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High-pressure synthesis and energetics of MgCu with a CsCl-type structure

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Abstract

The novel intermetallic compound of MgCu with a CsCl-type structure has been prepared under high pressure, and its energetics including the enthalpy of formation has been discussed by means of density functional calculations. The MgCu phase with a lattice constant of $a = 0.3161$ nm was prepared by using cubic anvil-type apparatus at 800 °C under 6 GPa. For the first-principles calculation, a full potential linearized augmented plane wave (FPLAPW) technique was used. The lattice constant obtained as a result of volume optimization showed a good agreement with the observed value with an accuracy of less than 0.3%. From the calculation of the total energy, the enthalpy of formation of the novel MgCu phase was estimated to be -18.4 kJ/mol. In addition, the MgCu phase decomposed into Mg_2Cu and $MgCu_2$ phases at around 520 K with $\Delta H = -2.2$ kJ/mol (exothermic). The calculated ΔH (-6.4 kJ/mol) also showed a fairly good agreement with the observed value.

Keywords: Hydrogen storage materials; Intermetallics; High pressure; Electronic band structure; Thermal analysis

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, a high-pressure synthesis technique has been increasingly utilized. Under high pressure on the order of GPa, the atomic radius of metallic elements changes in the range of a few percent to more than 10%, depending on elements, and the chemical potential of hydrogen can be enhanced. These advantages make it possible to prepare novel hydrides that are unstable under ambient pressure. For example, novel hydrides of Mg_3MnH_7 and $REMg_2H_9$ (RE = La, Ce) have been prepared by using either of anvil- or autoclave-type apparatuses [1,2]. Moreover, $Mg_2Ni_3H_{3.4}$, $(Ca, Mg)_2NiH_x$, and $MgY_2H_{7.8}$, Mg_3REH_9 (RE = La, Ce, Pr) have been prepared in our previous work [3–8]. As an another approach, novel Mg-based intermetallic compounds without hydrogen have been also prepared by under high-pressure in Mg–Cu and Mg–Ni systems. For example, MgCu with a CsCl-type structure, $Mg_{51}Cu_{20}$ with an $Mg_{51}Zn_{20}$-type structure, and Mg_4Ni with an FCC structure have been reported [9]. Among them, the MgCu phase with ordered structure is of interest, since the chemical composition of MgCu is the middle of Mg_2Cu that shows disproportionation reaction with hydrogen and $MgCu_2$ that is difficult to be hydrogenated.

This paper focuses on the novel intermetallic compound of MgCu with a CsCl-type structure. The enthalpy of formation and phase stability compared to equilibrium phases, i.e., Mg_2Cu and $MgCu_2$ will be discussed in the con-

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text of energetics calculated by means of the local density approximation of the density-functional theory. The possibility of the formation of its hydride phase is also examined.

2. Experimental procedure

The sample of MgCu with a CsCl-type structure was prepared by a cubic anvil-type apparatus at 800 °C under 6 GPa for 8 h. The details of preparation was described elsewhere [9]. The crystal structure of MgCu was determined by powder X-ray diffraction (XRD). The temperature and enthalpy of decomposition were measured by a differential scanning calorimeter (DSC) under argon gas flow.

To date, the first-principles calculations based on the density functional theory were widely adopted for hydrogen storage materials; it is well known that the calculated enthalpies of formation and hydrogenation for those materials show a good agreement with observed values [10–14]. The first-principles calculations for the novel MgCu intermetallic compound were performed by means of the full potential linearized augmented plane wave (FPLAPW) method. The same calculation was conducted for the Mg_2Cu and $MgCu_2$ phases in order to compare the phase stability. The program code used was WIEN2k developed by Blaha et al. [15]. For the exchange and correlation potentials, the generalized gradient approximation (GGA) was utilized [16]. Inside muffin-tin spheres, the wave function was expanded in spherical harmonics with $l_{\max} = 10$ for the potential and charge density representations, while non-spherical components of the density and potentials are included up to $l_{\max} = 6$. For the intermetallic phase of MgCu, Mg_2Cu, and $MgCu_2$, the muffin-tin radii of 0.116 nm (2.2 a.u.) were used. On the other hand, for a hydride phase, the muffin-tin radii of 0.095 nm (1.8 a.u.) and 0.080 nm (1.5 a.u.) were used for metallic elements and hydrogen, respectively. $RK_{\max}$ was fixed to 9.0.

