

High-pressure synthesis of novel hydride in Mg–Ni–H and Mg–Ni–Cu–H systems

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Abstract

Novel hydrides were synthesized in Mg–Ni–H and Mg–Ni–Cu–H systems by high-pressure technique using a cubic-anvil-type apparatus. Crystal structure and thermal stability of the hydrides were studied. The novel hydride with a composition of MgNi_2H_y was synthesized at 973 K for 2 h under the pressure of over 2 GPa. This hydride could be synthesized from each starting material, such as $\text{MgNi}_2(\text{C36})$ and mixture of MgH_{2-x} mol% Ni ($x = 65\text{--}70$). From fusion analysis, hydrogen content of the sample of MgH_{2-67} at.% Ni prepared with hydrogen source at 973 K for 2 h under 5 GPa was estimated to be 2.23 mass% and chemical formula was corresponding to be $\text{MgNi}_2\text{H}_{3.2}$. The novel hydride was found to exhibit the body-centered tetragonal structure (space group $I4/mmm$, No. 139) with lattice parameters of $a = 0.327(3)$ nm, $c = 0.878(9)$ nm. Moreover, crystal structure of novel hydride was distorted with varying Ni content, then it was found to exhibit C-faced based-centered orthorhombic structure (space group $Pmmm$, No. 47) with lattice parameters of $a = 0.460(1)$ nm, $b = 0.468(1)$ nm, $c = 0.893(1)$ nm. In Mg–Ni–Cu–H system, crystal structure and thermal stability of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2\text{H}_y$ ($x = 0.05, 0.10, 0.15, 0.20$) were investigated. The sample of $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ prepared with hydrogen source at 973 K for 8 h under 5 GPa was dehydrogenated at 446 K, which is 15 K lower than that of $\text{MgNi}_2\text{H}_{3.2}$. Moreover, $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ prepared with hydrogen source at 973 K for 2 h under 5 GPa, which did not react hydrogen sufficiently, was decomposed at 409 K. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Mg-based alloys will be good candidate for hydrogen storage media because of their high hydrogen capacity. But there are some problems of high working temperature and low kinetics. To overcome the problems, a number of studies exploring new Mg-based alloys and hydrides have been conducted with conventional metallurgy techniques such as melting, sintering and ball milling [1,2]. It seems to reach their limits to develop new compounds by conventional studies.

As another method, high-pressure synthesis is known to be an effective method to explore novel compounds. In the field of hydrogen storage media, many new hydrides have been obtained by using this technique. The high-pressure synthesis can be mainly classified into two groups according to manner of gen-

erating pressures, those are, autoclave-type with gas media and anvil-type 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] and $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ [6] and so on were reported to be synthesized under a high pressure up to GPa range by using anvil-type apparatus. In our previous work, $\text{Mg}_2\text{Ni}_3\text{H}_{3.4}$ [7,8], Mg_3MnH_y [9], MgY_2H_8 [10–13] Mg_6Ni [14], MgCu [14] and $\text{Mg}_{54}\text{Cu}_{17}$ [14] have been obtained by using anvil-type apparatus. The author group has conducted two approaches to explore new hydrides by using the high-pressure synthesis. One of the approach is exploring new hydrides by using high-pressure synthesis from the hydrides as raw materials with or without hydrogen source. An another approach is that high-pressure compounds which were synthesized from metals were tried to be hydrogenated under less than the pressure of MPa order. In this study, as a new approach, intermetallic compounds that were not hydrogenated under atmospheric pressure were tried to be hydrogenated under a high pressure of GPa range. In our previous study, it was reported that novel

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hydride was obtained from $\text{MgNi}_2(\text{C36})$ by using high-pressure synthesis [15]. In this study, we investigated structural and hydrogenation properties of this novel hydride.

To improve property of $\text{MgNi}_2\text{H}_{3.2}$, third element was substituted for Ni site. In this study, Cu was selected as a third element. It was reported that Cu substitution decreased dehydrogenation temperature of $\text{Mg}_2\text{NiH}_{3.2}$ [16] which is the same system as the $\text{MgNi}_2\text{H}_{3.2}$. In this study, we investigated thermal stability of $\text{Mg}(\text{Ni}_{1-x}\text{Cu}_x)_2\text{H}_y$.

