Hydrogenation Properties of CaMg$_2$ Based Alloys*

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Binary C14 Laves phase alloy CaMg$_2$ is expected to absorb hydrogen more than 6 mass%, when the H/M ratio reaches 2. We have found that the binary CaMg$_2$ did not absorb hydrogen at ambient temperature and hydrogen pressure but Ni added CaMg$_{1.8}$Ni$_{0.2}$ which is also C14 Laves phase absorbed 6.0 mass% of hydrogen at room temperature. CaMg$_{1.8}$Ni$_{0.2}$ formed hydrides of Mg and Ca, and the C14 Laves phase disappeared. Hydrogen desorption was not observed from hydrogenated CaMg$_{1.8}$Ni$_{0.2}$. (Ca$_{0.1}$La$_{0.2}$)Mg$_{2.2}$Ni$_{0.1}$ absorbed 5.1 mass% hydrogen and H/M ratio reached 1.8 at room temperature. After hydrogenation, the lattice of the Laves phase expands 4% in a-axis and 3% in c-axis. The volume expansion is 13%. The Laves phase structure is kept and hydrogen was absorbed in the lattice. The hydride of (Ca$_{0.1}$La$_{0.2}$)Mg$_{1.8}$Ni$_{0.1}$ decomposed from 470 K with increase at temperature and hydrogen was released from the products of decomposition from 610 K.

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1. Introduction

Hydrogen attracts attention from both environmental and energy resource issues that we are facing. In order to handle with a large amount of hydrogen safely, a system which uses a hydrogen absorbing alloy is suitable. Development of a hydrogen absorbing alloy which can reversibly absorb and desorb a large amount of hydrogen at ambient temperature and hydrogen pressure is indispensable to establish such hydrogen storage/transportation systems.

There are various types of hydrogen absorbing materials, for example, AB$_5$ (such as LaNi$_5$), AB$_2$ (such as ZrMn$_2$), and AB type (such as TiFe), and solid solution alloys with BCC structure (such as Ti-V-Cr system alloy). The hydrogen capacity of the alloys based on rare earth and transition metals does not meet the requirement for onboard hydrogen storage.

On the other hand, Mg-based intermetallic compound, Mg$_2$Ni, reversibly absorbs hydrogen to form Mg$_2$NiH$_4$ and the hydrogen content is as high as 3.6 mass%.$^{1}$ However, because working temperature of Mg$_2$Ni is above 550 K,$^{1}$ they have not been applied for actual applications. To lower hydrogen desorption temperature, amorphization and substitution of third elements for Mg or Ni of Mg$_2$Ni in order to changes hydrogenation/dehydrogenation properties is performed briskly.$^{2-5}$ However, the satisfying result has not been obtained yet.

Recently, a few studies on novel hydrogen absorbing intermetallic compounds containing Mg have been published. For example, these are the AB$_2$ Laves phase compounds MgNi$_{1.9}$M$_{0.1}$ (M=Cr, Mn, Fe) reported by Tsushio and Akiba,$^{4,5}$ the C15-b type AB$_2$ Laves compound MgYNi$_4$ reported by Aono et al.,$^5$ RMg$_2$Ni$_8$ (R=rare earth) reported by Kadir et al.$^7$-9 and La-Mg-Ni reported by Kohno et al.$^{10}$ We also have developed the novel Mg-based hydrogen absorbing alloy (Mg$_{0.67}$Ca$_{0.33}$)Ni$_2$ with C15 type Laves structure which can reversibly absorb and desorb hydrogen at room temperature.$^{11}$ The maximum hydrogen capacity of (Mg$_{0.67}$Ca$_{0.33}$)Ni$_2$ is 1.4 mass% (H/M=0.7) under hydrogen pressure of 4 MPa at temperature of 278 K.

In order to develop the alloy having a larger hydrogen capacity than the above alloys, we have been investigating CaMg$_2$ based compounds with C14 type Laves structure. CaMg$_2$ is expected to absorb hydrogen more than 6.0 mass%, when the H/M ratio reaches 2. We found that CaMg$_2$ did not absorb hydrogen at room temperature at hydrogen pressure of 4 MPa, but at temperature above 573 K hydrogen absorption occurred. With hydrogenation CaMg$_2$ disproportionated into CaH$_2$ and Mg. Desorption did not occur at temperature below 573 K from the mixture of CaH$_2$ and Mg. Ni substituted pseudo-binary alloy, CaMg$_{1.8}$Ni$_{0.2}$, absorbed 6.0 mass% of hydrogen at room temperature. However, hydride of Mg and Ca formed from CaMg$_{1.8}$Ni$_{0.2}$ and the Laves phase disappeared. Hydrogen desorption was not observed from hydrogenated CaMg$_{1.8}$Ni$_{0.2}$ at temperature below 523 K.

