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Investigation of hydrogen desorption from CaSiH by means of calorimetric method

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Abstract The present work deals with the study of the reaction of hydrogen desorption from the $CaSiH_X$ hydride by means of the calorimetric method. The dehydrogenation of the $CaSiH_X$ hydride was carried out at 548 K. For a calorimetric study, the installation composed of the differential heat-conducting Tian–Calvet type calorimeter connected with a conventional Sieverts-type apparatus was employed. Such installation permitted us to obtain simultaneously the P-X isotherms (P—equilibrium hydrogen pressure, $X = H/CaSi$) and variation of the partial molar enthalpies of the reaction of hydrogen desorption from $CaSiH_X$ with the hydrogen concentration in the metallic matrix. It was ascertained that in the CaSi-H_2 system there was one region where values of the partial molar enthalpy of the reaction of hydrogen desorption from the $CaSiH_X$ hydride remained constant. This means that formation of one hydride phase in the CaSi-H_2 system took place. The enthalpy and entropy values for the reaction of hydrogen desorption from the $CaSiH_X$ in the plateau range are $\Delta H_{des} = 53.8 \pm 1.2$ kJ mol^{-1} H_2 and $\Delta S_{des} = 94.2 \pm 2.7$ J mol^{-1} H_2 K^{-1} (ΔH_{des} and ΔS_{des}—the differential molar enthalpy and entropy desorption, respectively).

Keywords CaSi · Hydride · Calorimetry · Thermodynamic · Desorption

Introduction

The economic advancement raised two burning problems in front of humanity, which are necessary to determine: the first is the ecological problem, associated with burning of large amount of hydrocarbon fuel and discharge into the air of CO_2, and the second one is the exhaustion of world resources of fossil energy carrier (petroleum, coal and natural gas). The use of hydrogen as an ecologically pure energy carrier could permit to decide these problems. Therefore, scientists deal with the development of hydrogen energy, search of new compounds, which could be used for reversible hydrogen storage.

Libowitz et al. [1] in 1958 showed that the ZrNi compound easily and reversibly interacted with hydrogen that led to the formation of the $ZrNiH_3$ hydride. Later, the structure of the ZrNi hydride was studied by means of X-ray and neutron diffraction methods [2–9], and it was determined that ZrNi and $ZrNiH_X$ crystallized into the orthorhombic structure CrB (space group C*mcm*). As well, there are few works in which the thermodynamic properties of the ZrNi hydride were calculated using the van't Hoff equation [10, 11] and measured directly by reaction calorimetry [11–13]. Besides that in the works [5, 10, 14], it was ascertained that intermetallic compounds (IMC) such as HfNi, HfCo and ZrCo reversibly absorb hydrogen too. Nemirovskaya and Lunin studied [14] phase transformations in the IMC having CrB-type structure such as ZrNi, HfNi, ZrCo and HfCo during hydrogen sorption–desorption. And the reaction of hydrogen interaction with each of these IMC was studied by thermodynamic methods [15]. In the recent work, Jat et al. [16] studied the hydrogen interaction with ZrCo plotting PCI's and calculated the thermodynamic parameters according to van't Hoff equation. In addition, the authors found the activation energy

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for the absorption of hydrogen by ZrCo (120 ± 5 kJ mol^{-1} H_2).

The development of hydrogen storage materials makes expert community to analyse the cost of materials from which the sorbent is produced and its molecular weight though scientists drew attention on alkaline-earth silicides. It was found out that CaSi, SrSi and BaSi also crystallized in the CrB-type structure [17–22] and reversibly reacted with hydrogen [23, 24].

Japanese scientists [25–27] hydrogenated CaSi simultaneously to Swiss ones [28, 29] and for the first time studied hydrogen absorption by CaSi, and ascertained that CaSi reversibly absorbed hydrogen. Japanese scientists [25, 26] hydrogenated CaSi at 473 K and hydrogen pressure of 9 MPa and then they desorbed hydrogen from the obtained hydride $CaSiH_{1.3}$ on a Seiverts-type apparatus at three different temperatures.

