.1$) and body-centered tetragonal structures ($I4/mmm$, $x = 0.15-0.2$). Their hydrogen contents were estimated to be 2.23–2.32 mass%. Dehydrogenation temperature decreased from 460 K ($x = 0.0$) to 429 K ($x = 0.20$) with increasing amount of Cu substitution. After dehydrogenation, the C36-type phase was observed by X-ray diffraction (XRD). Consequently, it is noteworthy that $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ could be hydrogenated reversibly without disproportionation under high pressure of the order of gigapascals. [doi:10.2320/matertrans.MRA2008451]

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1. Introduction

Magnesium based alloys are considered to be useful as hydrogen storage media because of their high hydrogen-storage capacity. However, there are some problems of high working temperature and poor kinetics. In order to overcome these problems, a number of studies have been conducted for exploring new Mg-based alloys and hydrides using conventional metallurgy techniques such as melting, sintering, and ball milling.^{1,2)} However these conventional techniques have reached their limits with respect to the development of new compounds.

High pressure synthesis is known to be an effective method for exploring novel compounds. Several new hydrides that can be used for hydrogen storage have been prepared using this method. High pressure synthesis is mainly classified into two groups according to the pressure-transmitting medium: an autoclave apparatus with gas media and an anvil apparatus with solid media. For example, CsMgH_3 ,³⁾ LaMg_2H_7 ,⁴⁾ CeMg_2H_7 ⁴⁾ have been prepared under a high pressure of around 10 MPa by using the autoclave apparatus. On the other hand, Mg_3MnH_7 ,⁵⁾ $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ ⁶⁾ and several other compounds have been prepared under high pressure of the order of gigapascals by using the anvil apparatus. The author's group have also reported the synthesis of $\text{Mg}_2\text{Ni}_3\text{H}_{3.4}$,^{7,8)} Mg_3MnH_y ,⁹⁾ MgY_2H_8 ,¹⁰⁻¹³⁾ Mg_4Ni ,¹⁴⁾ MgCu ,¹⁴⁾ and $\text{Mg}_{50}\text{Cu}_{21}$ ¹⁴⁾ by using this method.

In our previous study, MgNi_2 (C36) was hydrogenated under a hydrogen pressure of the order of gigapascals rather than ambient hydrogen pressure.¹⁵⁾ The hydrogen content of a novel MgNi_2 hydride was estimated to be 2.23 mass% and their dehydrogenation temperature was approximately 460 K, which is approximately 100 K lower than those of MgH_2 and Mg_2NiH_4 . Moreover, $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0-0.2$) was found to be hydrogenated,¹⁴⁾ but the optimum condition of hydrogenation of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ was not investigated. Therefore, in this study, the optimum condition for hydrogenating $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0-0.3$) intermetallics was investigated. The effects of Cu substitution on their crystal structures,

thermal stabilities and hydrogen contents of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0-0.3$) hydrides were also investigated.

2. Experimental Procedures

Mg (99.9 mass%), Ni (99.9 mass%), and Cu (99.9 mass%) powders were used as raw materials. Powder mixtures with a nominal composition were pressed into pellets and placed into boron nitride (BN) containers. On the other hand, a NaCl container was used for synthesis using a hydrogen source. High pressure hydrogen was generated by the thermal decomposition of an internal hydrogen source ($\text{NaBH}_4 + \text{Ca}(\text{OH})_2$). The NaCl container was expected to work as a gas-sealer and an electrical insulator. Samples were heated with or without a hydrogen source at 973–1073 K for 2 to 8 h under high pressure in the order of gigapascals and then quenched. Phase identification was carried out by powder X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation. Then, lattice parameters were refined by using the CELL program.¹⁵⁾ The thermal stabilities of the hydrides were investigated using a differential scanning calorimeter (DSC) under Ar-gas flow. The hydrogen contents were measured by fusion extraction analysis (LECO).

3. Results and Discussion

Figure 1 shows XRD patterns of Mg-67 mol% ($\text{Ni}_{1-x}\text{Cu}_x$) ($x = 0.0-0.3$) prepared at 1073 K for 2 h under 2 GPa. Only the MgNi_2 (C36) phase was observed for each sample. Table 1 shows lattice parameters of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0-0.3$) calculated by using the CELL program.¹⁵⁾ The lattice volume increased with an increase in the Cu content. This implies that Cu is substituted for Ni, since the atomic radius of Cu is larger than that of Ni. These samples were used as starting materials.

