Calorimetric study of the hydrogen interaction with $Ce_6Ni_{1.67}Si_3$

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Abstract. In the present work at the first time the hydrogen interaction with $Ce_6Ni_{1.67}Si_3$ at pressure up to 45 atm and temperature 51°C has been investigated by means of the calorimetric method. The ΔHabs.-C dependence (ΔHabs. - the partial molar enthalpy of the reaction of the hydrogen interaction with IMC, C - hydrogen concentration, C=H/IMC) was obtained.

Introduction

For the first time Bodak and co-work. [1] described the formation of the ternary $Ce_6Ni_2Si_3$ compound in the Ce-Ni-Si system. The authors defined that a new compound crystallized in its own structure type: $Ce_6Ni_2Si_3$ (space group *P*6$_3$/*m, a*=1.211 nm, *c*=0.432 nm) [2]. Gaudin showed [3] that the ternary silicide $Ce_6Ni_2Si_3$ did not exist and he defined more exactly the stoichiometry of this compound, notably its precise chemical formula $Ce_6Ni_{1.67}Si_3$ and the crystal structure was determined. In Ref. [4, 5] the authors investigated the hydrogen interaction with $Ce_6Ni_2Si_3$ and carried out crystal-chemical analysis of the original compound and its hydride. Yaropolov [6] studied of the magnetic properties of $Ce_6Ni_{1.67}Si_3H_X$. However, there are not any thermodynamic data of the reaction of the hydrogen interaction with $Ce_6Ni_{1.67}Si_3$ in the scientific literature until now. As the $Ce_6Ni_{1.67}Si_3$ compound contains large quantity of cerium known as an active hydride forming element the interaction of the $Ce_6Ni_{1.67}Si_3$ compound with hydrogen, as one can suppose, would be accompanied by evolving of great quantity of heat, and the equilibrium hydrogen pressure in the $Ce_6Ni_{1.67}Si_3$-H system at the temperatures excepting disproportionation during the hydrogen absorption is very low. Therefore in this case it is impossible to determine the enthalpy of the absorption (desorption) reaction by the measurement of "pressure-composition" isotherms and calculate the thermodynamic functions according to the Van't-Hoff equation. That's why in the present work we studied the reaction of the hydrogen interaction with $Ce_6Ni_{1.67}Si_3$ by means of the calorimetric method that permitted us to derive the dependence of the partial molar enthalpy of hydrogen absorption vs the hydrogen concentration in the metal matrix.

Experimental details

The intermetallic compound $Ce_6Ni_{1.67}Si_3$ was prepared by arc melting in a furnace with a non-spending tungsten electrode on a copper water-cooled boat in a purified argon atmosphere under pressure 2 atm. The input materials were nickel (99.99%), cerium (99.9%) and silicon (99.99%). Titanium sponge was used as a getter for a purification of argon from impurities. The amount of cerium was chosen with some excess as compared with a stoichiometric composition to compensate the metal losses. The sample was turned over and re-melted several times to ensure homogeneity. Then as-cast alloy was subjected to homogenising vacuum annealing in a sealed silica ampoule at 900°C for 10 days with following fast quenching in cold water.

X-ray powder diffraction analysis of the phase composition and unit cell parameters of the starting alloy and its hydrides, containing the different amounts of hydrogen, were carried out on a diffractometer DRON with Cu Kα radiation.

A twin-cell differential conducting calorimeter of Tian-Calvet type, connected with an apparatus for hydrogenation, was employed for a study of a hydrogen reaction with $Ce_6Ni_{1.67}Si_3$. This permitted us to determine simultaneously the amount of hydrogen, absorbed or desorbed during the reaction, and to measure the amount of release (absorbed) heat corresponding this process. The installation diagram and the experimental technique were described elsewhere [7]. The reaction of hydrogen interaction with the sample under investigation was carried out at 51°C. The volumetric method was employed to quantify absorbed (desorbed) hydrogen. The hydrogen content in the sample was determined from the volumes of the apparatus and pressures before and after absorption (desorption) of H_2 and the hydrogen concentration in the sample was calculated using the Van-der-Waals equation of a gas law for pressure below 20 atm, the modified Van-der-Waals equation [8] for pressure above 20 atm and the equation for ideal gases at pressure below 1 atm.