The present work is devoted to the study of hydrogen interaction with CaSi by the calorimetric method.

Experimental

A CaSi sample was prepared by melting a starting mixture with the stoichiometric composition of Ca (purity 99.5 %) and Si (purity 99.999 %) in a high-frequency induction furnace under argon pressure of 2.0 atm. Then, the CaSi sample was subjected to homogenization in a fused quartz tube under residual argon pressure of 0.1 atm at 1,073 K for 240 h and finally quenched in cold water.

The sample of CaSi was examined by a powder X-ray diffraction analysis with a DRON-4 diffractometer at room temperature using monochromatic Cu K_α radiation, and the diffraction patterns were analysed by the Rietveld method with the computer program RIETAN [30].

In our work, we studied the reaction of hydrogen desorption from the $CaSiH_X$ hydride by the calorimetric method using the differential heat-conducting Tian–Calvet type calorimeter connected with the conventional Sieverts-type volumetric apparatus that permitted us to measure simultaneously the *P-X* isotherms (*P*—equilibrium hydrogen pressure, X = H/CaSi) and the relationship of the differential molar enthalpy versus the hydrogen concentration in the metallic matrix ($\Delta H_{des.} = f(X)$) of desorption reaction of hydrogen with the sample under investigation. The apparatus scheme, the experimental procedure and the treatment of obtained results were described elsewhere [31].

Previously, it was established [32] that according to the conditions of hydrogen reaction with CaSi, two hydride phases may be obtained, namely, $CaSiH_1$ and $CaSiH_{1.2}$, which have different structures. The $CaSiH_{1.2}$ hydride was obtained when hydrogenation of the CaSi sample was carried out at hydrogen pressure of 90 atm. If hydrogenation of CaSi took place under smaller values of the hydrogen pressure, then $CaSiH_1$ is obtained.

In the present work, we hydrogenated the CaSi sample at 548 K and hydrogen pressure of 52 atm for 1 day before each experiment.

Results and discussion

X-ray analysis

According to XRD data, the synthesized CaSi sample had the CrB-type structure (space group C*mcm*). Small amounts of CaO (0.82 mass%) and $Ca_{14}Si_{19}$ (1.77 mass%) were found as minor phases. In addition, the X-ray analysis of the $CaSiH_X$ sample was carried out after five cycles of hydriding/dehydriding. The refined unit lattice parameters for both samples are presented in Table 1 along with reference data.

As one can see from Table 1, the results obtained in the present work are in good agreement with the reference data. A small expansion of lattice parameters of the sample after five cycles of hydriding/dehydriding is due to the fact that a part of hydrogen remained in the matrix of CaSi after desorption, as hereof wrote in [25]. The crystal structure of CaSi after five cycles hydriding/dehydriding remained unchanged.

Hydrogen interaction with CaSi

In Fig. 1, the dependences of *P-X-T* (*T*—temperature of an experiment) are presented for the reaction of hydrogen desorption from the $CaSiH_X$ hydride for four different runs of determination. As one can see from Fig. 1, the CaSi sample absorbs 1.49 mass% hydrogen (548 K and 52 atm) that corresponds to the stoichiometric ratio of H/CaSi = 1.04 and formation of the $CaSiH_{1.04}$ hydride (as pointed out in Fig. 1). In the α-region during dehydrogenation, the equilibrium hydrogen pressure sharply decreases with decreasing of the hydrogen concentration in the metallic matrix (see Fig. 1). At 548 K, hydrogen did not desorb completely from the sample. Really in the work [25], the authors showed the data according to which the hydrogen concentration on the CaSi sample under study after evacuation it at 473 K, and the hydrogen pressure below 1×10^{-1} Pa was 0.2 mass%, that corresponded to formation of the $CaSiH_{0.13}$ composition.