2. Experimental procedures

Raw materials were MgH_2 (90 mass%, the major impurity was metallic Mg), Mg (99.9 mass%) and Ni (99.9 mass%), Cu (99.9 mass%) powder. The powders were mixed at nominal composition and pressed into pellets and put into BN containers. On the other hand, NaCl container was used in the case of synthesis with hydrogen source. High-pressure hydrogen was generated by 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 electrical insulator. Samples were heated with or without hydrogen source at 973–1073 K for 2 h under a high pressure up to GPa order range and then quenched. Phase identification was performed by powder X-ray diffraction (XRD) using Cu $K\alpha$ radiation. Then, lattice parameters were refined by CELL program. Thermal stability was investigated using a differential scanning calorimeter (DSC) under Ar-gas flow. The hydrogen content was measured by means of fusion extraction analysis (LECO).

3. Results and discussion

3.1. Mg–Ni–H system

Fig. 1 shows the X-ray diffraction (XRD) patterns of $\text{MgH}_{2-x}\text{at.}\% \text{Ni}$ prepared at 973 K for 2 h under 5 GPa. Two different kind of unknown peaks are observed for the sample of $x=65$ and 67, and for $x=70$. The crystal structure of the new

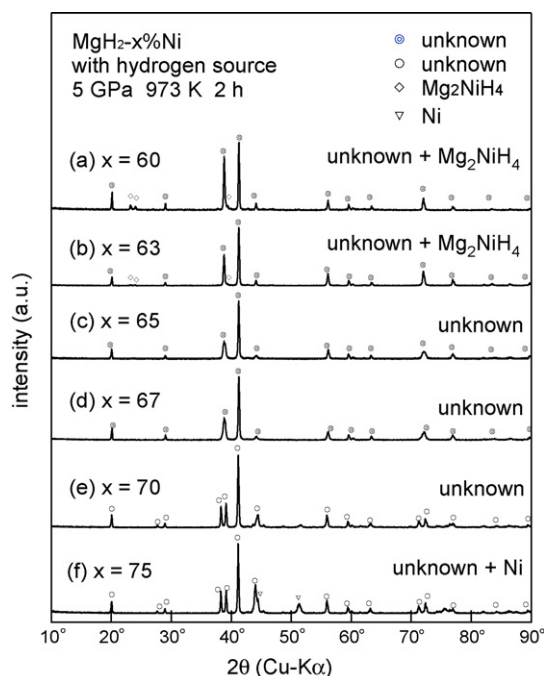


Fig. 1. XRD patterns of $\text{MgH}_{2-x}\text{at.}\% \text{Ni}$ ($x=60\text{--}75$) prepared at 973 K for 2 h under 5 GPa.

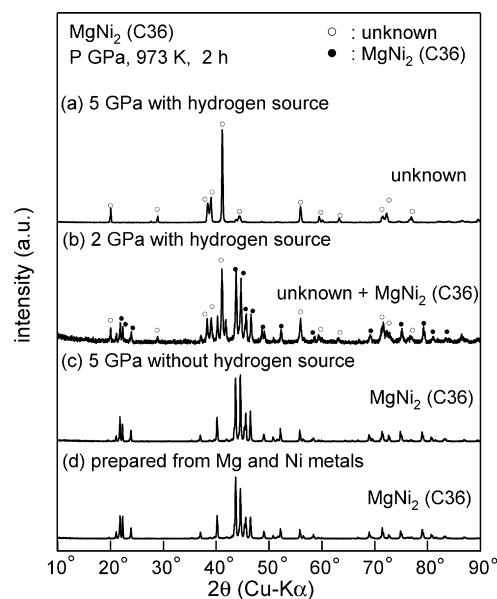


Fig. 2. XRD patterns of $\text{MgNi}_2(\text{C36})$ phase prepared at 973 K for 2 h under 2 or 5 GPa with or without hydrogen source in comparing with MgNi_2 .

