

Hydriding and dehydriding properties of Ca–Si–X

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Received 13 September 2006; received in revised form 30 November 2006; accepted 30 November 2006

Available online 29 December 2006

Abstract

We have already reported that CaSi reversibly absorbs and desorbs hydrogen. The maximum hydrogen content and the enthalpy of hydride formation of CaSi were 1.9 wt% (CaSiH_{1.3}) and –62 kJ/mol·H₂, respectively. However, further improvement of CaSi is required for its practical use as a hydrogen storage material. Therefore, we have investigated the effectiveness of partial substitution for Ca or Si. In order to select the substituent X, the stability of Ca–Si–X hydride has been theoretically studied using the first-principles calculations by the ultrasoft pseudopotential method based on the density functional theory. As a result, it was demonstrated that the hydrogen content is improved by the partial substitution of Al, Ge, Mg, Sr, etc. Encouraged by this theoretical result, we have conducted an experiment to investigate the hydriding and dehydriding properties of Ca–Si–X. In the case of X = Al, the experimental result was in close agreement with the theoretical calculation result. Therefore, we confirmed the effectiveness of the calculation in investigating the properties of Ca–Si–X.

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Keywords: Metal silicides; Hydrogen storage materials; First-principles calculation

1. Introduction

The use of hydrogen-based energy in practical applications such as fuel cell vehicles requires the development of safe and efficient hydrogen storage technologies. Although metal hydrides are considered to be one of the promising materials for hydrogen storage, those developed so far do not possess a sufficient gravimetric hydrogen storage capacity for practical applications. Therefore, the development of new light metal hydrides possessing large hydrogen storage capacities is strongly desired.

We have already reported that CaSi reversibly absorbs and desorbs hydrogen [1–3]. However, its maximum hydrogen content of 1.9 wt% is rather low for its practical use as a hydrogen storage material. Therefore, we investigated the effectiveness of partial substitution for Ca or Si in order to improve the hydriding and dehydriding properties of CaSi. In this study, we used the first-principles calculations for the selection of the substituent X to perform efficient development. We also confirmed the

effectiveness of the first-principles calculations in investigating the properties of Ca–Si–X.

2. Theoretical calculations

First-principles calculations were performed to investigate the stability of the Ca–Si–X hydride by the ultrasoft pseudopotential method [4] based on the density functional theory [5]. The generalized gradient approximation formula [6] was applied to calculate the exchange-correlation energy. The details of the computational procedure can be found in refs. [7,8].

Initially, the hydrogen site of the Ca–Si–X hydride was the same as that of CaSi hydride (*Pnma* space group) [3] and ZrNi hydride (*Cmcm* space group) [9,10]. Then, additional hydrogen atoms were placed at other sites according to the empirical criteria that the minimum H–H distance was 2.1 Å [11].

3. Experimental

A Ca–Si–X sample was prepared by melting a mixture of Ca (purity 99.5%), Si (purity 99.999% up) and X is equal to Al (purity 99.99%) or Ge (purity 99.99%) in a high-frequency induction furnace, under an argon pressure of 0.2 MPa. We finished melting a mixture at high temperature than a melting

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Table 1
The calculation results of the enthalpies of hydride formation of $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})$

	Hydride				
	$\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})$	$\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}$	$\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.3}$	$\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.5}$	$\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_2$
H site	Ca4	Ca4 Ca3Si Ca3Al	Ca4 Ca3Si Ca3Al	Ca4 Ca3Si Ca3Al Ca4Al	Ca4 Ca2Si2 Ca2Al2 Ca2Si3
Cohesive energy (hartree/atom)	0.1174	0.1163	0.1156	0.1156	0.1094
ΔH_{cal} (kJ/mol·H ₂)	−30	−53	−56	−56	−21
Hydrogen content (wt%)	1.5	1.9	2.2	2.2	2.9

The indication of H site, for example Ca2Si2, means that the H atom is surrounded by two Ca atoms and two Si atoms.

point of Ca. The alloys were then heat-treated in an argon atmosphere at 1273 K for 10 h and finally quenched in water.

The samples (Ca–Si–Al, Ca–Si–Ge) were examined by pressure–composition (*p–c*) isotherm measurement and X-ray diffraction (XRD) analysis (Rigaku RINT-TTR). The volumetric method was used to obtain the *p–c* isotherms. The XRD measurements were carried out with Cu K α radiation at room temperature.

4. Results and discussion

4.1. Partial substitution for Si

First, we discuss the hydriding and dehydriding properties of $\text{Ca}(\text{Si}_{1-y}\text{Al}_y)$ in which the Si atoms of CaSi are partially replaced by Al atoms. The calculation results of the enthalpy of hydride formation ΔH_{cal} for $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})$ hydride ($y = 0.25$) are shown in Table 1. The indication of H site, for example Ca2Si2, means that the H atom is surrounded by two Ca atoms and two Si. As an example of hydrogen sites, crystal structure of $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.5}$ is shown in Fig. 1(a).