The $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0-0.3$) reactivity with hydrogen was investigated. Figure 2 shows XRD patterns of MgNi_2 and $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ treated with the hydrogen source at 973 K for 2 and 8 h under 5 GPa. In our previous study,¹⁶⁾ a single phase of MgNi_2 hydride was obtained after it was treated for 2 h. However, the same result was not

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Fig. 1 XRD patterns of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ prepared at 1073 K for 2 h under 2 GPa ($x = 0.0\text{--}0.3$).

Table 1 Lattice constants of C36-type structure in $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0\text{--}0.3$).

x	Lattice constants
0	$a = 0.485(0) \text{ nm}$, $c = 1.590(0) \text{ nm}$
0.05	$a = 0.485(0) \text{ nm}$, $c = 1.590(0) \text{ nm}$
0.10	$a = 0.485(0) \text{ nm}$, $c = 1.593(1) \text{ nm}$
0.15	$a = 0.486(0) \text{ nm}$, $c = 1.590(0) \text{ nm}$
0.20	$a = 0.487(0) \text{ nm}$, $c = 1.593(1) \text{ nm}$
0.30	$a = 0.488(0) \text{ nm}$, $c = 1.597(1) \text{ nm}$

obtained when the $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ treated for 2 h. On the other hand, when the sample was treated for 8 h, only MgNi_2 -type hydride phase was obtained. Since Cu has lower catalytic effect of hydrogenation than that of Ni, longer synthesis time was required for the hydrogenation of Cu-substituted MgNi_2 .

Figure 3 shows XRD patterns of C36-type $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0\text{--}0.3$) prepared in the presence of the hydrogen source at 973 K for 8 h under 5 GPa, hydride phases were observed as almost single phases for $x = 0.0\text{--}0.20$. Therefore, the samples with $x = 0.0\text{--}0.2$ were thought to be almost entirely hydrogenated. On the other hand, for $x = 0.3$, only the C36 phase was identified, i.e., the hydride phase was not observed.

The crystal structures, lattice constants, thermal stabilities, hydrogen contents, and heat quantities of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0\text{--}0.2$) hydrides are summarized in Table 2.

$\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ hydrides with $x = 0.0\text{--}0.1$ had a primitive orthorhombic (PO) structure ($Pmmm$, No. 47). On the other hand, hydrides with $x = 0.15\text{--}0.2$ had a body centered

Fig. 2 XRD patterns of $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ treated with hydrogen source at 973 K for 2 and 8 h under 5 GPa and MgNi_2 treated with hydrogen source at 973 K for 2 h under 5 GPa.

Fig. 3 XRD patterns of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ treated with hydrogen source at 973 K for 8 h under 5 GPa ($x = 0.0\text{--}0.3$).

tetragonal (BCT) structure ($I4/mmm$, No. 139). These crystal structures appear to depend on the Cu content of MgNi_2 .

Table 2 Crystal structures, lattice constants, dehydrogenation temperatures, hydrogenation contents, and enthalpies of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2\text{H}_y$ ($x = 0.0\text{--}0.2$).

Composition	Crystal structure (Space group)	Lattice Constants	Dehydrogenation temperature	Hydrogen Content	Hydrogenation Enthalpy
$\text{MgNi}_2\text{H}_{3.2}$	PO (No. 47)	$a = 0.460\text{ nm}$, $b = 0.468\text{ nm}$ $c = 0.878\text{ nm}$, $V = 0.1900\text{ nm}^3$	460 K	2.23 mass%	-30.6 kJ/mol-H_2
$\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2\text{H}_{3.38}$	PO (No. 47)	$a = 0.460\text{ nm}$, $b = 0.469\text{ nm}$ $c = 0.881\text{ nm}$, $V = 0.1910\text{ nm}^3$	446 K	2.32 mass%	-31.1 kJ/mol-H_2
$\text{Mg}(\text{Ni}_{0.90}\text{Cu}_{0.10})_2\text{H}_{3.37}$	PO (No. 47)	$a = 0.463\text{ nm}$, $b = 0.469\text{ nm}$ $c = 0.880\text{ nm}$, $V = 0.1910\text{ nm}^3$	435 K	2.31 mass%	-25.4 kJ/mol-H_2
$\text{Mg}(\text{Ni}_{0.85}\text{Cu}_{0.15})_2\text{H}_{3.40}$	BCT (No. 139)	$a = 0.329\text{ nm}$, $c = 0.879\text{ nm}$ $V = 0.1910\text{ nm}^3$	437 K	2.32 mass%	-26.3 kJ/mol-H_2
$\text{Mg}(\text{Ni}_{0.80}\text{Cu}_{0.20})_2\text{H}_{3.40}$	BCT (No. 139)	$a = 0.331\text{ nm}$, $c = 0.878\text{ nm}$ $V = 0.1923\text{ nm}^3$	429 K	2.31 mass%	-23.6 kJ/mol-H_2

