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Citation: Applied Physics Letters **85**, 387 (2004); doi: 10.1063/1.1773930 View online: http://dx.doi.org/10.1063/1.1773930 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/85/3?ver=pdfcov Published by the AIP Publishing

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## Reversible hydriding and dehydriding properties of CaSi: Potential of metal silicides for hydrogen storage

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(Received 9 March 2004; accepted 21 May 2004)

We found that CaSi reversibly absorbs and desorbs hydrogen. First-principles calculations theoretically indicated that CaSi hydride is thermodynamically stable. The hydriding and dehydriding properties of CaSi were experimentally determined using pressure-composition (*p*-*c*) isotherms and x-ray diffraction analysis. The *p*-*c* isotherms clearly demonstrated plateau pressures in a temperature range of 473–573 K. The maximum hydrogen content was 1.9 wt % under a hydrogen pressure of 9 MPa at 473 K. The reversible hydriding and dehydriding properties of CaSi suggest the potential of metal silicides for hydrogen storage. © 2004 American Institute of Physics. [DOI: 10.1063/1.1773930]

Hydrogen is considered to be one of the new clean energy sources capable of replacing fossil fuels. The use of hydrogen-based energy in practical applications such as fuel cell vehicles, however, requires the development of safe and efficient hydrogen storage technology. Although metal hydrides hold promise for hydrogen storage, those developed so far do not possess sufficient storage capacity on a unit weight basis for practical applications.<sup>1–3</sup> Accordingly, the development of hydrides of light metals possessing large hydrogen storage capacities is an urgent necessity.

It is well known that ZrNi and LaNi with the CrB-type structure (space group *Cmcm*) absorb a large number of hydrogen atoms and form ZrNiH<sub>3</sub> and LaNiH<sub>4</sub>, respectively.<sup>4–16</sup> Other alloys with the same structure are also expected to have high hydrogen storage capacities. Therefore, we turned our attention to CaSi,<sup>17,18</sup> 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 those of ZrNi and LaNi on a unit weight basis, because Ca and Si are much lighter elements than Zr, La, and Ni. In addition, Ca and Si have the advantage of being lowcost elements.

First, we performed first-principles calculations to investigate the stability of CaSi hydride by the ultrasoft pseudopotential method<sup>19</sup> based on the density functional theory.<sup>20</sup> The theoretical calculations suggested that the enthalpy of formation of CaSi hydride is negative. Encouraged by this result, we conducted an experiment to investigate the hydriding and dehydriding properties of CaSi. The results are presented in this letter. The fact that CaSi reversibly absorbs and desorbs hydrogen is a new find, and neither theoretical nor experimental studies on this phenomenon have been reported.

A CaSi sample was prepared by melting a mixture of Ca (purity 99.5%) and Si (purity 99.999% plus) in a high-purity graphite crucible placed in a high-frequency induction furnace under an argon pressure of 0.2 MPa. The CaSi melt weighed  $\sim$ 400 g. 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, hydrogen analysis using the inert gas fusion method (Horiba EMGA-621), and x-ray diffraction (XRD) analysis (Rigaku RINT-TTR). The conventional volumetric method with a Sieverts apparatus (Suzuki Shokan Co., Ltd.) 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 99.999 99%) pressure of 9 MPa. The XRD measurements were carried out with Cu  $K\alpha$  radiation at room temperature, and the diffraction patterns were analyzed by the Rietveld method using the computer program RIETAN.<sup>21</sup>

Figure 1 shows the *p*-*c* isotherms of CaSi during dehydriding at 473, 523, and 573 K. The hydrogen contents at 473 K under 9 MPa and  $1 \times 10^{-3}$  MPa of hydrogen pressure were 1.9 wt % (CaSiH<sub>1.3</sub>) and 0.4 wt % (CaSiH<sub>0.26</sub>), respectively. These values were in agreement with those obtained by the hydrogen analysis. The hydrogen analysis also revealed that, after the sample was evacuated at 473 K at a pressure below  $1 \times 10^{-1}$  Pa, its hydrogen content was 0.2 wt % (CaSiH<sub>0.13</sub>). Each of the *p*-*c* isotherms in the temperature range selected for this work clearly showed a plateau pressure. The maximum hydrogen content per formula unit of CaSi in the plateau region (CaSiH) is comparable to the hydrogen content of ZrNiH.<sup>4–7</sup> The enthalpy and entropy



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FIG. 1. p-c isotherms of CaSi in dehydriding processes at 473, 523, and 573 K.