From Table 1, we can assume that the $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})$ absorbs hydrogen as follows:

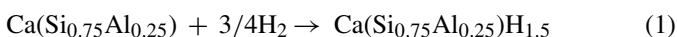


Fig. 1(a) shows the crystal structure of $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.5}$. The enthalpy of hydride formation for $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.5}$ is $-56 \text{ kJ/mol}\cdot\text{H}_2$, in this condition, it is too stable to desorb hydrogen at around room temperature. However, the hydrogen content per metal atom and per weight were $[\text{H}]/[\text{M}] = 0.75$ and 2.2 wt%, respectively, which are greater than those of CaSi ($[\text{H}]/[\text{M}] = 0.67$, 1.9 wt%). The charge density distribution of $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.5}$ on (004) plane is shown in Fig. 1(b). The distribution shows that the H atom is absorbed around the

Al atom because the Al atom has one valence electron lesser than the Si atom.

The above calculation results indicate that the hydrogen content is increased by the partial substitution of Al for Si. However, the enthalpy of the hydride formation was more negative than the calculated value for CaSi ($-45 \text{ kJ/mol}\cdot\text{H}_2$), suggesting that an effect that lowers the hydrogen desorption temperature cannot be expected. In order to confirm the above results, we actually produced $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})$ and evaluated its properties. Fig. 2 shows the XRD profiles of as prepared samples and those after hydrogenation at 573 K under a hydrogen pressure of 9 MPa. The as prepared sample was principally composed of the compound phase with the similar CrB-type crystal structure (*Cmcm* space group) to CaSi and included small quantities of CaAl_2 and CaSi_2 phases. If Si atoms were partly replaced by Al atoms, whose atomic radius is larger than that of Si, a lattice volume expands. Therefore, a diffraction peak position should shift to the low angle side in comparison with that of CaSi. A diffraction peak seen in Fig. 2(a) shifted to the low angle side in comparison with that of CaSi. Therefore, this main phase is considered to be $\text{Ca}(\text{Si}_{1-y}\text{Al}_y)$ phase in which the Si atoms were partly replaced by Al atoms. We think that substituting for Si generated the strain, so the “unknown peak” in Fig. 2(a) appears. On the other hand, the sample after hydrogenation shows a diffraction profile similar to that of $\text{CaSiH}_{1.3}$ (*Pnma* space group) [1]. Therefore, $\text{Ca}(\text{Si}_{1-y}\text{Al}_y)$ may have absorbed the hydrogen and formed the $\text{Ca}(\text{Si}_{1-y}\text{Al}_y)\text{H}_z$ phase (*Pnma*). This is in agreement with the calculation result. Fig. 3 shows the *p–c* isotherms of $\text{Ca}(\text{Si}_{1-y}\text{Al}_y)$ at 573 K. The maximum hydrogen content was 2.0 wt% at 573 K under a hydrogen pressure of 9 MPa. The experimental value is 0.2 wt% less than the calculated value. The small hydrogen content loss appears to be attributable to

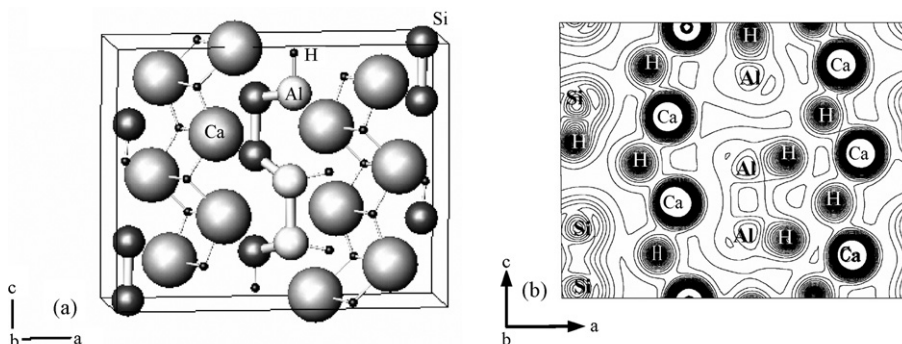


Fig. 1. H interstitial sites in $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.5}$; (a) crystal structure, (b) the charge density distribution of $\text{Ca}(\text{Si}_{0.75}\text{Al}_{0.25})\text{H}_{1.5}$ on (004) plane. The range of $0\text{--}0.5 \text{ e}/\text{bohr}^3$ was drawn at $0.01 \text{ e}/\text{bohr}^3$ intervals.