compound will be sensitive to Ni content, and some diffracted peaks of $\text{MgH}_2\text{--}70\text{at.}\% \text{Ni}$ split. Fig. 2 shows XRD patterns of MgNi_2 prepared from Mg and Ni metals, or ones of Mg and Ni synthesized with or without hydrogen source under 2 or 5 GPa. Figure indicated that the sample prepared under 5 GPa with hydrogen source has different diffracted peak, which will be resulted from hydrogenation. It is well known that MgNi_2 cannot be hydrogenated under atmospheric pressure. But this figure suggests that MgNi_2 can be hydrogenated under 5 GPa with hydrogen source. This unknown peaks agree with that of $\text{MgH}_{2-x}\text{at.}\% \text{Ni}$ in Fig. 1. Therefore, this MgNi_2H_y hydride can be formed by high-pressure under 5 GPa with hydrogen source starting from either metals or hydride as raw materials. From Fusion analysis, the hydrogen content of the sample of $\text{MgH}_{2-67}\text{at.}\% \text{Ni}$ prepared with hydrogen source at 973 K for 2 h under 5 GPa was estimated to be 2.23 mass%. So the chemical formula of novel hydride was described to $\text{MgNi}_2\text{H}_{3.2}$.

Fig. 3 shows result of Rietveld analysis of the hydride prepared from $\text{MgH}_{2-67}\text{at.}\% \text{Ni}$. The metal sublattice of the hydride is found to be MoSi_2 -type in our previous study [15]. The new $\text{MgNi}_2\text{H}_{3.2}$ has body-centered MoSi_2 type structure ($I4/mmm$, No. 139) with lattice parameters of $a=0.327(3)\text{ nm}$, $c=0.878(9)\text{ nm}$ and $Z=2$. It implies that the new hydride $\text{MgNi}_2\text{H}_{3.2}$ has the metal atomic positions and fitting parameters shown on the inset table in Fig. 3.

With increasing Ni content, some diffracted peaks of the hydride split. Probable unit cell of the hydride with split patterns was found to have orthorhombic structure by using ITO13. Lattice constants of the hydride prepared from $\text{MgH}_{2-70}\text{mol}\% \text{Ni}$ was refined to be $a=0.460(1)\text{ nm}$, $b=0.468(1)\text{ nm}$, $c=0.883(1)\text{ nm}$ by CELL. Structure model was determined in order to form similar structure of hydride with tetragonal structure obtained from $\text{MgH}_{2-67}\text{mol}\% \text{Ni}$. Fig. 4 shows results of Rietveld analysis of the hydride obtained from $\text{MgH}_{2-70}\text{mol}\% \text{Ni}$. So the metal sublattice of the hydride was

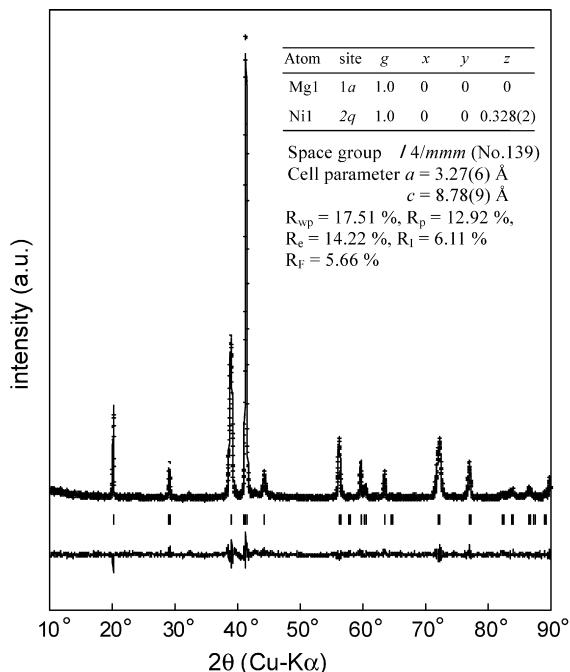


Fig. 3. Result of Rietveld analysis of the new hydride with a tetragonal structure.

found to exhibit primitive orthorhombic structure ($Pmmm$, No. 47) with lattice parameters of $a = 0.460(1)$ nm, $b = 0.468(1)$ nm, $c = 0.883(1)$ nm and $Z = 4$. It implies that the new hydride prepared from MgH_2 –70 mol% Ni has the metal atomic positions and fitting parameters shown on the inset table in Fig. 4.