The heat effect of the reaction was calculated according to the equation:

Q=S•A/Δn, where   (1)

S – area of voltage-time plot,

A – receptiveness, determined from an electrical calibration

Δn – the number of absorbed/desorbed H_2 mole

It should be noted that the study of the hydrogen reaction with $Ce_6Ni_{1.67}Si_3$ was carried out on a non-activated sample IMC. It was connected with the physicochemical peculiarities of the present reaction, which was accompanied by the great quantity of releasing heat that resulted in forming of a very stable hydride. At 51°C hydrogen did not eliminate from the hydrogenated sample completely and at high temperatures $Ce_6Ni_{1.67}Si_3$ hydride was subjected to disproportion. Therefore we carried out our experiments every time on a new portion of the sample (2.0000 – 2.6000g).

Results and discussion

According to the X-ray diffraction data the synthesized $Ce_6Ni_{1.67}Si_3$ sample had the hexagonal structure, space group *P6$_3$/m*, with the unit cell parameters close to those reported previously [3, 4]. The impurity content in the annealing sample was below 5%. The hydrogen interaction with $Ce_6Ni_{1.67}Si_3$ resulted in the formation of the hydride which had following composition $Ce_6Ni_{1.67}Si_3H_{11.3}$ without any change of an original structure type but as one can see from the Table 1 a pronounced anisotropic distortion of the unit cell was observed.

In the Table 1 the X-ray characteristics of the origin sample and its hydrides are presented. The hydride with the minor hydrogen concentration ($Ce_6Ni_{1.67}Si_3H_{10.0}$) was obtained as a result of partial dehydrogenation of $Ce_6Ni_{1.67}Si_3H_{11.3}$.

Table 1. Crystallografic data for the $Ce_6Ni_{1.67}Si_3$ compound and its hydrides.

Composition	*a*, [Å]	*c*, [Å]	V, [Å^3]	ΔV/V, [%]
$Ce_6Ni_{1.67}Si_3$	12.071(3)	4.299(7)	542.3(2)	-
$Ce_6Ni_{1.67}Si_3H_{10.0}$	12.800(5)	4.141(1)	587.6(4)	8.0
$Ce_6Ni_{1.67}Si_3H_{11.3}$	13.004(4)	4.134(1)	605.4(5)	11.3

The calorimetric measurements showed that the hydrogen reaction with $Ce_6Ni_{1.67}Si_3$ started without any induction period in practice and the formation of hydride was accompanied by the release of the great quantity of heat. ΔHabs.-C plot (ΔHabs - the partial molar enthalpy of the reaction of the hydrogen interaction with IMC, C - hydrogen concentration, C=H/IMC) is presented on the Fig.1

for one of the run. The plot shows that the process of hydrogen absorption by $Ce_6Ni_{1.67}Si_3$ passes through the several stages where the enthalpy values remain constant on every stage at the change of the hydrogen concentration in the metallic matrix.
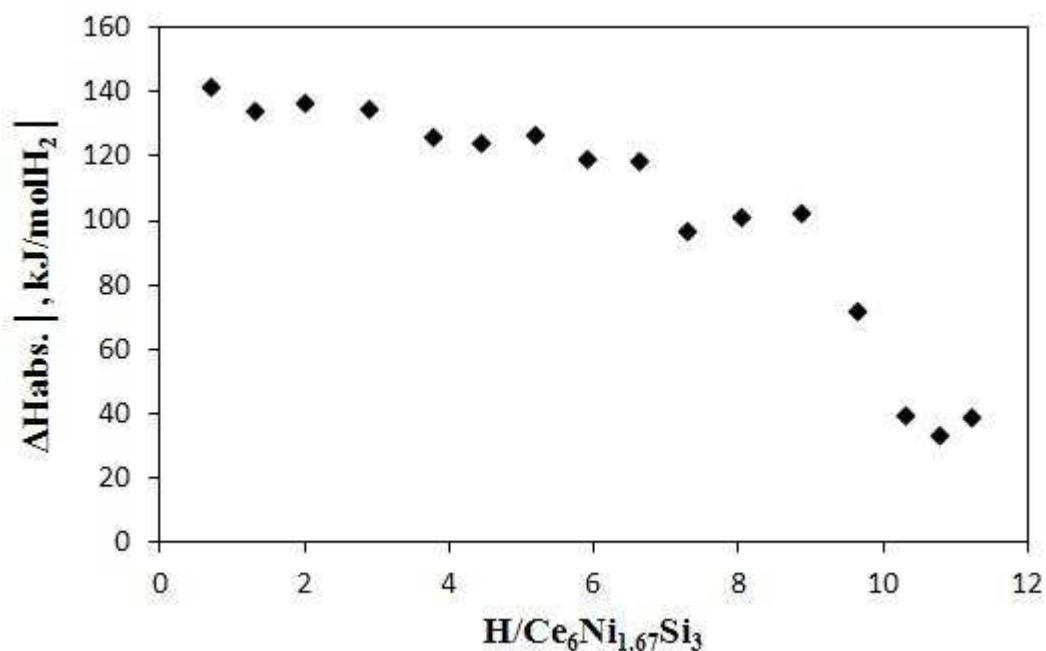

Fig.1. Changes in the partial molar absorption enthalpies vs. composition for the $Ce_6Ni_{1.67}Si_3$-H_2 system at 51°C.