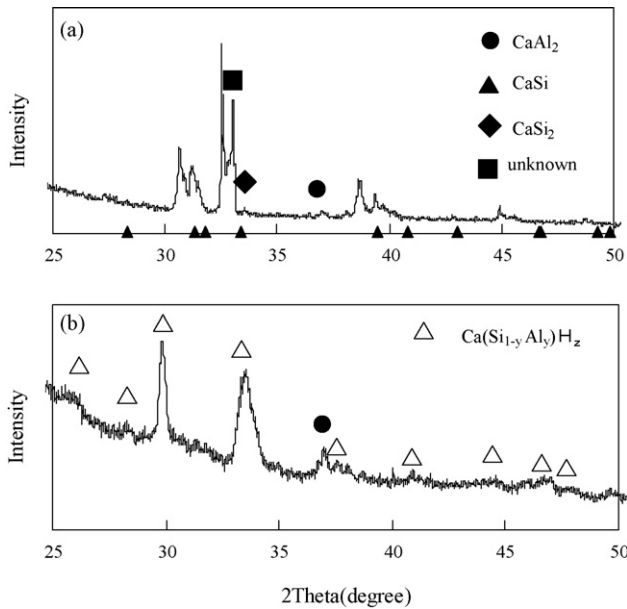


Fig. 2. X-ray diffraction profile of $\text{Ca}(\text{Si}_{1-y}\text{Al}_y)$; (a) as prepared, (b) after hydrogenation.

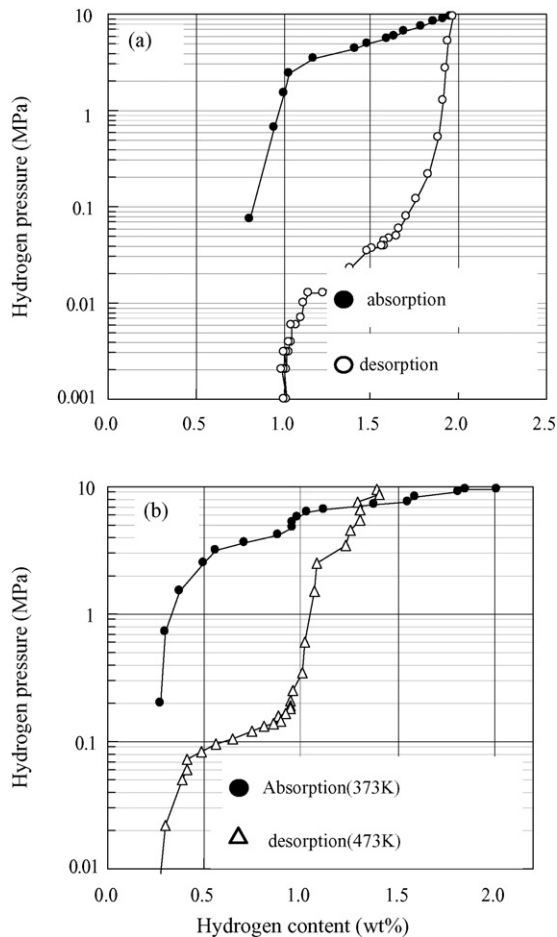
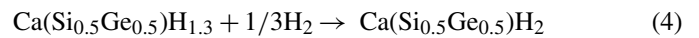
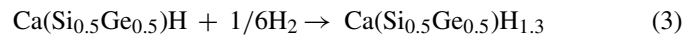
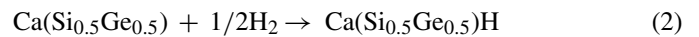


Fig. 3. The p - c isotherms of Ca-Si-X ; (a) $X = \text{Al}$ (573K), (b) $X = \text{Ge}$.

presence of CaAl_2 and CaSi_2 , which did not absorb the hydrogen. Moreover, since the hydrogen desorption pressure becomes lower than that of CaSi (about 0.3 MPa at 573 K), the hydrogen in the alloy could have become stable by the partial substitution of Al for Si.

The above experimental results suggest that the hydrogen content increases over that of CaSi by the partial substitution of Al for Si. However, since the $\text{Ca}(\text{Si}_{1-y}\text{Al}_y)$ hydride stabilizes, the hydrogen desorption temperature becomes higher than that of CaSi . This is in close agreement with the calculation result.