Fig. 5 shows XRD patterns of synthesized samples of MgH_2 –67 at.% Ni before and after DSC measurement up to 573 K. After DSC measurement, $MgNi_2(C36)$ phase was

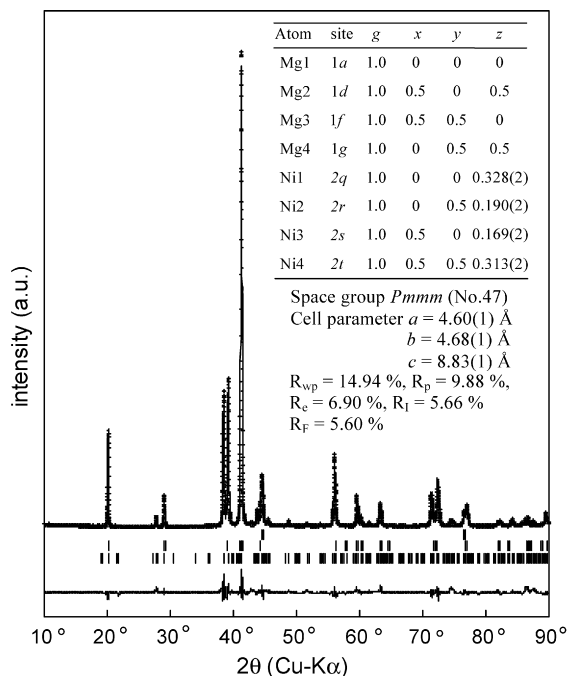


Fig. 4. Result of Rietveld analysis of the new hydride with an orthorhombic structure.

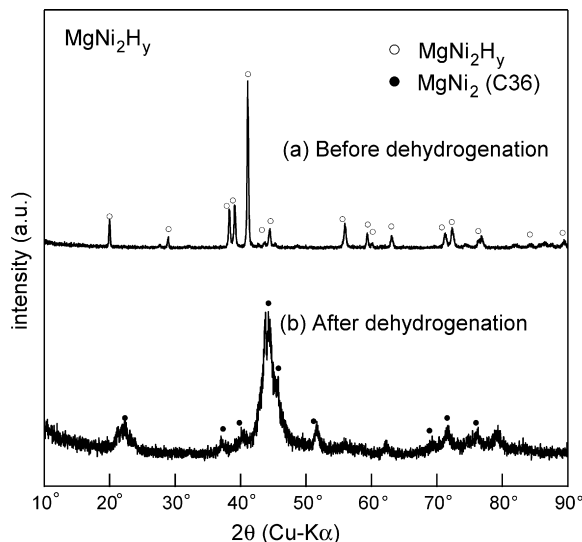


Fig. 5. XRD patterns of $MgNi_2H_y$ before and after DSC measurement up to 573 K.

observed. This means that $MgNi_2H_y$ hydride was dehydrogenated and some defects are introduced.

Since $MgNi_2H_y$ dehydrogenated into $MgNi_2$, $MgNi_2H_y$ will show reversal absorption–desorption reaction as far as hydrogenation of the compound was done under 5 GPa. Consequently, $MgNi_2H_y$ was found to be able to reversibly absorb hydrogen under the pressure of GPa order.

3.2. Mg–Ni–Cu–H system

To decrease dehydrogenation temperature of $MgNi_2H_{3.2}$, Cu was substituted for Ni site, as third element. Enthalpy of hydrogenation of Cu has negative value, which is higher than that of Ni. It was reported that dehydrogenation temperature of Mg_2NiH_4 decreased by Cu substitution. Therefore, it is expected that Cu substitution affects the temperature of decomposition of $MgNi_2$ hydride.

