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Hydride formation in Ce(La)–Ni–Si ternary compounds

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Abstract

Hydrogen interaction with $R_2Ni_{0.8}Si_{1.2}$, R_2NiSi, $R_2Ni_{1.2}Si_{0.8}$ and $R_6Ni_2Si_3$ (R=La, Ce) compounds were studied. The new hydride phases, namely, $La_2Ni_{0.8}Si_{1.2}H_{3.75}$, $La_2NiSiH_{3.9}$, $La_2Ni_{1.2}Si_{0.8}H_{4.4}$, $Ce_2Ni_{0.8}Si_{1.2}H_{3.7}$, $Ce_2NiSiH_{4.4}$, $Ce_2Ni_{1.2}Si_{0.8}H_{4.9}$, $La_6Ni_2Si_3H_{12}$ and $Ce_6Ni_2Si_3H_{10.9}$ have been synthesised and characterised by X-ray diffraction and thermodesorption methods. All hydrides retained the structure type of the starting compounds with pronounced anisotropic distortion of crystal lattice: the increase of the «a» parameter at decreasing «c». Variation of the Ni/Si ratio in $R_2Ni_{1-x}Si_{1+x}$ (x=0, 0.4 and −0.4) markedly affected the hydrogen capacity and crystal lattice extension. The Ce-containing hydrides possessed a higher hydrogen contents but significantly smaller specific unit cell volume expansion per one hydrogen atom in comparison with La-based compounds. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cerium–nickel–silicon compounds; Hydride; Crystal structure

1. Introduction

Formation of ternary R_2NiSi and $R_6Ni_2Si_3$ compounds in the R–Ni–Si system (R=La,Ce) has been described in Ref. [1]. Both La- and Ce-containing compounds crystallise in the Ce_2NiSi ($P6_3/m$, $a=1.612$ nm, $c=0.4309$ nm) and $Ce_6Ni_2Si_3$ ($P6_3/m$, $a=1.211$ nm, $c=0.432$ nm) structure types [2,3]. R_2NiSi possesses a large homogeneity area with possible variation of Ni and Si contents from 20 to 30 at.%.

Hydrogen interaction with this type of compounds was not investigated until now, meanwhile they can be considered as promising matrices for hydrogen intercalation due to a high content of cerium which is known as an active hydride forming metal. On the other hand, the presence of silicon, which usually suppresses hydrogen absorption, and the opportunity to vary the Ni/Si ratio within the limits of the same structure type causes a special interest in such studies.

2. Experimental details

The $R_2Ni_{0.8}Si_{1.2}$, R_2NiSi, $R_2Ni_{1.2}Si_{0.8}$ and $R_6Ni_2Si_3$ (R=La,Ce) compounds were prepared by arc melting under an argon atmosphere in a furnace with a non-consumable tungsten electrode and water-cooled copper tray. Silicon (purity of 99.99%), nickel (99.99%) and cerium (99.85%) were used as the starting components and a titanium sponge as a getter.

Sample hydrogenation was performed at hydrogen pressures up to 50 MPa. The composition of hydrides formed was calculated from volumetric measurements and controlled by a high-temperature vacuum extraction method.

X-ray powder diffraction studies for starting alloys and synthesised hydrides were conducted on DRON-3.0. The characteristic X-ray used was Cu Kα and the measurement was scanning for the angle from 20 to 70°C, step 0.05°C, 5 s per point). The X-ray patterns obtained were examined with the CSD [4] and Rietan [5] software.

3. Results

The prepared alloys were single-phase compounds crystallised in the structure types mentioned above. We would like to note that the *a* and *c* periods, and so the unit cell volume, of the $R_2Ni_{0.8}Si_{1.2}$, R_2NiSi and $R_2Ni_{1.2}Si_{0.8}$ compounds were nearly independent on the nature of R element (see Table 1).

All samples reacted with hydrogen even at room temperature and pressures of 0.1–0.5 MPa. Temperature

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Table 1
Crystallographic data for $R_2Ni_{0.8...1.2}Si_{1.2...0.8}$, $R_2Ni_{0.8...1.2}Si_{1.2...0.8}H_x$, $R_6Ni_2Si_3$ and $R_6Ni_2Si_3H_x$ compounds