We have tried to prevent decomposition or disproportionation of CaMg$_2$ with substitution of other elements for Ca or Mg. In this paper, we report on the effect of substitution of La for Ca of CaMg$_2$ and its hydrogenation/dehydrogenation properties.

2. Experimental Details

2.1 Sample preparation

CaMg$_2$ based C14 Laves phase alloys were prepared by melting in high-purity (more than 97%) alumina crucible using an electric furnace and casting into a Cu mold under 0.1 MPa argon atmosphere. Commercial grade Mg (3–5 mm in diameter), Ca (3–5 mm in diameter), Ni (1F × 10 mm) and La (5–10 mm in diameter) granules were used as raw materials. The shape of the cast alloys was button-like and three centimeters in diameter and one centimeter in thickness. The weight of each cast alloys was approximately ten-twenty grams. The ingots were powdered to the size appropriate for each measurement using a hand mill in argon atmosphere for preventing ignition and oxidation.

2.2 Characterization

The chemical compositions of the cast alloys were...
analyzed using a conventional inductively coupled plasma analyzer (ICP, Seiko Instruments Inc., SP54000).

The crystal structures of each alloy and its lattice parameters were determined by powder X-Ray Diffraction (XRD, Rigaku Inc., RINT2000). The X-ray tube with Cu Kα radiation was operated at a voltage of 40 kV and at a current of 40 mA, and the scanning rate of the goniometer was 0.01°/s.

The pressure-composition (p-c) isotherms were measured at temperatures 313, 523 and 573 K under hydrogen pressure from 1.0 × 10⁻³ to 3.5 MPa by use of a homemade automatic Sieverts'-type apparatus.

The thermal stability of hydride was examined by differential thermal analysis (DTA, Seiko Instruments Inc., SSC5200) simultaneously with thermogravity (TG) measurements at temperature range from 300 to 950 K in a flowing argon (99.999%) atmosphere. The heating rate was 0.083 K/s.

3. Results and Discussions

3.1 Chemical analysis

Table 1 shows the results of chemical analysis. The results of chemical analysis agree with those of the target compositions. It should be pointed out that the estimation of the amount of Ca and Mg vaporizing during melting, temperature of molten metal and sufficient stir are keys to prepare the alloy close to the target composition. Our applied calculations of a yield rate and melting conditions were pertinent.

3.2 Hydrogenation properties

Table 2 shows the condition of hydrogenation and the results of hydrogenation for sample 1, 2 and 3. Moreover, Fig. 1 shows the X-ray diffraction profiles of sample 1, 2 and 3 before hydrogenation (a, c, e) and after hydrogenation (b, d, f) measured in air. The lattice constants and the cell volumes of C14 Laves phases calculated from the XRD profiles are summarized in Table 3.

2

3

Sample | State | Ca (at%) | La | Mg | Ni | Compositions formula
--- | --- | --- | --- | --- | --- |
No. 1 | Target | 33.33 | — | 66.67 | — | CaMg2
No. 1 | Analyzed | 34.97 | — | 65.03 | — | CaMg_{1.9}
No. 2 | Target | 33.33 | — | 60.00 | 6.67 | CaMg_{1.8}Ni_{0.2}
No. 2 | Analyzed | 34.79 | — | 58.85 | 6.36 | CaMg_{1.2}Ni_{0.2}
No. 3 | Target | 24.24 | 6.06 | 66.67 | 3.03 | (Ca_{0.9}La_{0.1})Mg_{2.2}Ni_{0.1}
No. 3 | Analyzed | 24.51 | 6.22 | 65.78 | 3.49 | (Ca_{0.9}La_{0.1})Mg_{2.1}Ni_{0.1}

Table 2 The conditions of hydrogenation and the results of hydrogenation for sample 1, 2 and 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition of hydrogenation</th>
<th>H/M Mass%</th>
<th>Condition of C14 phase (after hydrogenation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>573 K, 4 MPa</td>
<td>0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>No. 2</td>
<td>Room temperature, 4 MPa</td>
<td>1.9</td>
<td>6.0</td>
</tr>
<tr>
<td>No. 3</td>
<td>Room temperature, 4 MPa</td>
<td>1.8</td>
<td>5.1</td>
</tr>
</tbody>
</table>

While sample 1 did not absorb hydrogen at room temperature and hydrogen pressure of 4 MPa, it absorbed 2.3 mass% hydrogen at temperature of 573 K. Sample 1 disproportionated into CaH2 and Mg after hydrogenation at 573 K. On the other hand, Ni substituted CaMg_{1.8}Ni_{0.2} (sample 2) absorbed 6.0 mass% hydrogen at room temperature. Sample 2 decomposed and the C14 Laves phase disappeared with hydrogenation. The alloy substituted La for Ca (sample 3) absorbed 5.1 mass% hydrogen at room temperature. After hydrogenation, the lattice of the C14 Laves phase expanded 4% in a-axis and 3% in c-axis, respectively. The volume expansion was 13%. In the case of sample 3, the C14 Laves phase structure kept after hydrogenation. It means that a hydride with C14 Laves type structure formed.