Fig. 6 shows XRD patterns of $Mg(Ni_{1-x}Cu_x)_2$ ($x = 0, 0.05, 0.1, 0.15$ and 0.2) prepared at 1073 K for 2 h under 5 GPa. $MgNi_2$ phase was obtained in each sample, and secondly phase was not observed. This means that Cu can be contains in $MgNi_2$ phase. Fig. 7 shows XRD patterns of $Mg(Ni_{1-x}Cu_x)_2$ treated with hydrogen source at 973 K for 2 h under 5 GPa. $MgNi_2H_y$ phase and $MgNi_2$ phase were observed. Although $MgNi_2H_y$ was obtained as a single phase in Mg–Ni–H system, small addition of Cu may retard the hydrogenation reaction of $MgNi_2$. Fig. 8 shows XRD patterns of $Mg(Ni_{0.95}Cu_{0.05})_2$ treated with hydrogen source at 973 K for 2 or 8 h under 5 GPa. As a result of prolonging of synthesis time, $MgNi_2$ hydride with Cu was obtained as a single phase.

Fig. 9 shows DSC curves of $Mg(Ni_{1-x}Cu_x)_2$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) prepared with hydrogen source at 973 K for 2 h under 5 GPa. The decomposition temperature of $MgNi_2H_y$ is found to be 460 K. Endothermic peaks of the samples of $x = 0.05, 0.10, 0.15, 0.20$ were observed at about 409, 422, 426 and 431 K, respectively. Then small addition of Cu decreases

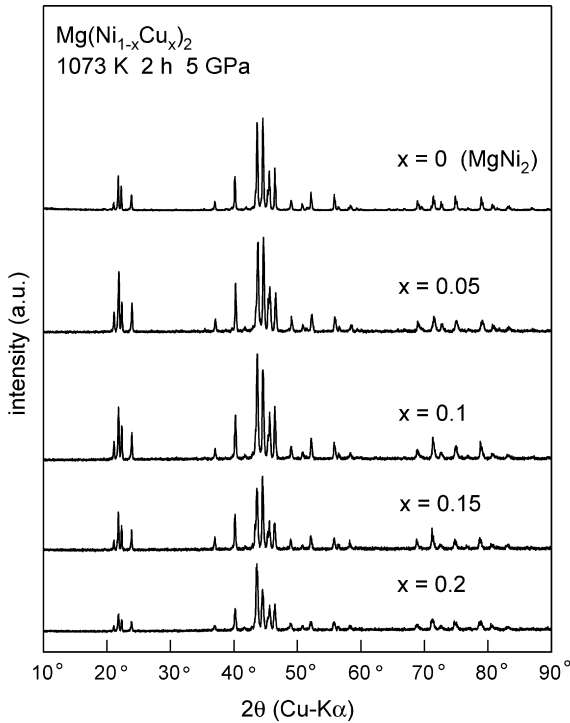


Fig. 6. XRD patterns of the Mg–67 at.% (Ni_{1-x}Cu_x)₂ ($x=0-0.20$) prepared at 1073 K for 2 h under 5 GPa.

the temperature of dehydrogenation. Dehydrogenation temperature of Mg(Ni_{0.95}Cu_{0.05})₂ sample was the lowest in this study. Secondly phase was included in the samples with 2 h treatment, and this phase might affect the dehydrogenation of Mg(Ni_{0.95}Cu_{0.05})₂ hydride probably due to the decrease of