The reaction enthalpy gradually decreases on absolute value from ~ -137kJ/molH$_2$ to ~ -97kJ/molH$_2$ along the C axis and in the range of hydrogen concentration about C≈9.1 the sharp reduction of the enthalpy values was observed (till ~ - 38kJ/molH$_2$). In the Table 2 the constant enthalpy values of absorption (desorption) and corresponded them the hydrogen concentration ranges are presented.

Table 2. The values of absorption and desorption partial molar enthalpy for the $Ce_6Ni_{1.67}Si_3$ –H_2 system at 51°C at different composition range.

Range	ΔHabs., [kJ]/[molH$_2$]	ΔHdes., [kJ]/[molH$_2$]
1.0 < C < 2.8	-137.64±2.27	
3.7 < C < 6.6	-118,86±2.07	
7.2 < C < 9.6	-97.79±1.97	
10.2 < C < 11.2	-38.96±1.36	38.36±1.11

As there is a sufficient length range where the equilibrium pressures of hydrogen are too small for to make pressure measurement by a membrane vacuum gauge used in our Sivert-type volumetric apparatus (<0.02 atm) so we obtained the P-C isotherms diagram for the absorption and desorption processes only from 10.2 to 11.2 C (see fig.2).

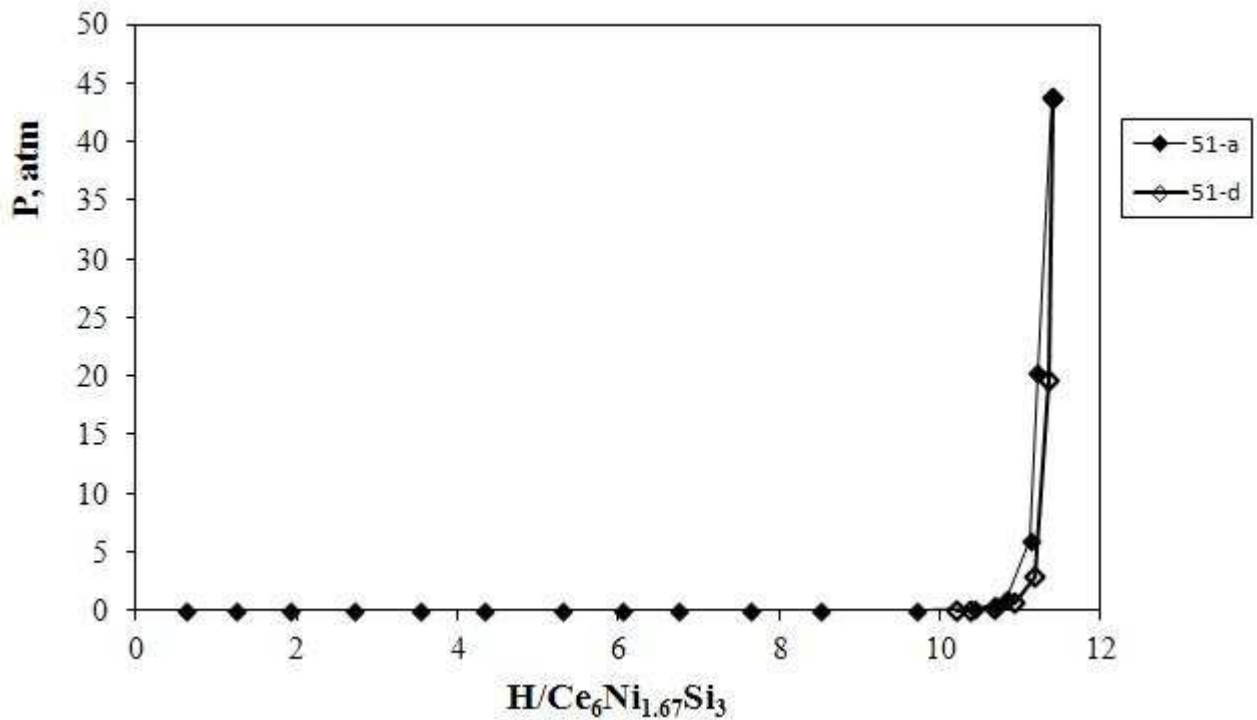Fig.2 Pressure-composition isotherms: absorption (filled) and desorption (opened) symbols for the $Ce_6Ni_{1.67}Si_3$ – H_2 system at 51°C.