Compound	Structure	*a*, nm	*c*, nm	*c*/*a*	*V*, nm^3	Δ*V*/*V*,%	Δ*V*/*H*, $nm^3 10^3$	*H*/*M*
$Ce_6Ni_2Si_3$	$Ce_6Ni_2Si_3$	1.2016	0.4299	0.3578	0.5375	–	–	–
$Ce_6Ni_2Si_3H_{10.9}$	$Ce_6Ni_2Si_3$	1.2829	0.4129	0.3218	0.5885	9.48	2.34	0.99
$La_6Ni_2Si_3$	$Ce_6Ni_2Si_3$	1.2212	0.4385	0.3591	0.5664	–	–	–
$La_6Ni_2Si_3H_{12}$	$Ce_6Ni_2Si_3$	1.3365	0.4152	0.3106	0.6423	13.39	3.16	1.09
$Ce_2Ni_{0.8}Si_{1.2}$	Ce_2NiSi	1.5965	0.4271	0.2675	0.9429	–	–	–
$Ce_2Ni_{0.8}Si_{1.2}H_{3.7}$	Ce_2NiSi	1.7027	0.4100	0.2408	1.0294	9.18	2.34	0.93
$La_2Ni_{0.8}Si_{1.2}$	Ce_2NiSi	1.6208	0.4349	0.2683	0.9893	–	–	–
$La_2Ni_{0.8}Si_{1.2}H_{3.75}$	Ce_2NiSi	1.7461	0.4165	0.2385	1.0997	11.16	2.95	0.94
Ce_2NiSi	Ce_2NiSi	1.5969	0.427	0.2674	0.9430	–	–	–
$Ce_2NiSiH_{4.4}$	Ce_2NiSi	1.6936	0.4105	0.2424	1.0197	8.13	1.74	1.10
$Ce_2NiSiH_{3.7}$	Ce_2NiSi	1.6781	0.4114	0.2452	1.0033	6.39	1.63	0.93
La_2NiSi	Ce_2NiSi	1.6213	0.4351	0.2684	0.9905	–	–	–
$La_2NiSiH_{3.9}$	Ce_2NiSi	1.7468	0.4171	0.2388	1.1025	11.13	2.87	0.98
$La_2NiSiH_{3.3}$	Ce_2NiSi	1.7288	0.4204	0.2432	1.0881	9.86	2.96	0.83
$Ce_2Ni_{1.2}Si_{0.8}$	Ce_2NiSi	1.5968	0.4268	0.2673	0.9424	–	–	–
$Ce_2Ni_{1.2}Si_{0.8}H_{4.9}$	Ce_2NiSi	1.6816	0.4121	0.2451	1.0091	7.08	1.36	1.23
$La_2Ni_{1.2}Si_{0.8}$	Ce_2NiSi	1.6220	0.4351	0.2682	0.9913	–	–	–
$La_2Ni_{1.2}Si_{0.8}H_{4.4}$	Ce_2NiSi	1.7398	0.4183	0.2404	1.0964	10.61	2.39	1.10

lowering to 243 K did not result in visible changes in the hydrogen capacity of the reaction products. The composition of the hydrides formed and their structural parameters are presented in Table 1. Analysis of the X-ray diffraction patterns showed that the hydride phases retained the structure type of their parent compounds with pronounced anisotropic distortion of the crystal matrix (Fig. 1). While the *a* parameter increased up to 6–10%, value of *c* decreased down to 4–5.5% during hydrogen intercalation for all the alloys studied.

To characterise the thermal stability of the hydrides their behaviour during heating in vacuum has been studied. It was establish that hydrogen release began at 520–570 K. Thermodesorption was a monotonic process up to 850–900 K that corresponded to loss of approximately 40% of the hydrogen absorbed. At those temperatures a phenomenon of partial re-absorption has been observed. Complete desorption and restoration of the starting intermetallic compounds occurred at a temperature of 1250 K. In order to define the nature of the re-absorption effect an X-ray