The total energies as a function of cell volumes were calculated around the equilibrium volumes to obtain the minimum energy. For the hydride phase, in addition to the volume optimization, the optimization of c/a ratio was performed. The criterion of energy convergence was set to be 0.1 mRy. This criterion of convergence ensures that the error of the enthalpy of formation is less than 1 kJ/mol.

3. Results and discussion

3.1. High-pressure synthesis and thermal stability of MgCu

Fig. 1 shows X-ray diffraction patterns of Mg–X at.% Cu prepared at 800 °C under 6 GPa for 8 h. As can be seen, a single phase of intermetallic compounds, MgCu, was prepared at $X = 50$. Judging from the presence of a (1 0 0) reflection around 28°, the crystal structure of the novel MgCu phase is considered to be CsCl-type (B2). The lattice constant was refined and found to be 0.3161 nm.

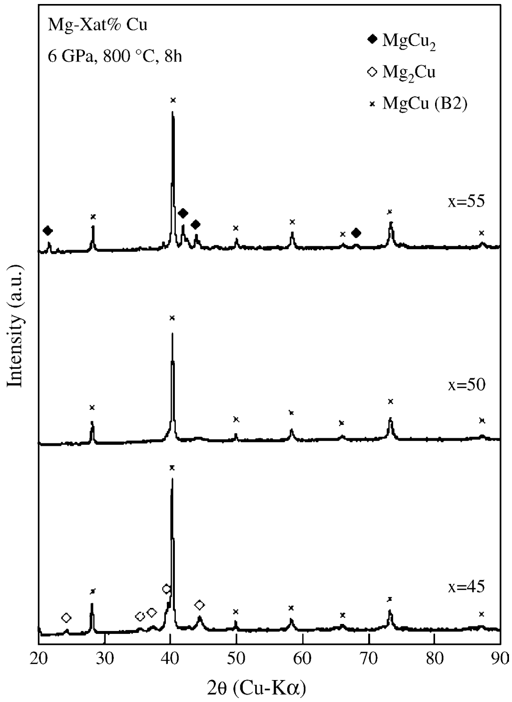

Fig. 1. X-ray diffraction patterns of Mg–X at.% Cu prepared at 800 °C under 6 GPa.

The thermal stability of the MgCu intermetallic compound was examined by DSC under Ar flow atmosphere. As shown in Fig. 2, an exothermic peak with approximately $\Delta H = -2.2$ kJ/mol was observed between 480 and 560 K. The XRD pattern of the sample after the DSC measurement was plotted in Fig. 3 along with that for the original sample before DSC. In Fig. 3, the equilibrium phases of Mg_2Cu and $MgCu_2$ appeared after the DSC measurement. From these observations, it can be said that the exothermic peak of −2.2 kJ/mol in Fig. 2 corresponds to the decomposition reaction of MgCu as follows:

$$MgCu = 1/3Mg_2Cu + 1/3MgCu_2 \qquad (1)$$

This also implies that the MgCu phase newly developed is a semi-stable phase. The energetics of MgCu, including the relations to equilibrium phases of Mg_2Cu and $MgCu_2$, were then examined by using first-principles calculations.

3.2. Energetics of Mg–Cu-based intermetallic compounds

In order to obtain precise minimum total energies for the intermetallic compounds in Mg–Cu system, first of all, total energies were calculated as a function of lattice volume. For example, Fig. 4 shows the total energy of MgCu as a function of an unit cell volume. The volume of unit cell was varied in the range of −10 to 10% with respect to the observed value. As can be seen, the total energy of MgCu showed a

