High-Pressure Synthesis of Novel Hydride in Mg-Ni (-H) System

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A novel hydride was synthesized in Mg-Ni-H system by high pressure technique using a cubic-anvil-type apparatus. Crystal structure, thermal stability and hydrogen content of the hydride were studied. The novel hydride with a composition of MgNi2H8 was synthesized at 973 K for 2 h under the pressure of more than 2 GPa, and was found to exhibit the body-centered tetragonal structure (space group I4/mmm, No.139) with lattice parameters of $a = 0.3273(3)$ nm, $c = 0.8789(9)$ nm. Moreover, this hydride could be synthesized from each starting material, such as MgNi2 high pressure phase, MgNi2 (C36) and mixture of MgH2-x mol% Ni ($x = 65$–$70$). Its hydrogen content was estimated to be 2.23 mass% from fusion analysis and corresponding chemical formula was found to be MgNi2H3. This hydride was decomposed into MgNi2 (C36) over 460 K, and has solubility of Ni content and thermal stability of the novel hydride was decreased with increasing Ni content.

Keywords: magnesium, hydride, high pressure

1. Introduction

Mg-based alloys are expected to be important for hydrogen storage media because of their high hydrogen capacity. But there are some problems of high working temperature and slow 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)

As another method, high pressure synthesis is known as an effective method to explore novel compounds. In the field of hydrogen storage media, many new hydrides have been obtained by this technique. The high pressure synthesis can be mainly classified into two groups according to manner of generating pressures, those are, autoclave-type with gas media, and anvil-type apparatus with solid media. For generating pressures, those are, autoclave-type with gas media, and anvil-type apparatus with solid media. For example, CsMgH3,3) LaMg3H7,4) CeMg2H7,5) have been prepared under a high pressure of about 10 MPa by using the autoclave apparatus. On the other hand, Mg5MnH5,6) and Sr6Mg17H6,7) and so on, were reported to be synthesized under a high pressure up to GPa range using anvil-type apparatus. In our previous work, Mg2Ni3H7,8) Mg2-MnH7,9) Mg2-Y3H8,9-12) Mg5Ni,13) MgCu,13) Mg5Cu7,13) and Mg2Ni2 high pressure14) phase have been obtained by using anvil-type apparatus. The author’s group has conducted two approaches to explore new hydrides by the high pressure synthesis. We have explored new hydrides by using high pressure synthesis from raw materials. Another approach that utilize high pressure compounds were tried to be hydrogenated under less than 10 MPa. In this study, as a new approach, intermetallic compounds that were not hydrogenated under normal pressure were tried to be hydrogenated under a high pressure in GPa range. There is no report of hydrogenation of MgNi2. On the other hand, it is expected that MgNi2 hydride decomposes at lower temperature than conventional Mg-based alloys such as Mg2NiH4. So it was investigated whether a novel hydride was synthesized from MgNi2 phase. Furthermore it was investigated whether a new hydride can be obtained from raw materials. The crystal structure, thermal stability, and hydrogen content of the newly found compound are also investigated.

2. Experimental Procedures

Raw materials were MgH2 (90 mass%, the major impurity was metallic Mg), Mg (99.9 mass%) and Ni (99.9 mass%) powder. MgNi2 high pressure phase was prepared by high pressure method. 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 (NaBH4 + Ca (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 2–8 h under a high pressure up to GPa range and then quenched. Synthesis temperature was controlled by electric power which was calibrated in advance. However, it is difficult to measure the accurate temperature of the sample during synthesis in closed cell. Phase identification was performed by powder X-ray diffraction (XRD) using Cu-Kα radiation. Then, the lattice parameters were refined by freeware called “CELL.”15) 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

To investigate reactivity between highly-pressurized hydrogen and MgNi2 high pressure phase, MgNi2 high pressure phase prepared at 1073 K for 2 h under 5 GPa was treated with hydrogen source at 973 K for 2 h under 2–5 GPa. Figure 1 shows XRD patterns of the samples of MgNi2 high pressure phase before and after the treatment under high

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pressure and that of MgNi$_2$ high pressure phase after the treatment without hydrogen source. After the treatment without highly-pressurized hydrogen, MgNi$_2$ high pressure phase was obtained. After the treatment with highly-pressurized hydrogen, unknown phases marked by opened (○) and double (⊗) circle were obtained by the treatment at 973 K under 2 and 5 GPa, respectively. The obtained samples showed black color and were stable under the atmospheric pressure in air. In the same way, reactivity of MgNi$_2$ with hydrogen was investigated. Figure 2 shows XRD patterns of MgNi$_2$ treated with hydrogen source at 973 K for 2 h under 2–5 GPa, MgNi$_2$ (C36) treated without hydrogen source at 973 K for 2 h under 5 GPa and MgNi$_2$ (C36) phase prepared from raw materials. After the treatment without highly-pressurized hydrogen, MgNi$_2$ (C36) phase was obtained. There is the patterns marked by opened circle (○) of the samples prepared under 2 GPa or above was similar to the phase with the preconceived MgNi$_2$ high pressure phase. As shown in Fig. 2, the sample prepared under 2 GPa, unknown phase (○) and MgNi$_2$ (C36) phase were observed. Figure 3 shows XRD patterns of the samples prepared at 973 K for 2–8 h under 2 GPa. As shown in Fig. 3, the sample prepared at 973 K for 8 h under 2 GPa sufficiently reacted with hydrogen, (○) phase was observed as a single phase. C36-type MgNi$_2$ was found to react with hydrogen under GPa order high pressure. This might be first observation in MgNi$_2$.