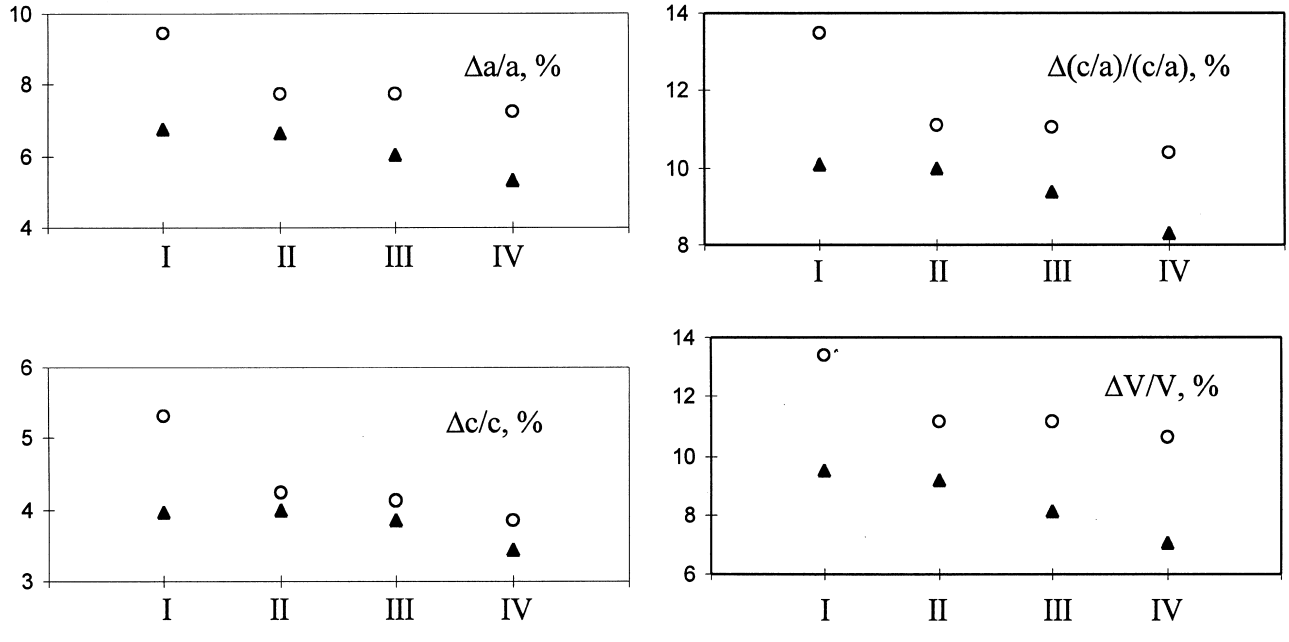

Fig. 1. Dependance of relative change of unit cell parameters at hydrogenation versus type of compounds. I-$R_6Ni_2Si_3$, II-$R_2Ni_{0.8}Si_{1.2}$, III-R_2NiSi, IV-$R_2Ni_{1.2}Si_{0.8}$. ○–La-compounds, ▲–Ce-compounds.

study of the intermediate reaction products has been performed. The data obtained for the $R_2NiSi–H_2$ system showed that when the hydrogen content in the hydride became close to $R_2NiSiH_{2.7}$ (870 K) a decomposition of the intermetallic matrix took place and the formation of cerium (lanthanum) dihydride and RNi_2Si_2 phase was registered:

$$2R_2NiSiH_{2.7}+0.3H_2=3RH_2+RNi_2Si_2$$

According our experimental data $CeNi_2Si_2$ did not react with hydrogen over a wide pressure–temperature range.

It is necessary to note that the studied hydrides lost partially absorbed hydrogen during a prolonged exposure to air in spite of their stability at room temperature in a hydrogen atmosphere or in vacuum. One month of exposure led to the hydrogen content decreasing by 15–20%, probably due to oxidation by air.