On the *P-X* isotherms obtained at 548 K, one can separate three regions: the α-solid solution of hydrogen in CaSi ($0 < X < 0.35$), the region of two-phase coexistence or "plateau" where the α ↔ ß transition takes place ($0.35 < X < 0.80$) and the region of hydrogen solid solution in the ß-hydride of $CaSiH_X$ ($X > 0.80$). For the first

Table 1 Lattice parameters (*a*, *b*, *c*) and cell volumes (*V*) of CaSi and $CaSiH_X$ with CrB-type structure (space group C*mcm*)

	a/Å	*b*/Å	*c*/Å	*V*/Å^3	Reference
CaSi	4.556(0)	10.74(0)	3.892(5)	190.44	This work
CaSi	4.5589(1)	10.7250(2)	3.8930(1)	190.35	[24]
CaSi	4.5594(9)	10.731(1)	3.8900(7)	190.33	[21]
CaSi	4.559(1)	10.731(1)	3.890(1)	189.67	[23]
$CaSiH_{0.19}$ (after 5-th desorption)	4.531(6)	10.854(1)	3.890(2)	191.31	This work
$CaSiH_{0.26}$ (after desorption)	4.5336(7)	10.839(2)	3.8913(6)	191.22	[24]

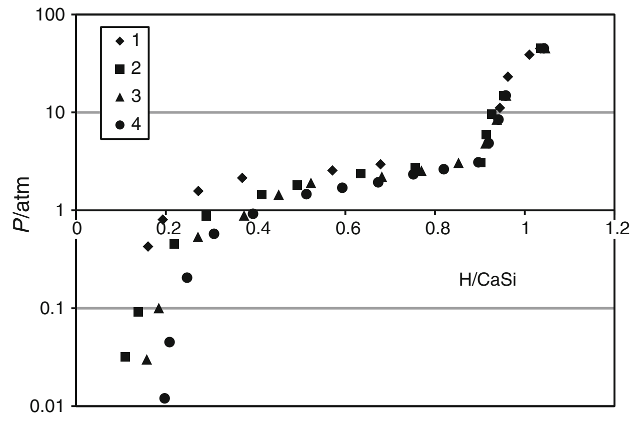

Fig. 1 Desorption isotherms for the CaSi-H_2 system at 548 K for four runs

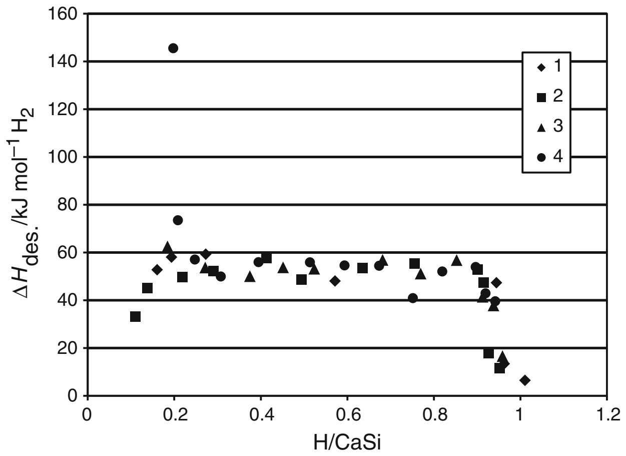

Fig. 2 Desorption enthalpies versus composition for the CaSi-H_2 system at 548 K for four runs

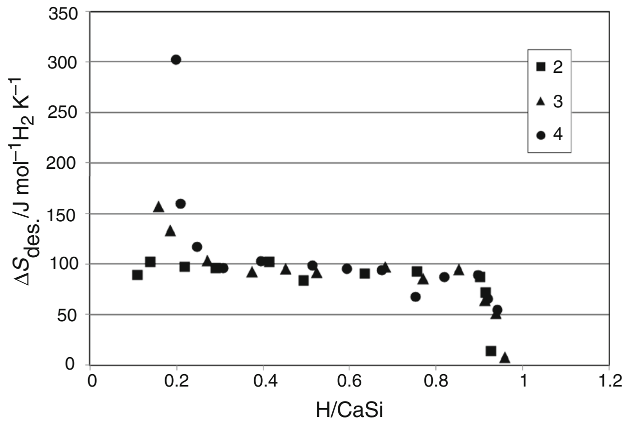

Fig. 3 Desorption entropies versus composition for the CaSi-H_2 system at 548 K for three runs