The sharp decrease of exothermicity of the hydrogenation reaction of the studied IMC permitted us to desorb reversibly about one hydrogen atom. The enthalpy value of the desorption process on the range $10.0 < C < 11.2$ is equal to 38.36 ± 1.11 kJ/molH_2 (see fig.3). According to the X-ray diffraction data the sample under investigation did not decompose after partial desorption i.e. it remained the hexagonal structure $P6_3/m$ of the original sample but the lattice parameters changed slightly. Then we repeated the reaction of the hydrogen absorption on the same region of the hydrogen concentrations in the IMC and obtained the enthalpy value of the hydrogen absorption equalled to -38.96 ± 1.36kJ/molH_2. On basis of the obtained data it could draw a conclusion that in the range of the hydrogen concentration in the IMC $10.0 < C < 11.2$ the enthalpy values for the absorption and desorption processes coincide in magnitude.
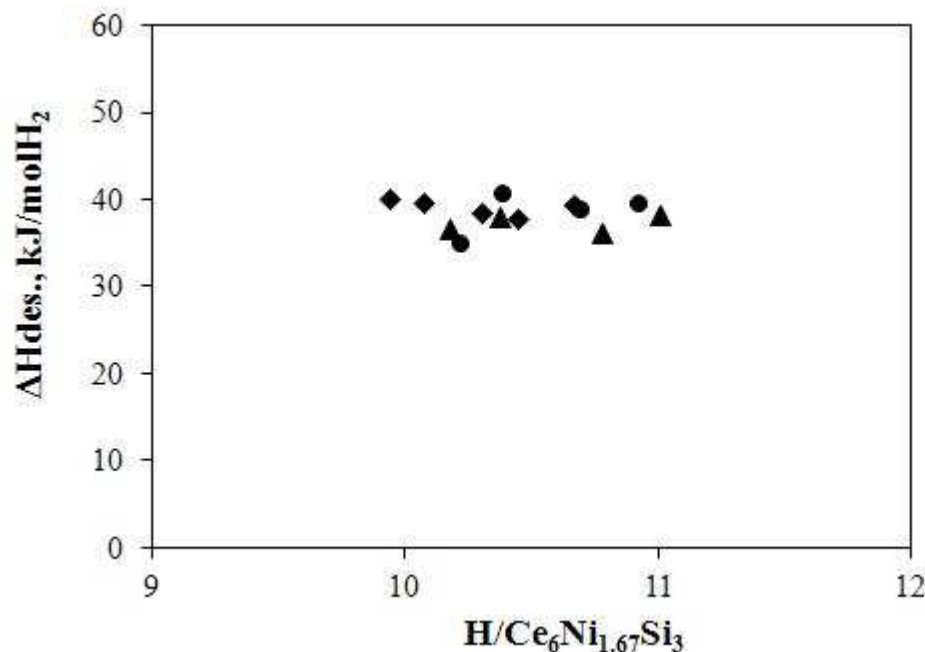
Fig.3. Partial molar desorption enthalpy for the $Ce_6Ni_{1.67}Si_3$-H_2 system at 51°C.The different symbols refer to different series of determinations.

The integral enthalpy (ΔHint) of hydrogenation of the sample up to the composition $Ce_6Ni_{1.67}Si_3H_{11.3}$ can be calculated by integrating the partial molar enthalpies of hydrogen absorption within the range $0<C<11.3$.

$$Ce_6Ni_{1.67}Si_3 +11.3/2\ H_2 \rightarrow Ce_6Ni_{1.67}Si_3H_{11.3} \tag{2}$$

The enthalpy of absorption calculated in this way is equal to -106.40 kJ/molH_2.

