

Hydriding and dehydriding properties of CaSi

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Received 28 May 2004; received in revised form 2 November 2004; accepted 8 November 2004

Available online 21 July 2005

Abstract

The hydriding and dehydriding properties of CaSi were investigated both theoretically and experimentally. First-principles calculations suggested that CaSiH_n is thermodynamically stable. Experimentally, the *p*–*c* isotherms clearly demonstrated plateau pressures in a temperature range of 473–573 K and the maximum hydrogen content was 1.9 weight % (wt.%) under a hydrogen pressure of 9 MPa at 473 K. The structure of CaSiH_n is different from those of ZrNi hydrides, although CaSi has the CrB-type structure as well as ZrNi.

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Keywords: Metal silicides; Hydrogen storage materials; CrB-type structure

1. Introduction

Metal hydrides are considered to be one of promising materials for hydrogen storage, however, those which possess sufficient storage capacities for practical applications have not been developed. Accordingly, the development of hydrides of light metals possessing large hydrogen storage capacities is required.

It is well known that ZrNi with the CrB-type structure (space group *Cmcm*) absorbs a large number of hydrogen atoms and forms ZrNiH₃ [1–4]. Other alloys with the same structure are also expected to have high hydrogen storage capacities. Therefore, we turned our attention to CaSi [5,6], which has the CrB-type structure, and studied its hydriding and dehydriding properties both theoretically and experimentally. We expected the hydrogen storage capacity of CaSi to be much larger than that of ZrNi on a unit weight basis, because Ca and Si are much lighter elements than Zr and Ni.

2. Theoretical calculations

First-principles calculations were performed to investigate the stability of CaSi hydride by the ultrasoft pseudopotential

method [7] based on the density functional theory [8]. The generalized gradient approximation formula [9] is applied to the exchange-correlation energy. The details of computational procedure can be found in Refs. [10,11].

In the present calculations, hydrogen was put on the same sites as for ZrNiH (4c site surrounded by four Ca atoms [1]) and ZrNiH₃ (4c site surrounded by three Ca and two Si atoms and 8f site surrounded by three Ca and one Si atoms [1,2]) because CaSi has the CrB-type structure as well as ZrNi. Calculations about CaSiH and CaSiH₃ were performed, respectively, and then the optimized structure of each hydride was acquired by the structural relaxation.

3. Experimental

A CaSi sample was prepared by melting a mixture of Ca and Si in a high-frequency induction furnace under an argon pressure of 0.2 MPa. The alloy was then heat-treated in an argon atmosphere at 1223 K for 30 h and finally quenched in water.

The sample was examined by pressure–composition (*p*–*c*) isotherm measurement and X-ray diffraction (XRD) analysis (Rigaku RINT-TTR). The volumetric method was used to obtain *p*–*c* isotherms when CaSi was dehydrided at 473, 523, and 573 K. Before each measurement, the sample was hydrogenated at 473 K under a hydrogen (purity

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Table 1
Lattice constants of CaSi with the CrB-type structure (space group *Cmcm*)

	Lattice constants (Å)			Reference
	<i>a</i>	<i>b</i>	<i>c</i>	
Calculation	4.517	10.725	3.886	This work
Experiment	4.561	10.735	3.891	[5]
Experiment	4.545	10.728	3.890	[6]

99.99999%) pressure of 9 MPa. The XRD measurements were carried out with Cu K α radiation at room temperature.

4. Results and discussion

4.1. Theoretical calculation on CaSi hydride

The optimized lattice constants of CaSi are shown in Table 1. The calculation values are in agreement with experimental ones [5,6], and it is confirmed that our calculation has been performed in sufficient accuracy.

The enthalpy of hydride formation was obtained by subtracting the total energies of CaSi and the hydrogen molecule from that of its hydride. The calculation for the hydrogen molecule was performed using a cubic supercell with size of 6 Å \times 6 Å \times 6 Å. The bond length and the binding energy are predicted to be 0.755 Å and 4.536 eV/H₂, respectively, which agree with the experimental values of 0.741 Å [12] and 4.747 eV/H₂ [13]. The enthalpies of formation for CaSiH and CaSiH₃ were -27 and $+33$ kJ/mol H₂, respectively. Although the value of the enthalpy for CaSiH₃ is positive, that for CaSiH is negative. These theoretical calculations suggest that CaSi absorbs hydrogen and forms CaSi hydride (CaSiH). The structure model of CaSiH is shown in Fig. 1.