Figure 4 shows XRD patterns of MgH$_2$-$x$ mol%Ni ($x = 60$–75) samples prepared with hydrogen source at 973 K for 2 h under 5 GPa. As shown in Fig. 4, unknown phase (⊗) was obtained as a single phase for the samples of $x = 65$–67 and the unknown phase (○) was appeared as a single phase for the sample of $x = 70$. Figure 4 shows XRD patterns of MgH$_2$-67 mol%Ni prepared with hydrogen source at 973 K for 2 h under 2 and 5 GPa. As a result, unknown phase was also found to be obtained above 2 GPa. It suggests that the newly found phases were also synthesized from raw materials with hydrogen source.

It seems that XRD patterns of unknown phase (⊗) and (○) were similar each other. As shown in Fig. 3, some peaks separated with increasing Ni content, and the other peaks did not shift significantly. So unknown phase (○) was thought to have a deformed structure which changes the parameters such as axis ratio or angle. It was seemed that crystal structure of newly found compound was very sensitive to the Ni composition, however, synthesis condition of new compound was independent on the state of the starting materials.

Figure 6 shows XRD patterns of new phase of $x = 67$ and that of simulated body-centered tetragonal MoSi$_2$ ($I4/mmm$, No.139) type structure. These patterns were similar each other. Refining lattice parameters by freeware called “CELL”, the parameters were estimated to be $a = 0.327(3)$ nm, $c = 0.878(9)$ nm. By fusion extraction analysis,
for the sample of $x = 67$, the amount of hydrogen was estimated to be 2.23 mass% and corresponding chemical formula of tetragonal new phase can be expressed as MgNi$_2$H$_3$ and $H/M = 1.07$.

To investigate thermal stability of new hydride, DSC measurement was performed under Ar flow. Figure 7 shows DSC curves of MgH$_{2-x}$mol%Ni ($x = 63, 67, 70$) samples prepared at 973 K for 2 h under 5 GPa. For each composition, endothermic peaks were observed at about 483 K, 460 K, 449 K, respectively. Since Ni has negative hydrogenation enthalpy value, the decomposition temperature was decreased with increasing Ni content. Hydrogenation enthalpy of the sample of MgH$_{2-67}$mol%Ni at decomposing temperature was estimated by integration value of the endothermic peak area. As a result, hydrogenation enthalpy was calculated to be $-30.6$ kJ/mol-H$_2$. Figure 8 shows XRD patterns of the sample of MgH$_{2-67}$mol%Ni before and after DSC measurement. From XRD analysis, MgNi$_2$ (C36) phase was observed.
after DSC measurement. Therefore it can be said that MgNi$_2$H$_{3.2}$ was decomposed into MgNi$_2$ (C36) at about 460 K. From this result, MgNi$_2$ (C36) may be capable of reversible hydrogenation-dehydrogenation under high pressure in GPa range.

It is known that almost Mg-based hydrides, such as the compounds prepared by high pressure method in our previous work, have ionic-bond between metal and hydrogen atoms. Metal sublattice of MgNi$_2$H$_{3.2}$ was similar to that of K$_2$MgH$_4$, which is known to have ionic-bond of hydrogen. Assumed that MgNi$_2$H$_{3.2}$ was ionic-bonded compound, hydrogen atoms could occupy around O-sites of Mg and formed [MgH$_6$]$^{4-}$ complexes. On the other hand, the sample of MgNi$_2$H$_{3.2}$ showed black color, and the decomposition temperature of the sample was relatively low in comparing with other Mg-based hydrides synthesized by high pressure method. From these results, it is supposed that MgNi$_2$H$_{3.2}$ might have metallic-bond of hydrogen.

4. Conclusion

The novel hydride is synthesized in Mg-Ni-H system by high pressure technique using a cubic-anvil-type apparatus. The new hydride with a composition of MgNi$_2$H$_{x}$ is synthesized at 973 K for 2 h under the pressure of more than 2 GPa. The new hydride of MgNi$_2$H$_{x}$ is found to exhibit the body-centered tetragonal structure (space group $I\overline{4}$/$mmm$, No.139) with lattice parameters of $a = 0.327(3)$ nm, $c = 0.878(9)$ nm. Its hydrogen content is estimated to be 2.23 mass% from fusion analysis and corresponding chemical formula is found to be MgNi$_2$H$_{3.2}$. This hydride is decomposed into MgNi$_2$ (C36) over 460 K. The hydride has solubility of Ni content and its thermal stability is decreased with increasing Ni content.

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