Figure 2 shows the p-c isotherms of sample 3 at temperature of 313, 523, and 573 K. In sample 3, hydrogen desorption did not occurred, while absorption occurred at temperature of 313 K. At temperature above 523 K, hydrogen
desorption occurred and the amount of desorbed hydrogen was 3.2 mass%. The enthalpy of hydride formation was calculated from the Van’t Hoff plot at temperatures of 523 and 573 K. The midpoint of the plateau was used as the equilibrium pressure for this calculation. The value of enthalpy of hydride formation for sample 3 was \( C_0 = 85 \text{ kJ/mol H}_2 \). Therefore, at temperature above 523 K, it suggests that the hydrogen desorption from the hydride of Mg formed from the C14 Laves phase has occurred.

3.3 Structural stability of the C14 Laves phase hydride

The results of DTA/TG measurements of the hydrogenated sample 3 are shown in Fig. 3. From the TG curve of upper case, it can be seen that the reduction of the weight by desorption of hydrogen was observed at temperature from 610 K. Moreover, the amount of desorbed hydrogen content was equivalent to the result of the PCT measurement shown in Fig. 2. From the DTA curve of upper case, the exothermic reaction existed at temperature near 493 K. As the TG curve shows, this exothermic reaction is not accompanied by weight change. Therefore, this exothermic reaction is based on a structural change of the hydride of sample 3.

Figure 4 shows the XRD profiles of the hydride of sample 3 after heating to temperatures shown by the arrows in Fig. 3. The XRD profile (ii) shows the hydride of sample 3 after heating to 446 K. Just higher this temperature the exothermic reaction appeared but the same XRD pattern of the hydride before heating (i) was shown. Furthermore, a difference was not observed by both lattice constants as shown in Table 3. The XRD profile of the hydride after heating to 525 K (iii) showed a few broad peaks, but did not show any sharp Bragg peaks except CaO peaks. Consequently, we can see that the C14 Laves structure of the hydride of sample 3 decomposed into hydrides of Mg and Ca by this exothermic reaction. In the XRD profile of the hydride after heating to 648 K (iv), new Bragg peaks of Mg and CaH\(_2\) appeared.

By substitution of La with a smaller atomic radius than Ca, the value of atomic radius ratio \( R_A/R_B \) in AB\(_2\) Laves phase approaches to 1.225 which is an ideal value. Structural stability of the C14 Laves phase increases with substitution of La for Ca. As the result, the C14 Laves phase can withstand the expansion of lattice by hydrogenation. The similar phenomena have been reported by Aoki et al.\(^{13,14}\) for C15 Laves phase alloys.

4. Summary and Conclusions

Binary C14 Laves phase alloy CaMg\(_2\) did not absorb hydrogen at room temperature and hydrogen pressure of 4 MPa. In the case of temperature above 573 K, it absorbed 2.3 mass% hydrogen and disproportionated into CaH\(_2\) and...
Mg simultaneously. The alloy Ni added multi-phase CaMg$_{1.8}$Ni$_{0.2}$ absorbed 6.0 mass% hydrogen at room temperature and hydrogen pressure of 4 MPa. However, CaMg$_{1.8}$Ni$_{0.2}$ decomposed and the C14 Laves phase disappeared after hydrogenation. The alloy substituted La for Ca (Ca$_{0.8}$La$_{0.2}$)Mg$_{2.2}$Ni$_{0.1}$ absorbed 5.1 mass% hydrogen at room temperature and hydrogen pressure of 4 MPa. After hydrogenation, the C14 Laves structure kept and expanded 13% in volume of C14 lattice. As the result of decrease of the atomic radius ratio by substitution La for Ca, C14 Laves structure of (Ca$_{0.8}$La$_{0.2}$)Mg$_{2.2}$Ni$_{0.1}$ may become stable. The C14 Laves structure of hydrogenated (Ca$_{0.8}$La$_{0.2}$)Mg$_{2.2}$Ni$_{0.1}$ changed and decomposed at temperature from 470 K accompanied by the exothermic reaction.

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REFERENCES