two runs of the hydrogen desorption, plateau on the *P*-*X* isotherm is well defined and in practice there is no slope (see Fig. 1). However, one peculiarity of the measured *P*-*X*-*T* dependence should be noticed, notably, every new process of hydrogen desorption from the $CaSiH_X$ hydride results in a slight increase of the plateau slope and the length of plateau reduces, that is the α-region length widens. In whole, the presented plot of the *P*-*X*-*T* is in good agreement with the reference data [25, 26].

In Fig. 2, the plot of the $\Delta H_{des} = f(X)$ function (ΔH_{des}—the differential molar enthalpy of the reaction of hydrogen desorption from the $CaSiH_X$ hydride) is obtained directly by calorimetric measurements for four runs of experiments. As one can see from the presented plot, there is one region where the enthalpy values are constant that correlates with the process of the hydride formation. The behaviour of the curve of the $\Delta H_{des} = f(X)$ dependence in the α-region should be noticed. For the first two runs of experiments, the decrease of the hydrogen concentration in the metallic matrix results in reduction of the enthalpies values in the interval $0.10 < X < 0.15$, while for the third and fourth runs, the decrease of the hydrogen concentration in the α-region results in the increase of the enthalpy values in the interval $0.16 < X < 0.30$. It may be assumed that during the absorption/desorption process in the sample under investigation, "traps" form. These traps have greater affinity for hydrogen than the normal interstitial sites. Flanagan et al. [33] suppose that the trapping sites most probably arise from the imperfect nature of intermetallic structure, i.e. metal atoms in wrong positions. The same trapping phenomenon is observed for $LaNi_5$ [34] and ZrNi [35]. In the range of the hydrogen solution in the ß-hydride, the enthalpy values sharply decrease with the rise of the hydrogen concentration in the metallic matrix.

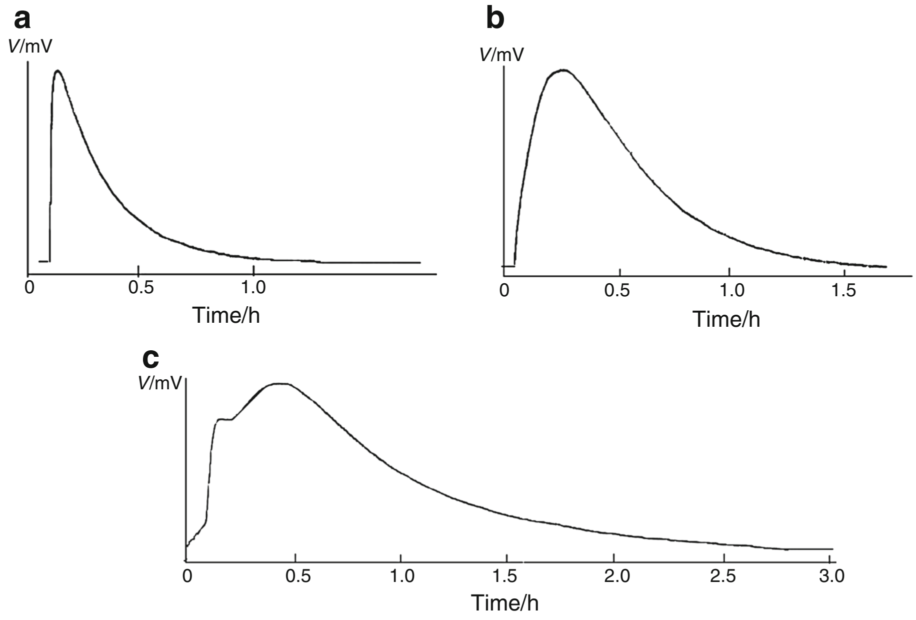

Fig. 4 The shape of curves of heat generation for hydrogen desorption from the CaSi-H_2 system obtained in different parts of this system: **a** hydrogen solid solution in the β-hydride, **b** α-region, **c** plateau region (α ↔ β)

