High-Pressure Synthesis of MgNi Intermetallic Compound and Its Thermal Stability

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A novel intermetallic compound of MgNi was synthesized from amorphous MgNi by high pressure technique. Crystal structure, thermal stability and hydrogenation property of the compound were studied. The crystallized MgNi was synthesized at 573 K for 2 h under the pressure of more than 5 GPa, and was found to exhibit a CuTi-type structure with lattice parameters of $a = 0.2997(1)$ nm, $c = 0.3166(2)$ nm. The MgNi was decomposed into Mg₂Ni and amorphous phase at 575 K and decomposed into Mg₂Ni and MgNi₂ over 682 K. Moreover the MgNi was hydrogenated into novel hydride with a CsCl-type structure at 355 K under 2 MPa hydrogen. This novel hydride with a lattice parameter of $a = 0.3215(1)$ nm was decomposed into Mg₂Ni and MgNi₂ over 428 K under an Ar atmosphere. [doi:10.2320/matertrans.MBW200782]

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1. Introduction

Mg-based alloys and their hydrides have been extensively studied because of their promising applications as hydrogen storage media. However, it is well known that the Mg-based hydrides need high operating temperatures, especially for dehydrogenation. To improve their hydrogenation and dehydrogenation properties, it is important to explore new Mg-based hydrides and intermetallic compounds.

For that purpose, high pressure synthesis is known to 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 pressure transmitting media, those are, gases media in autoclave, and solid ones such as anvil-type apparatus. For example, CsMgH₃,¹⁾ LaMg₂H₇,²⁾ and CeMg₂H₇,²⁾ have been prepared under a high pressure of about 10 MPa by using the autoclave apparatus. On the other hand, Mg₃MnH₇,³⁾ and Sr₆Mg₇H₂₆,⁴⁾ and so on, were reported to be synthesized under a high pressure up to GPa range using anvil-type apparatus. In our previous work, Mg₂Ni₃H_{3.4},^{5,6)} Mg₃MnH_y,⁷⁾ MgY₂H₈,⁷⁻¹⁰⁾ Mg₅₄Cu₁₇,¹¹⁾ and MgNi₂ high pressure phase¹²⁾ have been obtained by using anvil-type apparatus.

MgCu¹¹⁾ with a CsCl-type structure has been obtained by using anvil-type apparatus in our previous work. The crystal structure and chemical formula of MgCu are the same as that of MgAg and MgAu which are equilibrium phases obtained under ambient pressure while both Ag and Au are homologous elements with Cu. There is a tendency that compounds which has homologous elements have similar crystal structure and chemical formula.

In Mg-10group system, MgPd and MgPt intermetallic compounds have CsCl-type and FeSi-type structure, respectively. On the other hand, (Mg_{1-x}Al_x)Ni ($x = 0.3 \sim 0.5$) prepared by mechanical alloying have CsCl-type structure,¹³⁾ however MgNi binary compound has not been reported. By

the way, amorphous MgNi phase has been synthesized by mechanical milling method.¹⁴⁾ So, there is a possibility to synthesize crystallized MgNi by high pressure technique.

In this work, we investigated novel MgNi compound and the possibility of hydrogenation of the compound. The crystal structure, thermal stability, hydrogenation property and hydrogen content of the newly found compounds are also investigated.

2. Experimental Procedures

Raw materials were Mg (99.9 mass%) and Ni (99.9 mass%) powders. Mg₂Ni was prepared by sintering at 803 K for 5 h under Ar-3 mol% H₂ atmosphere from mixture of Mg and Ni powders. Amorphous MgNi was obtained after 80 h of milling at 200 rpm by mechanical alloying from Mg₂Ni and Ni powders. The amorphous MgNi was used as a precursor and was pressed into a pellet. On the other hand, mixtures of Mg and Ni were also used as precursors. The pellet was put into a BN container, which is expected to work as electric insulator. 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 high-pressure synthesis was carried out by using anvil-type apparatus. Samples were heated at 573–973 K for 2 h under 2–6 GPa and then quenched into ambient temperature and pressure. Phase identification was carried out by X-ray diffractometry (XRD). Then, lattice parameters were refined by CELL¹⁵⁾ 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 2 MPa hydrogen. The hydrogen content of hydrides was measured by means of a fusion extraction analysis.

3. Results and Discussion

Figure 1 shows XRD patterns of an amorphous MgNi precursor and the MgNi samples prepared at 573 K and 673 K

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Fig. 1 XRD patterns of an amorphous MgNi precursor and the MgNi samples prepared at 573 K and 673 K for 2 h under 6 GPa.