Yaropolov et al. [6] ascertained that the interaction of $Ce_6Ni_{1.67}Si_3$ with hydrogen resulted in the formation of $Ce_6Ni_{1.67}Si_3H_{12.3}$. In this case three types of tetrahedral interstices (4f, 12i$_1$ and 12i$_2$) are occupied. Among three mentioned above tetrahedral interstices the 4f tetrahedron, formed by three cerium atoms and one nickel atom, possesses the largest volume as the tetrahedrons 12i$_1$ and 12i$_2$ are formed by three cerium atoms and one silicon atom. Therefore, it is possible to assume that hydrogen atoms will occupy the 4f interstice in the first place and it will be accompanied by the most release of heat. However, the authors in the work [6] established that 4f interstices were occupied by hydrogen atoms only half that is 0.96 hydrogen atoms are located in the 4f tetrahedron and the subsequent filling these sites are blocked by hydrogen atoms which occupy tetrahedral interstices 12i$_1$ and 12i$_2$. These last interstices are occupied by hydrogen on 96% and 93%, respectively, i.e. 5.76 hydrogen atoms locate in 12i$_1$ sites and 5.58 hydrogen atoms locate 12i$_2$. If we compare these data with the plot of the ΔH-C dependence (see Fig.1 and Table 2) we can notice that the length of the range where the enthalpy values have the maximum magnitude (-137.64±2.27 kJ/molH_2) equals nearly 2 hydrogen atoms after that the enthalpy decreases on absolute values and once more range appears where the enthalpy values are constant (-118.86±2.07 kJ/molH_2). The length of this range is equal to ~ 3.0 hydrogen atoms. And finally, there is one more range with the constant enthalpy values of hydrogen reaction with IMC ($7.2 < C < 9.6$, -97.79±1.97kJ/molH_2). On the base of these data we can draw a conclusion that filling of the crystallographic positions by hydrogen in the IMC matrix occurs on the complex path and when non-activated samples are studied it is difficult to establish relation among the filling of some definite interstitial site and the realise of definite quantity of heat.

Conclusion

For the first time the reaction of the hydrogen interaction with $Ce_6Ni_{1.67}Si_3$ was studied by means of the calorimetric method. The dependence of ΔHabs.(des.)-C at 51ºC and the value of the integral hydrogenation enthalpy up to the composition $Ce_6Ni_{1.67}Si_3H_{11.3}$ which was equalled to -106.4 kJ/molH$_2$, were obtained.

It was shown that the calorimetric method of the study the hydrogen interaction with IMCs, hydrides of which possess a very low hydrogen dissociation pressure and a high temperature causes their disproportion, is one of the most informative methods that permitted to determine the calorific effect of the reaction of hydrogenation directly.

References

[1] O.I. Bodak, E.J. Gladyshevsky, O.I. Kharchenko, Crystal structure of $Ce_6Ni_2Si_3$ and related compounds, Crystallogr. Rep. №1 (v.19) (1974) 80-83.

[2] Yu.M. Prots, W. Jeitschko, Lanthanum Nickel Silicides with the General Formula $La_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$ and Other Series of Hexagonal Structure with Metal: Metalloid Ratios Close to 2:1, Inorg. Chem. 37 (1998) 5431-5438.

[3] E. Gaudin, B. Chevalier, On the structural and magnetic properties of the ternary silicides $Ce_6M_{1.67}Si_3$ (M=Co, Ni) and $Ce_5Ni_{1.85}Si_3$, J. Solid State Chem. 180 (2007) 1397-1409.

[4] S.A. Lushnikov, S.N. Klyamkin, A.V. Morozkin, V.N. Verbetsky, Hydride formation in Ce(La)–Ni–Si ternary compounds, J. Alloys and Compd. 293–295 (1999) 429–432.

[5] A.V. Morozkin, S.N. Klyamkin, V.N. Verbetsky, Yu.D. Seropegin, V.K. Portnoy, Hydrogen in $Ce_2Ni_{1-X}Si_{1+X}$ and $Ce_6Ni_2Si_3$ compounds, International Journal of Hydrogen Energy 24 (1999) 141-143.

[6] Yu.L. Yaropolov, A.S. Andreenko, S.A. Nikitin, S.S. Agafonov, V.P. Glazkov, V.N. Verbetsky, Structure and magnetic properties of RNi (R=Gd, Tb, Dy, Sm) and $R_6Ni_{1.67}Si_3$ (R=Ce, Gd, Tb; M=Ni, Co) hydrides, J. Alloys Compd. 509 (2) (2011) S830-S834.

[7] Anikina E.Yu., Verbetsky V.N, Calorimetric investigation of the hydrogen interaction with $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$, J. Alloys and Compd. 330-332 (2002) 45-47.

[8] H. Hemmes, A. Drissen, R. Griessen, Thermodynamic properties of hydrogen at pressure up to 1 Mbar and temperature between 100 and 1000K, J. Phys. C: Solid State Phys. 19 (1986) 3571-3885.

Solid Compounds of Transition Elements II

Calorimetric Study of the Hydrogen Interaction with Ce$_6$Ni$_{1.67}$Si$_3$