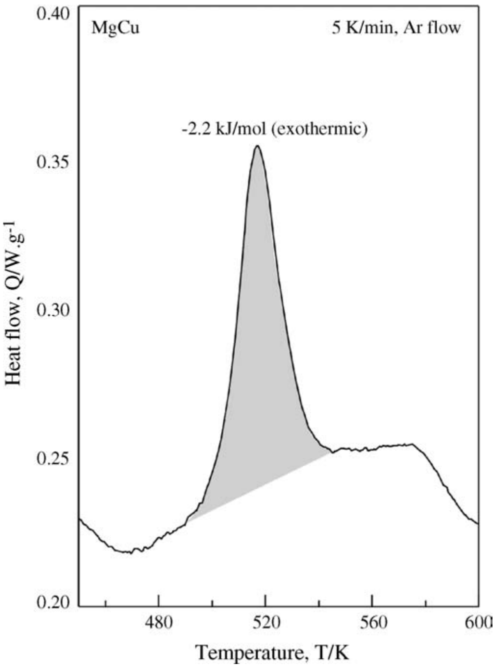

Fig. 2. The curve of differential scanning calorimetric measurement for MgCu.

minimum value at 211.506 a.u.^{3}, corresponding to the lattice constant of $a = 0.31530$ nm. This calculated value shows a good agreement with the observed value ($a = 0.3161$ nm at room temperature). The difference is less than 0.3%. This good agreement suggests that the crystal structure of MgCu may be same as the calculation model, i.e., CsCl-type. The volume optimization for Mg_2Cu and $MgCu_2$ phases, and raw materials (Mg and Cu) was performed in the same manner.

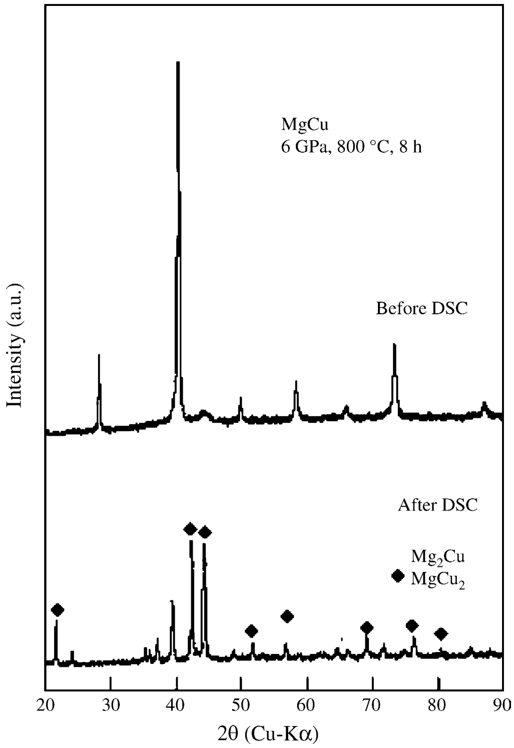

Fig. 3. X-ray diffraction patterns of MgCu (a) before DSC and (b) after DSC.

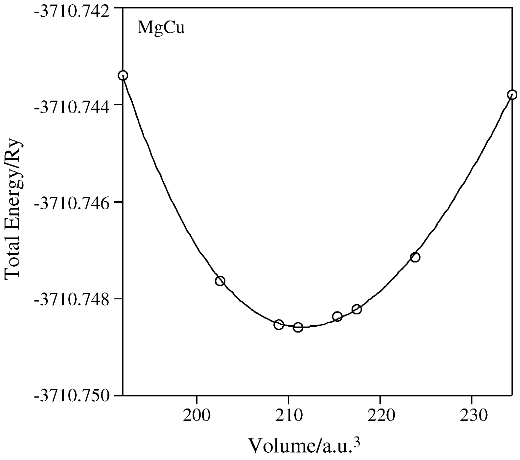

Fig. 4. Total energy of MgCu as a function of lattice volume.

Table 1 summarizes the results of volume optimization for Mg, Cu, Mg_2Cu, $MgCu_2$ and the novel MgCu intermetallic compound. In which, the equilibrium lattice constant, the corresponding minimum total energies, and bulk modulus that can be calculated by fitting the equation of status to the results of volume optimization are listed. As can be seen, the deference between calculated and observed lattice constants was less than 1% for all cases. In addition, bulk modulus of Mg and Cu showed a relatively good agreement with the observed values. These agreements suggest that the calculation conditions used in this study are appropriate and it is possible to discuss about the enthalpy of formation for intermetallic compounds in Mg–Cu system.