Fig. 2 XRD pattern of MgNi sample prepared at 573 K for 2 h under 6 GPa and simulated pattern as a CuTi-type structure.

for 2 h under 6 GPa. The halo pattern from amorphous phase was disappeared and unidentified phase was observed as an almost single phase for the sample prepared at 573 K. However only identified phases such as MgNi₂ high pressure phase and Mg₂Ni were appeared for the sample prepared at 673 K.

Figure 2 shows XRD patterns. A simulated pattern as a primitive tetragonal structure (CuTi-type; $P4/mmm$, No. 123) is also shown in this figure. This pattern was similar to that of the sample prepared at 573 K. So the novel phase was found to be MgNi as a high pressure phase and then the lattice parameters were estimated to be $a = 0.2997(1)$ nm, $c = 0.3166(2)$ nm. The CuTi-type structure is similar to a CsCl-type structure such as MgPd. The occupation of atoms in these crystal structures is similar each other. However the difference between CuTi and CsCl is their structure types of tetragonal or cubic. So the structure of MgNi is similar to that of MgPd.

Figure 3 shows XRD patterns of the MgNi samples prepared at 573 K for 2 h under varying pressure of 4–6 GPa. As a result, the MgNi was obtained above 5 GPa.

Figure 4 shows XRD patterns of the samples, which was used by precursor of Mg-50 mol%Ni mixture, prepared at 573–973 K for 2 h under 6 GPa. However, the MgNi was not obtained and only raw materials were observed. In addition, only identified phases were appeared for the samples prepared at 773 K and 973 K. So in this synthesis condition novel phase was obtained by the use of only amorphous MgNi as a precursor.

To investigate thermal stability of novel MgNi compound, DSC measurement was performed under an Ar atmosphere. Figure 5 shows DSC curve of the MgNi. Two exothermic

Fig. 3 XRD patterns of MgNi samples prepared at 573 K for 2 h under 4–6 GPa.

peaks were observed at 575 K and 682 K. From X-ray diffraction results after the DSC measurement, MgNi decomposed to Mg₂Ni and amorphous phase at 575 K, and MgNi₂ appeared over 682 K.

Fig. 4 XRD patterns of Mg-50 mol%Ni samples prepared at 573–973 K for 2 h under 6 GPa.

Fig. 5 DSC curve of MgNi under an Ar atmosphere.

To investigate hydrogenation property of the MgNi, DSC measurement was performed under 2 MPa hydrogen atmosphere (Fig. 6). An exothermic peak was observed at 355 K. From X-ray diffraction results after the DSC measurement, the MgNi was disappeared and an unidentified phase was obtained as an almost single phase. Figure 7 shows XRD patterns of the unidentified phase and that of simulated primitive cubic structure (CsCl-type; $Pm\bar{3}m$, No. 221). These patterns were similar each other. The hydrogen amount of the hydrogenated sample was estimated to be 1.89 mass% by fusion analysis and the corresponding chemical formula of the novel phase can be expressed as $\text{MgNiH}_{1.6}$.

Figure 8 shows DSC curve of the novel hydride measured under Ar atmosphere. An endothermic peak was observed at about 428 K. From X-ray diffraction results after the DSC

Fig. 6 DSC curve of MgNi under 2 MPa hydrogen.

Fig. 7 XRD pattern of the sample after hydrogenation of MgNi and simulated pattern as a CsCl-type structure.

Fig. 8 DSC curve of MgNiH_y under an Ar atmosphere.

measurement up to 670 K, Mg_2Ni and MgNi_2 were observed. A decomposition with dehydrogenation would occur.

4. Conclusion

The novel intermetallic compound of MgNi is synthesized by high pressure technique at 573 K for 2 h under the pressure of more than 5 GPa. The novel phase is found to exhibit a CuTi-type structure (space group $P4/mmm$, No. 123) with lattice parameters of $a = 0.2997(1)$ nm, $c = 0.3166(2)$ nm. The MgNi hydrogenated into novel hydride with a CsCl-type structure at 355 K under 2 MPa hydrogen. This novel hydride with a lattice parameter of $a = 0.3215(1)$ nm was decomposed into Mg_2Ni and MgNi_2 over 428 K under an Ar atmosphere. Its hydrogen content is estimated to be 1.89 mass% from fusion analysis and corresponding chemical formula is found to be $\text{MgNiH}_{1.6}$.

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