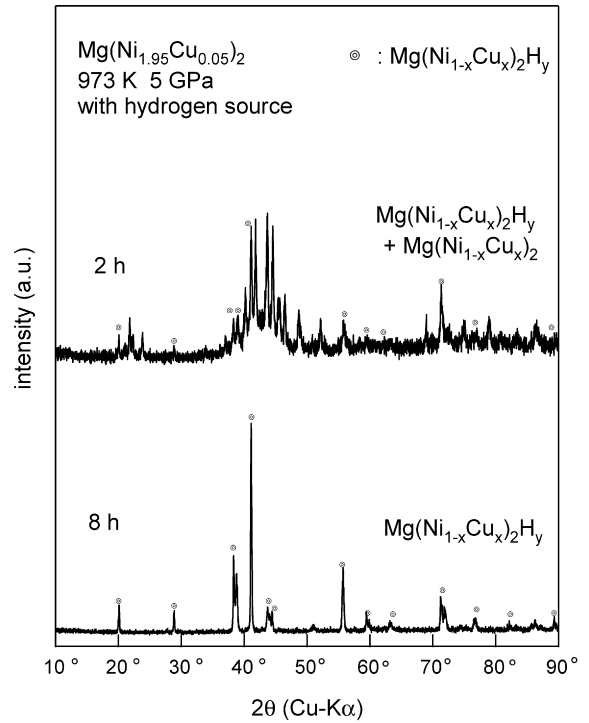


Fig. 8. XRD patterns of Mg(Ni_{0.95}Cu_{0.05})₂ prepared at 973 K for 2 or 8 h under 5 GPa.

dehydrogenation temperature as a catalyst. Fig. 10 shows DSC curves of Mg(Ni_{0.95}Cu_{0.05})₂ treated at 973 K for 2 or 8 h under 5 GPa. Decomposition temperature of the sample with 8 h treatment was 446 K, it was about 40 K higher than that of the sample with 2 h treatment. However, dehydrogenation temperature of Mg(Ni_{0.95}Cu_{0.05})₂ prepared with hydrogen source at

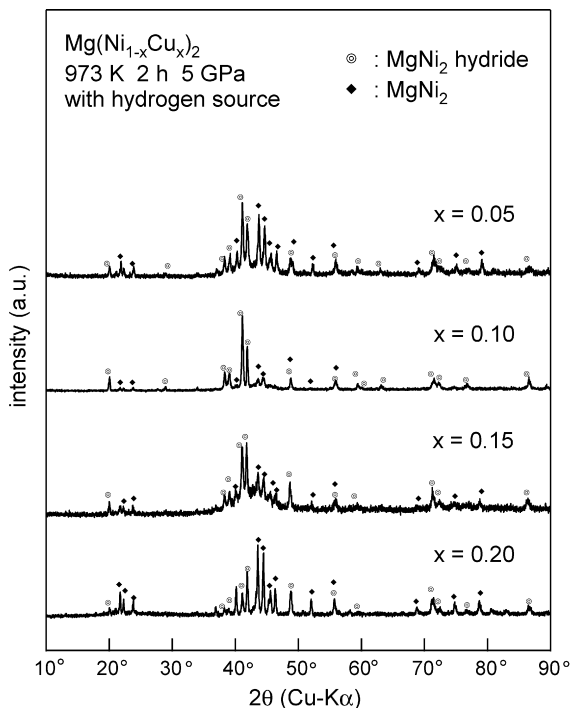


Fig. 7. XRD patterns of Mg(Ni_{1-x}Cu_x)₂ ($x=0.05-0.2$) treated with hydrogen source at 973 K for 2 h under 5 GPa.