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FIG. 2. van't Hoff plot of CaSi in the dehydriding process.

of hydride formation calculated using a van't Hoff plot (shown in Fig. 2) were  $-62 \text{ kJ/mol } \text{H}_2$  and  $-116 \text{ J/mol } \text{H}_2 \text{ K}$ , respectively. This value of the enthalpy, which is less negative than those of ZrNiH, ZrNiH<sub>3</sub>, and LaNiH<sub>4</sub>, <sup>5-9</sup> shows that CaSiH<sub>1.3</sub> is unstable as compared with these hydrides.

Figure 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 CaSi phase and a small quantity of CaO phase. The lattice parameters of the CaSi phase determined by a Rietveld analysis of the XRD profile were a=4.5589(1) Å, b =10.7250(2) Å, and c=3.8930(1) Å, which are in agreement with the values reported in the previous work.<sup>17,18</sup> After the sample was hydrogenated at 9 MPa, the diffraction peaks of the CaSiH<sub>1,3</sub> phase appeared, while those of the CaSi phase disappeared. The CaSiH<sub>1.3</sub> phase was indexed on an orthorhombic lattice with the parameters a=11.217(1) Å, b =14.615(2) Å, and c=3.8165(3) Å. The diffraction intensities suggested the space group to be Pbcn (No. 60). Rietveld refinements based on a metal atom sublattice in the space group *Pbcn* converged at  $R_{wp}=5.7\%$  and  $R_{I}=11.4\%$ , where  $R_{\rm wp}$  and  $R_{\rm I}$  are the weighted profile reliability factor and the reliability factor based on integrated intensities, respectively. The structure of the CaSiH<sub>1.3</sub> phase (space group *Pbcn*) is different from those of  $ZrNiH^{12}$  and  $ZrNiH_3$ .<sup>12,15</sup> After 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 the *p*-*c* isotherm measurement was carried out to  $1 \times 10^{-3}$  MPa of hydrogen pressure. Both hydrogenation and dehydrogenation were performed at 473 K.

*p*-*c* isotherm measurement was carried out to  $1 \times 10^{-3}$  MPa of hydrogen pressure to dehydrogenate the sample, the diffraction peaks of the CaSiH<sub>1.3</sub> phase disappeared, and those of the CaSi phase appeared with 131 and 200 reflections for the orthorhombic lattice splitting as indicated in Fig. 3. The lattice parameters estimated by the Rietveld analysis were a=4.5336(7) Å, b=10.839(2) Å, and c=3.8913(6) Å. These changes in the lattice parameters are attributed to the hydrogen dissolved in the CaSi phase.

We will systematically investigate the detailed structure of CaSi hydride by synchrotron radiation x-ray diffraction and neutron diffraction measurements to understand the hydriding and dehydriding properties of CaSi, through an experiment and theoretical discussion.

In conclusion, we found that CaSi reversibly absorbs and desorbs hydrogen in a temperature range of 473–573 K. CaSi has the same CrB-type structure as ZrNi and LaNi, however, it shows different hydriding and dehydriding properties. Therefore, it is important to investigate the detailed structure of CaSi for improving its performance as a practical hydrogen storage material. CaSi is a new hydrogen storage alloy, and its reversible hydriding and dehydriding properties suggest great potential of metal silicides for hydrogen storage. We are also investigating the hydriding and dehydriding properties of other metal silicides.

The authors would like to thank K. Miwa for his valuable comments and suggestions regarding this study and Y. Kondo for conducting the valuable hydrogen analysis.

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