PO: primitive orthorhombic

BCT: body-centered tetragonal

Fig. 4 DSC curves of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ hydrides measured under Ar flow ($x = 0.0\text{--}0.2$).

Although the affinity of hydrogen with Cu is less than that with Ni, the hydrogen contents of hydrides with $x = 0.05\text{--}0.20$ were higher ($\sim 2.3\text{ mass\%}$) than that of the MgNi_2 hydride.

Figure 4 shows DSC curves of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0.0\text{--}0.2$) hydrides. For each sample, endothermic peaks attributed to dehydrogenation were observed. The dehydrogenation temperature decreased with increasing Cu content. Particularly, the dehydrogenation temperature of $\text{Mg}(\text{Ni}_{0.8}\text{Cu}_{0.2})_2$ hydride was 429 K, which was approximately 30 K

lower than that of MgNi_2 hydride. Hydrogenation enthalpies of the hydrides at the dehydrogenation temperature were estimated from the endothermic peaks (Table 2). The estimated values were 23–30 kJ/mol- H_2 , which are similar to those of well-known hydrogen storage alloys such as LaNi_5 and TiFe . It appeared that C36-type $\text{Mg}(\text{Ni}_{0.7}\text{Cu}_{0.3})_2$ has been hydrogenated under hydrogen pressure of 5 GPa; however, as mentioned previously, it was not hydrogenated at all. This behavior might be due to the fact that catalytic rate of Cu than Ni. The activation energy required for the hydrogenation of C36-type MgNi_2 increased with an increasing Cu content. As a result, $\text{Mg}(\text{Ni}_{0.7}\text{Cu}_{0.3})_2$ could not be hydrogenated under hydrogen pressure of 5 GPa. On the basis of this assumption, it might be possible that $\text{Mg}(\text{Ni}_{0.7}\text{Cu}_{0.3})_2$ is hydrogenated under higher pressure.

Figure 5 shows XRD patterns of $\text{Mg}(\text{Ni}_{0.8}\text{Cu}_{0.2})_2\text{H}_{3.4}$ before and after DSC measurements up to 623 K and 773 K. The diffraction peaks of the sample after heat treatment up to 623 K were broadened. On the other hand, the peaks after heat treatment up to 773 K were attributed to the C36-type phase. According to results of DSC measurements shown in Fig. 4, no thermal reactions were observed in the range of 623 K to 773 K. Therefore, the broadened patterns might not be due to the existence of an intermediate phase such as an amorphous phase, but C36-type phase with refined grains. Consequently, it should be noted that $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ can be hydrogenated reversibly without disproportionation under high pressure of the order of gigapascals.

4. Conclusion

Hydrides of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ ($x = 0\text{--}0.2$) were synthesized at high pressure. These new hydrides were synthesized at 973 K for 8 h under 5 GPa. The hydrides had primitive orthorhombic ($Pmmm$, No. 47) ($x = 0.0\text{--}0.1$), and body-centered tetragonal structures ($I4/mmm$, No. 139) ($x = 0.15\text{--}$

Fig. 5 XRD patterns of $\text{Mg}(\text{Ni}_{1.6}\text{Cu}_{0.4})_2\text{H}_{3.40}$ before and after DSC measurement up to 623 K and 773 K.

0.20). Volume expansions were observed with increasing Cu content. The dehydrogenation temperature of these hydrides decreased from 460 K ($x = 0.0$) to 429 K ($x = 0.20$). The dehydrogenation temperature decreased by about 30 K due to Cu substitution. From fusion analysis, hydrogen content of the new hydrides were estimated to be 2.23–2.32 mass%. The H/M ratio of the hydrides increased with increasing Cu content. After dehydrogenation, $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ hydrides decomposed into $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ compounds and hydrogen. It should be noted that $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2$ could be hydro-

genated reversibly without disproportionation high pressure of the order of gigapascals.

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