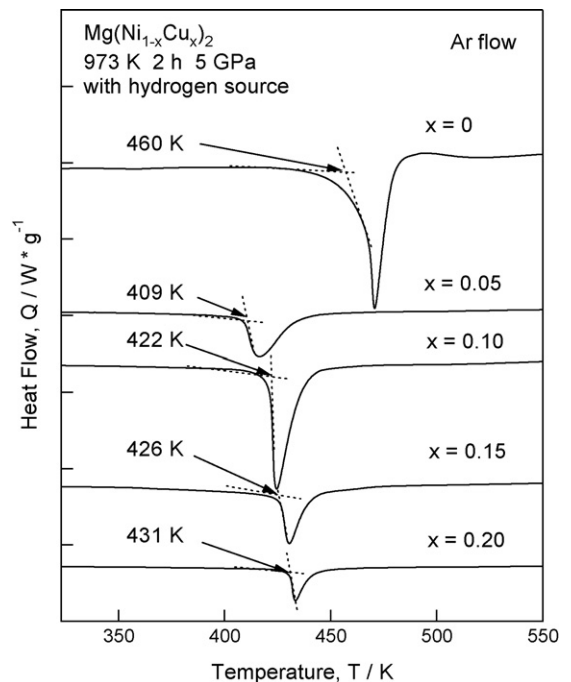


Fig. 9. DSC curves of Mg(Ni_{1-x}Cu_x)₂ ($x=0-0.20$) treated with hydrogen source at 973 K for 2 h under 5 GPa.

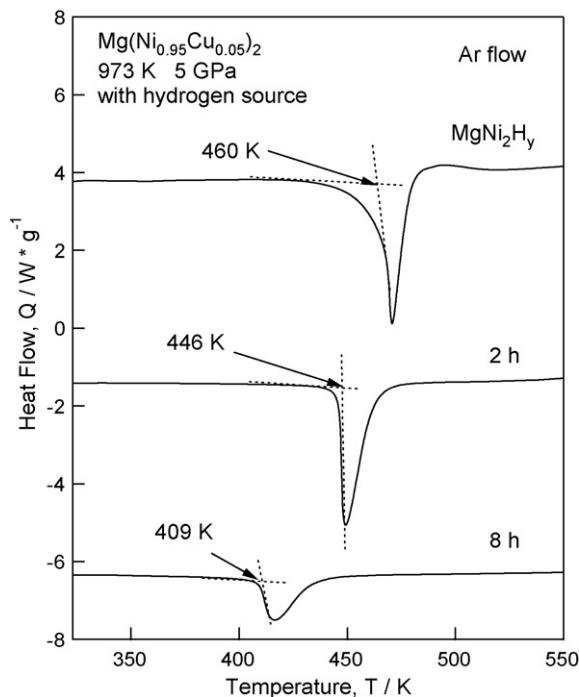


Fig. 10. DSC curves of $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ prepared at 973 K for 2 or 8 h under 5 GPa.

973 K for 8 h under 5 GPa was lower than that of $\text{MgNi}_2\text{H}_{3.2}$. Consequently, Cu substitution might decrease dehydrogenation temperature of $\text{MgNi}_2\text{H}_{3.2}$.

4. Conclusions

In Mg–Ni–H system, MgNi_2H_y was synthesized over 2 GPa with hydrogen source either from Mg and Ni metals or from MgH_2 and Ni. From fusion analysis, hydrogen content of novel hydride was 2.23 mass% and chemical formula was described as $\text{MgNi}_2\text{H}_{3.2}$. With increasing Ni content, crystal structure of $\text{MgNi}_2\text{H}_{3.2}$ changed from body-centered tetragonal structure (MoSi_2 type, $I4/mmm$, No. 139) with lattice parameters of $a = 0.327(3)$ nm, $c = 0.878(9)$ to C-faced based-centered orthorhombic structure ($Pmmm$, No. 47) with lattice parameters of $a = 0.460(1)$ nm, $b = 0.468(1)$, $c = 0.883(1)$ nm. Comparing with estimated tetragonal structure, an orthorhombic structure of the new hydride is regarded as to be distorted with changing the parameters, such as axis ratio, angle and coordination

of Ni site. MgNi_2H_y was dehydrogenated into MgNi_2 at around 460 K. MgNi_2 was found to be hydrogenated under the pressure of GPa.

In Mg–Ni–Cu–H system, dehydrogenation temperature of MgNi_2H_y was decreased by Cu substitution. The sample of $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ treated with hydrogen source at 973 K for 8 h under 5 GPa dehydrogenated at 446 K that was about 15 K lower than that of MgNi_2H_y . Moreover, the sample of $\text{Mg}(\text{Ni}_{0.95}\text{Cu}_{0.05})_2$ treated with hydrogen source at 973 K for 2 h under 5 GPa dehydrogenated at 409 K, although secondly phase was observed in this sample.

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