Based on the minimum total energies listed in Table 1, the enthalpy of formation of each intermetallic compound was calculated by using the following relationships:

$$\Delta H(\mathrm{Mg_2Cu}) = E(\mathrm{Mg_2Cu}) - 2E(\mathrm{Mg}) - E(\mathrm{Cu}) \tag{2}$$

$$\Delta H(\mathrm{MgCu_2}) = E(\mathrm{MgCu_2}) - E(\mathrm{Mg}) - 2E(\mathrm{Cu}) \tag{3}$$

$$\Delta H(\mathrm{MgCu}) = E(\mathrm{MgCu}) - E(\mathrm{Mg}) - E(\mathrm{Cu}) \tag{4}$$

The enthalpy of formation for these compounds was summarized in Table 2. For the equilibrium phases of Mg_2Cu and $MgCu_2$, the calculated values of the enthalpy of formation were slightly larger than reported values; however, differences between them are less than 10 kJ/mol. Compared to the error of enthalpy of formation obtained by using the same technique for other materials such as $LaNi_5$ [10–12,14], this difference seems to be within the acceptable range. For the novel MgCu phase, the enthalpy of formation was estimated to be −18.4 kJ/mol. Based on Eq. (1), the MgCu phase is considered to be a semi-stable phase compared to the mixture of equilibrium Mg_2Cu and $MgCu_2$ phases, since the value of $1/3\{\Delta H(\mathrm{Mg_2Cu}) + \Delta H(\mathrm{MgCu_2})\}$

Table 1
Calculated lattice constant, total energy, and bulk modulus for Mg, Cu, Mg_2Cu, $MgCu_2$, and MgCu

	Space group	Lattice constants		Total energy Ry/f.u.	Bulk modulus	
		Calculated (nm)	Difference (%)		Calculated (GPa)	Observed (GPa)
Cu	225 ($Fm\bar{3}m$)	0.36296	−0.40	−3310.0648	151.9	140
Mg	194 ($P63/mmc$)	0.31875; 0.51760	0.67; 0.67	−400.6697	36.5	45
Mg_2Cu	70 ($Fddd$)	0.90700; 0.52840; 1.82500	0.00; −0.02; −0.05	−4111.4283	57.1	–
$MgCu_2$	227 ($Fd\bar{3}m$)	0.70433	0.05	−7020.8321	91.6	–
MgCu	221 ($Pm\bar{3}m$)	0.31530	0.25	−3710.7486	68.7	–

1 Ry = 13.6058 eV; 1 eV = 96.485 kJ/mol.

Table 2
The enthalpy of formation for Mg_2Cu, $MgCu_2$ and MgCu (kJ/mol)

	$\Delta H_{calc.}$	ΔH_{298}	
Mg_2Cu	−31.6	−29.497[a]	$E(Mg_2Cu)-2E(Mg)-E(Cu)$
$MgCu_2$	−43.0	−35.145[a]	$E(MgCu_2)-E(Mg)-2E(Cu)$
MgCu	−18.4	–	$E(MgCu)-E(Mg)-E(Cu)$

[a] Kubaschewski, Termochemistry of Mg-alloys, NPL-DCS, Rep.2, 1968.

Table 3
The optimized lattice constant and total energy for MgCuH ($H/M = 0.5$)

	Lattice constant (nm)	Total energy, E (Ry/f.u.)
MgCu	$a = 0.31530$	−3710.7486
H_2	–	−2.3270
MgCuH	$a = 0.30437$ $c = 0.37071$ ($c/a = 1.2180$)	−3711.8665

is lower than that for MgCu by −6.4 kJ/mol. This mutual relation of the enthalpy of formation among raw materials (Mg + Cu), the equilibrium Mg_2Cu and $MgCu_2$ phases, and the MgCu phase is schematically illustrated in Fig. 5. From these calculations, it is expected that the decomposition of MgCu into Mg_2Cu and $MgCu_2$ phases is exothermic reaction with $\Delta H_{decomp.} = -6.4$ kJ/mol. This value shows a fairly good agreement with the observed value of −2.2 kJ/mol in Fig. 2.