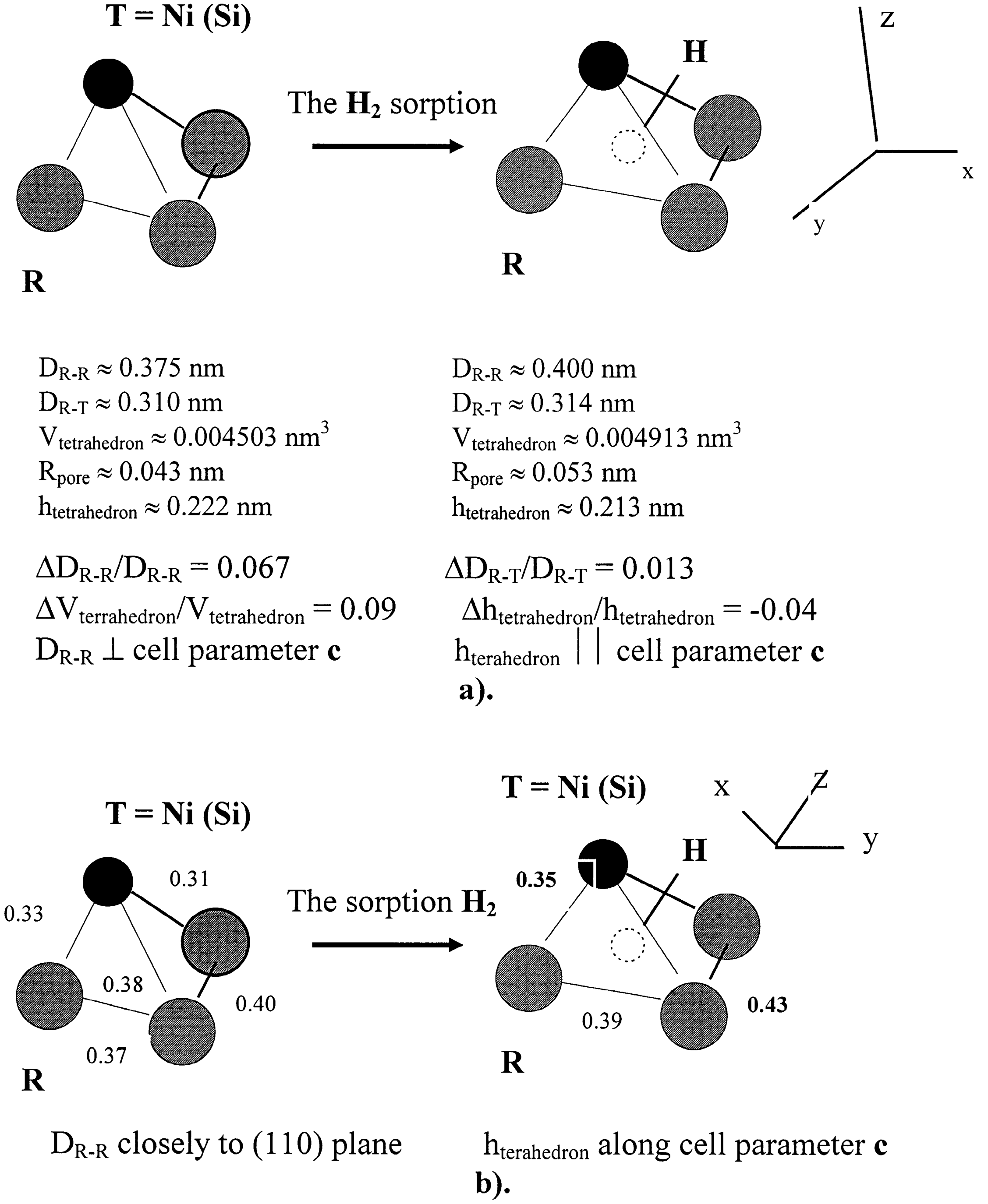

Fig. 2. Distortion of the two types of R_3T tetrahedra at hydrogen intercalation in R_2NiSi compounds.

4. Discussion

The crystal chemical analysis of the Ce_2NiSi and $Ce_6Ni_2Si_3$ structures shows that both lattices possess a large number of similar interstitial positions potentially available for hydrogen intercalation. All interstices can be shared in two groups. The first one includes the two types of R_3T tetrahedra (T=Ni, Si) which have a *R*3 base in the [*110*] crystallographic plane (or close to this plane) (Fig. 2). According to experimental X-ray data these tetrahedra are characterised by extension of all interatomic distances and tetrahedra volumes during hydride formation (Fig. 2). Other interstitial positions pertaining to the second group possess in their environment a R–R pair oriented in the (*001*) direction and compressed in hydrides taking into account the decrease of *c* lattice parameter mentioned above. Those particularities and the correlation between hydrogen capacity and the Ni/Si ratio (i.e. number of Ni and Si atoms in T positions) allow us to deduce that the filling with hydrogen of the R_3T interstices is the main factor influencing the formation and composition of hydride in the investigated compounds.

The Ce-containing hydrides demonstrated a significantly smaller specific unit cell volume expansion per one hydrogen atom than La-based compounds. This phenomenon can be attributed to the known ability of cerium ions, unlike lanthanum, to assume 3+ and 4+ valency states and change them during hydride formation and decomposition [6]. A $Ce^{3+} \rightarrow Ce^{4+}$ transition during hydrogenation is connected with a decrease of the effective metallic radius and, therefore, a relatively smaller expansion of crystal lattice. Final conclusions needs some additional studies, for example, magnetic measurements.

5. Conclusions

The hydrides formed in $R_6Ni_2Si_3$ and $R_2Ni_{1-x}Si_{1+x}$ ($x=0$, 0.4, -0.4) where R=La, Ce, retained the structural type of the parent compounds with pronounced anisotropic distortion of the crystal lattice. In a series of $R_2Ni_{1-x}Si_{1+x}$–H_2 systems the absorption capacity increased with increasing Ni/Si ratio. The Ce-containing hydrides possessed a higher hydrogen content but smaller specific lattice volume expansion in comparison with La-based compounds which can be attributed to the change of the Ce valency state during hydrogenation.

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