Figure 3 shows the ΔS_{des}-X dependence (ΔS_{des}—the differential molar entropy of hydrogen desorption from the $CaSiH_X$ hydride). The values of ΔS_{des} were calculated on the basis of the calorimetric data and the data obtained from the P-X measurements according to the following equation:

$$\Delta S_{\mathrm{des}} = \frac{\Delta H_{\mathrm{des}}}{T} + R \ln P_{\mathrm{H2des}}. \qquad (1)$$

In the Fig. 3, the plots of the ΔS_{des}-X dependences were presented for three runs of the carried out desorption experiments (for 2nd, 3rd and 4th). As seen from Fig. 3, there is one region with the constant entropy values on the plot of the ΔS_{des}-X dependence ($0.25 < X < 0.85$). The increase in the hydrogen concentration ($X > 0.85$) leads to a sharp decrease of the entropy values. In the α-region, the same picture as for the $\Delta H_{\mathrm{des}} = \mathrm{f}(X)$ is observed, namely, the entropy values of the second run decrease with the decreasing hydrogen concentration in the range $0.10 < X < 0.15$ in the metallic matrix, and on the contrary, the entropy values collected in the third and forth runs increase with the decreasing hydrogen concentration in the range $0.16 < X < 0.30$.

The average values of enthalpy and entropy desorption in the plateau region at 548 K are equal to 53.7 ± 1.2 kJ mol^{-1} H_2 and 94.2 ± 2.7 J mol^{-1} H_2 K^{-1}, respectively. These results differ from those obtained from earlier studies—in Aoki et al. [25, 26] for $CaSiH_{1.3}$ the authors calculated the enthalpy and entropy of the hydride formation using the van't Hoff plot and obtained the data as -62 kJ mol^{-1} H_2 and -116 $\mathrm{mol}^{-1} H_2$ K^{-1}, respectively, and in Ohba et al. [27], the enthalpy of the hydride formation of $CaSiH_{1.3}$ was estimated as -42 kJ mol^{-1} H_2 from the calculation based on crystal structure symmetry determined by the Rietveld refinements of synchrotron X-ray diffraction data and -27 kJ mol^{-1} H_2 for the formation of monohydride CaSiH. It may be connected with either the past history of the sample or the feature behaviour of the hydrogen absorption–desorption reaction.

It is worthwhile to draw attention to one feature that we noticed during our calorimetric study of the hydrogen desorption from $CaSiH_X$. The duration of the experiment was different depending on which part of the CaSi-H_2 system the reaction of hydrogen desorption took place, namely, if hydrogen was desorbed from the dilute α-solution, the reaction would finish in 1.0–1.5 h; the reaction of hydrogen desorption from the hydrogen solid solution in the β-hydride finished in 0.5–1.0 h after removing the next portion of hydrogen. If the reaction of the hydrogen desorption takes place in the plateau region, then it would finish in 2.5–3.0 h. To illustrate the above-described situation in Fig. 4, the shape of curves of heat generation is presented for three parts we mentioned. It should be noted that on the shape of curve corresponding to the reaction in the plateau region, there is some inflection that testifies about the complex character of reaction of the hydrogen desorption from the CaSi-H_2 system in the current region.

Conclusions

1. For the first time, the hydrogen interaction with CaSi was studied by the calorimetric method.

2. The dependences of P-X, ΔH_{des}-X and ΔS_{des}-X were obtained at 548 K for the CaSi-H_2 system. The average values of the enthalpy and entropy for the reaction of the hydrogen desorption in the plateau region are $\Delta H_{\mathrm{des}} = 53.7 \pm 1.2$ kJ mol^{-1} H_2 and $\Delta S_{\mathrm{des}} = 94.2 \pm 2.7$ J mol^{-1} H_2 K^{-1}, respectively.
3. It was established on the basis of the obtained curves of the heat generation that the process of the hydrogen desorption from the CaSi-H_2 system in the plateau region has a complex character.

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