3.3. Energetics of hydrogenated MgCu phase (MgCuH; $H/M = 0.5$)

Based on the rule of Miedema's reverse stability and a magnitude relation of the enthalpy of formation between MgCu and $MgCu_2$ as mentioned above, the newly developed MgCu phase seems to have more possibility to form a hydride phase than $MgCu_2$. The hydrogenation of MgCu phase has been examined at temperature just below its decomposition temperature under pH_2 of 7 MPa for 24 h; however, to date, the hydrogenation reaction has not been observed. The enthalpy of hydrogenation for MgCu was therefore estimated by using the first-principles calculation as well. As a calculation model, a super cell with dimensions of 2 × 2 × 1 was used. Hydrogen atoms were distributed on a part of O-sites, i.e., (0, 0, 1/2) and (1/2, 1/2, 0), to be $H/M = 0.5$ (MgCuH). For the calculation of a partially hydrogenated phase, the optimization of c/a ratio is required in addition to the volume optimization. To obtain an equilibrium lattice parameters and the corresponding minimum total energy, the volume optimization under constant c/a ratio and the c/a optimization by fixing the cell volume were repeatedly performed two times. To calculate the enthalpy of hydrogenation, the total energy of an H_2 molecule is required. For that purpose, an H_2 molecule was put in a cell with dimensions of 0.9 nm × 0.9 nm × 0.9 nm, and the total energy was calculated with respect to one k-point, i.e., only the Γ-point.

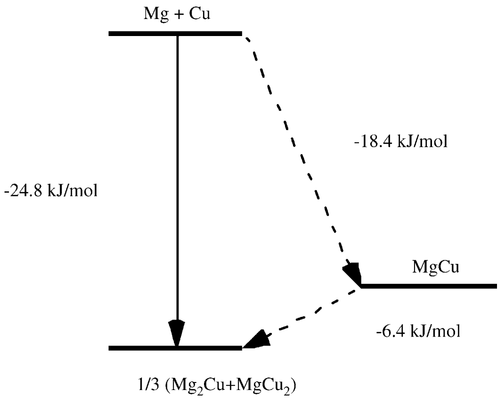

Fig. 5. Schematic diagram of the enthalpy of formation for MgCu.

Table 3 summarizes the optimized lattice parameters and the corresponding total energy. The minimum total energy of MgCuH was obtained for the crystal structure with $a =$ 0.30437 nm and $c = 0.37071$ nm ($c/a = 1.2180$). Based on these total energies, the enthalpy of hydrogenation was calculated as follows:

$$\Delta H = 2\{E(\mathrm{MgCuH}) - E(\mathrm{MgCu}) - E(\mathrm{H_2})/2\} \qquad (5)$$

As a result, ΔH of 119 kJ/mol-H_2 was derived for the hydrogenation reaction of MgCu. Judging from this large positive value of ΔH, the hydrogenation reaction seem to unlikely happen by using a conventional p-c-T apparatus. However, further calculations, including the use of structure model with H atoms on T-sites and/or various H/M ratios, appear to be required to precisely predict the enthalpy of hydrogenation for the newly developed MgCu phase.

4. Conclusions

High-pressure synthesis of MgCu with a CsCl-type structure, and its energetics including the enthalpy of formation have been investigated. The MgCu phase with a lattice constant of $a = 0.3161\,\text{nm}$ was prepared by using a cubic anvil-type apparatus at 800 °C under 6 GPa. The calculated lattice constant showed a good agreement with the observed value with an accuracy of less than 0.3%. Based on the minimized total energies for intermetallic compounds in Mg–Cu system, the enthalpy of formation for the MgCu phase was estimated to be $-18.4\,\text{kJ/mol}$. In addition, the MgCu phase decomposed into Mg_2Cu and $MgCu_2$ phases at around 520 K with $\Delta H = -2.2\,\text{kJ/mol}$. The calculated value of the exothermic reaction ($-6.4\,\text{kJ/mol}$) also showed a fairly good agreement with the observed value. The enthalpy of hydrogenation for MgCu was estimated to be 119 kJ/mol-H_2, when O-site occupation with $H/M = 0.5$ was assumed.

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