4.2. Hydriding and dehydriding properties of CaSi

Fig. 2 shows the *p*-*c* isotherms of CaSi during dehydriding at 473, 523, and 573 K. The maximum hydrogen content at 473 K under 9 MPa of hydrogen pressure was 1.9 wt.% (CaSiH_{1.3}), which is large compared with that suggested by theoretical calculations (CaSiH). Each of the *p*-*c* isotherms in the temperature range selected for this work clearly showed a

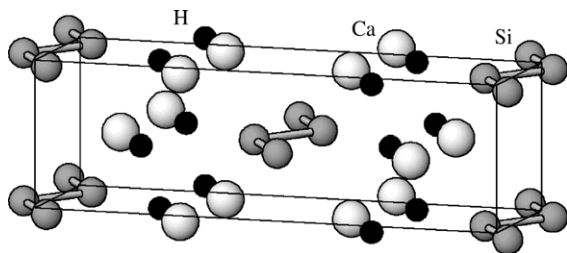


Fig. 1. The structure model of CaSiH. White, grey, and black spheres denote Ca, Si, and H, respectively.

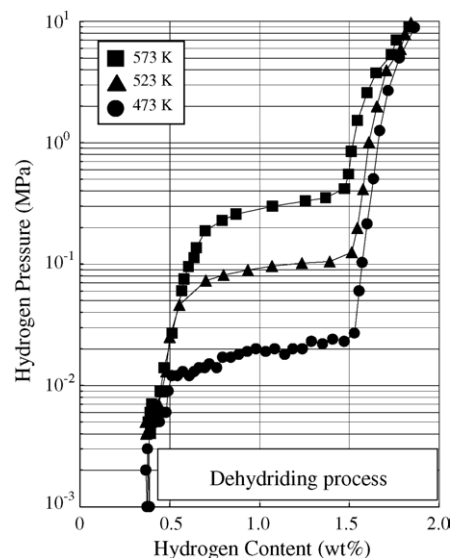


Fig. 2. The *p*-*c* isotherms of CaSi during dehydriding at 473, 523, and 573 K.

plateau pressure and the enthalpy of hydride formation estimated using a van't Hoff plot was -62 kJ/mol H₂. This value is more negative than that theoretically calculated for CaSiH (-27 kJ/mol H₂).

Fig. 3 shows the XRD profiles of the sample as prepared, after hydrogenation and after dehydrogenation at 473 K in all cases. The sample as prepared was composed of the

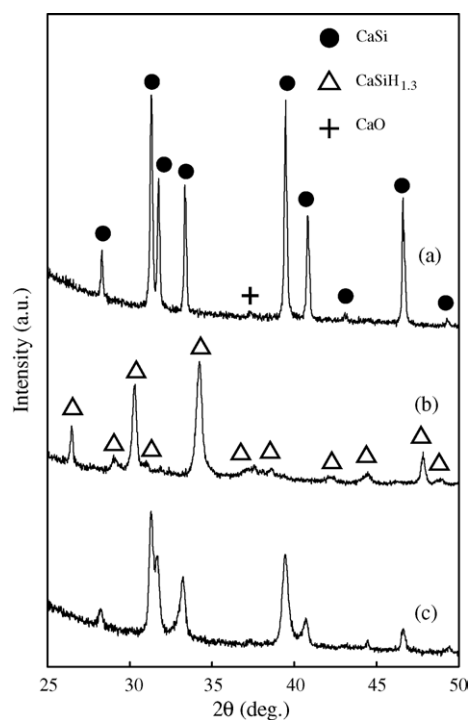


Fig. 3. X-ray diffraction profiles of CaSi (a) as prepared, (b) after hydrogenation under 9 MPa of hydrogen pressure, and (c) after dehydrogenation as evacuation below 1×10^{-3} Pa. Both hydrogenation and dehydrogenation were performed at 473 K.

CaSi phase and a small quantity of CaO phase. After the sample was hydrogenated at 9 MPa, the diffraction peaks of the CaSiH_{1.3} phase appeared, while those of the CaSi phase disappeared. After evacuation below 1×10^{-3} Pa at 473 K to dehydrogenate the sample, the diffraction peaks of the CaSiH_{1.3} phase disappeared, and those of the CaSi phase appeared again. These results of XRD analysis indicate that CaSi reversibly absorbs and desorbs hydrogen at 473 K.

The structure of the CaSiH_{1.3} phase [14] (space group *Pnma*) is different from those of ZrNiH and ZrNiH₃ [1–4], while hydrogen was put on the same sites as for ZrNiH and ZrNiH₃ in the calculations on CaSiH and CaSiH₃, respectively. We think that these cause the differences between the calculated and experimental values of the maximum hydrogen content and the enthalpy of hydride formation.

To understand the hydriding and dehydriding properties of CaSi through an experiment and theoretical discussion, we are systematically investigating the detailed structure of CaSi hydride by synchrotron radiation X-ray diffraction and neutron diffraction measurements.

5. Conclusions

It was found that CaSi reversibly absorbs and desorbs hydrogen through both theoretical and experimental investigations. First-principles calculations suggested that CaSiH is thermodynamically stable. Experimentally, 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. These are different from the calculated values, which

is most likely caused by the difference of structures between CaSi and ZrNi hydrides.

Acknowledgment

The authors would like to thank Dr. K. Miwa for his valuable comments and suggestions regarding this study.

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