The calculations and the experiment were performed in the case of $X = \text{Ge}$ using the same procedure as that for $X = \text{Al}$. From the calculation, we can assume that $\text{Ca}(\text{Si}_{0.5}\text{Ge}_{0.5})$ absorbed the hydrogen in the following three stages:



The enthalpy of hydride formation ΔH_{cal} in each reaction was evaluated to be -31 , -16 and -9 kJ/mol $\cdot\text{H}_2$, respectively. From the calculation results, we estimated that the maximum hydrogen content was $[\text{H}]/[\text{M}] = 1$, 2.2 wt% and becomes greater than those of CaSi by the partial substitution of Ge for Si. We thought that $[\text{H}]/[\text{M}]$ is larger than that of CaSi , because the lattice volume expands by partial substitution of Ge, whose atomic radius is larger than that of Si, and the number of H interstitial sites increased. Moreover, since the enthalpy of hydride formation for $\text{Ca}(\text{Si}_{0.5}\text{Ge}_{0.5})$ was higher than that for CaSi , we expected that the desorption temperature would become lower than that of CaSi .

Fig. 3 shows the p - c isotherms of absorption at 373 K and desorption at 473 K of $\text{Ca}(\text{Si}_{0.5}\text{Ge}_{0.5})$. We confirmed that $\text{Ca}(\text{Si}_{0.5}\text{Ge}_{0.5})$ absorbed the hydrogen in the three stages, as predicted by the calculations. Therefore, the calculation result was almost in agreement with the experimental result. Moreover, since the hydrogen desorption pressure becomes higher than that of CaSi (about 0.02 MPa at 473 K), the hydrogen in the alloy could have become unstable by the partial substitution of Ge for Si. So we can expect that the desorption temperature would become lower than that of CaSi .

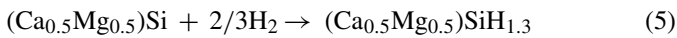
From the above results for X is equal to Al and Ge, we confirmed that the first-principles calculation is effective for studying the hydriding reaction in Ca-Si-X , and the hydriding and dehydriding properties of CaSi can be improved by the partial substitution for Si. In particular, in the case of $X = \text{Ge}$, we can expect that the hydrogen content increases and the hydrogen desorption temperature decreases.

4.2. Partial substitution for Ca

Mg and Sr, which are in the same periodic table group(2A) as Ca, were selected as substitution elements for Ca. The purpose of the partial substitution of Mg for Ca is to achieve lower weight. In the case of $X = \text{Sr}$, since SrSi has the same crystal structure as

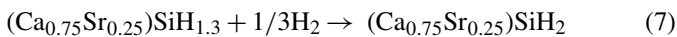
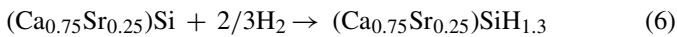
CaSi, we consider that stable (Ca, Sr)Si is formed and it absorbs the hydrogen, while maintaining the *Cmcm* symmetry.

In the case of X = Mg, based on the calculation results, we consider that (Ca_{0.5}Mg_{0.5})Si absorbs hydrogen as follows:



The enthalpy of hydride formation ΔH_{cal} for (Ca_{0.5}Mg_{0.5})SiH_{1.3} was evaluated to be $-9 \text{ kJ/mol}\cdot\text{H}_2$, which is higher than that of CaSi ($-45 \text{ kJ/mol}\cdot\text{H}_2$). Therefore, the hydrogen desorption temperature appears to have become lower than that of CaSi. Moreover, although the hydrogen content per metal atom [H]/[M] is 0.67, which is equal to that of CaSi, the hydrogen content per unit weight increases up to 2.2 wt%, which is greater than that of CaSi.

From the calculation results in the case of X = Sr, we assume that (Ca_{0.75}Sr_{0.25})Si absorbs hydrogen in the two stages as follows:



The enthalpies of hydride formation ΔH_{cal} were evaluated to be -36 and $-20 \text{ kJ/mol}\cdot\text{H}_2$, respectively, both of which are higher than that of CaSi. Therefore, we can expect that the hydrogen desorption temperature becomes lower than that of CaSi. Moreover, the hydrogen content per metal and per unit weight are [H]/[M] = 1 and 2.4 wt%, respectively, which are greater than those of CaSi as desired. We regard these reason as a stability of (Ca, Sr)Si or a lattice expansion.

From the above results for X is equal to Mg and Sr, we can expect that the hydriding and dehydriding properties of CaSi are improved by the partial substitution of Mg or Sr for Ca.

5. Summary

We confirmed the effectiveness of the first-principles calculation for the hydriding and dehydriding properties of Ca–Si–X formed by the substitution for Si in CaSi by other elements X. We predicted the following results based on the first-principles calculation. By partially substituting of Al for Si, the hydrogen content increased, although the hydrogen desorption temperature increased. By partially substituting of Ge for Si, we can expect both an increase in the hydrogen content and a decrease in the hydrogen desorption temperature. In the case of Ca, we can expect that the hydriding and dehydriding properties of CaSi are improved by the partial substitution of Mg or Sr for Ca.

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