Interaction of $R_{1-x}Zr_xSi$ (R = La, Ce, Nd, Dy; x = 0-0.05) Silicides with Hydrogen

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Abstract—The interaction of $R_{1-x}Zr_xSi$ (R = La, Ce, Nd, Dy; x = 0-0.05) silicides with hydrogen has been studied at hydrogen pressures of up to 250 MPa. At a high pressure and a temperature of 20°C, hydrogen solubility in the solid phase is very low. Raising the reaction temperature leads to disproportionation of the silicides. According to X-ray diffraction data, the disproportionation reaction yields a rare-earth hydride and RSi₂ disilicide.

Keywords: rare-earth silicides, hydrogen, hydrides, high pressure **DOI:** 10.1134/S0020168518010077

INTRODUCTION

RSi equiatomic silicides crystallize in the FeB and CrB structures [1, 2]. Such compounds are known to possess unique magnetic properties [3, 4]. The incorporation of hydrogen into an RSi lattice may lead to significant changes in the physicochemical properties of the material, but the hydriding of these compounds has not yet been studied in detail.

In this paper, we report a study of interaction of undoped and partially zirconium-doped RSi binary compounds with hydrogen.

EXPERIMENTAL

RSi silicides and $R_{1-x}Zr_xSi$ (R = La, Ce, Nd, Dy; x = 0-0.05) solid solutions were prepared by reacting pure components (R, 99.9%; Zr, 99.99%; Si, 99.99%) in an electric arc furnace under an inert atmosphere. Interaction with hydrogen and silicide-hydrogen equilibrium were investigated using an experimental setup that ensured hydrogen pressures of up to 250 MPa [5]. Before each experiment, silicide samples were ground in an agate mortar to a particle size near 5-7 mm for placing them in a reactor. Next, the samples were preactivated in vacuum at a temperature near 300°C for 1 h in order to remove the residual moisture from their surface.

Prior to X-ray diffraction characterization, the samples were thoroughly ground in an agate mortar into fine powder. The phase composition of the samples hydrided at high pressures was determined after passivation in air. To this end, an autoclave containing a sample was cooled to liquid nitrogen temperature (77 K) and then the pressure in the autoclave was lowered to atmospheric pressure. Next, the open autoclave containing the sample was held at liquid nitrogen temperature in air for 1 h. This procedure was used to passivate high-pressure hydride phases based on various alloys and intermetallic compounds [6, 7].

X-ray diffraction patterns of the samples were collected on a DRON-3M diffractometer (Co radiation). The X-ray diffraction data obtained were used to determine the phase composition of the samples.

RESULTS AND DISCUSSION

According to X-ray diffraction data, the samples of the equiatomic compounds CeSi, LaSi, and NdSi, as well as the zirconium-doped samples $Ce_{0.97}Zr_{0.03}Si$ and $La_{0.99}Zr_{0.01}Si$, were single-phase and crystallized in the FeB structure (Table 1). The $Dy_{0.95}Zr_{0.05}Si$ sample crystallized in the CrB structure and was also single-phase (Table 1). The lattice parameters of the synthesized equiatomic compounds are in reasonable agreement with data in the literature [8].

When interacting with hydrogen at a high pressure (250 MPa) and 20°C, the CeSi, LaSi, NdSi, $Ce_{0.97}Zr_{0.03}Si$, and $Dy_{0.95}Zr_{0.05}Si$ samples dissolve an extremely small amount of hydrogen: the composition of the limiting solid solution can be represented as $RSiH_{0.1}$. At the same time, after exposure to a high hydrogen pressure, the X-ray diffraction patterns of the passivated samples showed only reflections from the starting phases (Table 2). It is reasonable to assume that this type of passivation was ineffective in the case of the compounds under investigation. In a number of

Compound	Structure type	Lattice parameters, nm		
		а	b	С
LaSi	FeB	0.8403(2)	0.4011(2)	0.6070(3)
CeSi	FeB	0.8309(2)	0.3960(2)	0.5957(3)
NdSi	FeB	0.8160(3)	0.3917(3)	0.5889(3)
Ce _{0.97} Zr _{0.03} Si	FeB	0.8301(3)	0.3941(2)	0.5902(3)
$La_{0.99}Zr_{0.01}Si$	FeB	0.8398(2)	0.4020(3)	0.6052(3)
Dy _{0.95} Zr _{0.05} Si	CrB	0.4240(1)	1.0502(2)	0.3801(2)

Table 1. Structural data for the as-prepared compounds

 Table 2. Phase composition of the hydrided silicides

Compound	<i>p</i> , MPa; <i>t</i> , °C	Phase composition of the hydriding products	
LaSi	200; 20 5; 400	LaSi LaH ₂ solid solution, LaSi ₂ solid solution	
CeSi	200; 20 5; 300	CeSi CeH ₂ solid solution, CeSi ₂ solid solution	
NdSi	200; 20 5; 300	NdSi NdH ₂ solid solution, NdSi ₂ solid solution	
Ce _{0.97} Zr _{0.03} Si	200; 20 5; 300	$\frac{Ce_{0.97}Zr_{0.03}Si}{CeH_2 \text{ solid solution, } Ce_{0.97}Zr_{0.03}Si_2 \text{ solid solution}}$	
La _{0.99} Zr _{0.01} Si	200; 20 5; 300	$\label{eq:constraint} \begin{array}{l} La_{0.99}Zr_{0.01}Si\\ LaH_2 \mbox{ solution, } La_{0.99}Zr_{0.01}Si_2 \mbox{ solution} \end{array}$	

experiments, we identified rare-earth disilicides with the general formula RSi_{2-x} (x = 0-0.4) [9, 10], which points to partial disproportionation of the RSi compounds at high hydrogen pressures (Table 2).

The disproportionation process can be represented by the following scheme:

 $RSi + H_2 \rightarrow RH_2 + RSi_2$.

By analogy with previous findings [11], it is worth noting that the disproportionation of various rare-earth compounds is favored by the considerable heats of formation of binary hydrides and RSi₂ disilicides. For $R_{1-x}Zr_xSi$ solid solutions, the disproportionation reaction scheme is the same as for the interaction of RSi with hydrogen. Possible precipitation of zirconium dihydride or disilicide as an individual phase was not confirmed by X-ray diffraction data. Most likely, the zirconium dissolves in the rare-earth disilicide. For example, it is seen from the Ce–Zr–Si phase diagram [12] that zirconium solubility in CeSi₂ is about 5%.

Raising the temperature considerably increases the disproportionation rate. For example, in the case of NdSi, reaction occurred at a pressure of 5 MPa and temperature of 300°C. Analogous reaction products were obtained for LaSi and CeSi. In this case, however, the disproportionation reaction took place at a

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higher pressure (15 MPa) and higher temperature $(500^{\circ}C)$ (Table 2).

For the LaSi compound, Hennenberg [13] obtained neutron diffraction data using a sample that was exposed to a hydrogen atmosphere at a pressure of 0.65 MPa and temperature 520°C for 1.5 h. The data reported by Hennenberg [13] can be interpreted in the same manner as those obtained for hydrided CeSi in this study. At the same time, the interpretation of our X-ray diffraction data for LaSi differs from what was reported by Bohmhammel and Henneberg [14]: at a pressure of 1.2 MPa and temperature of 500°C, they observed the formation of a compound with the composition LaSiH₁₀ and an expanded crystal lattice of the parent lanthanum silicide. Bohmhammel and Henneberg [14] used differential thermal analysis and observed hydrogen absorption by their sample, but they presented no X-ray diffraction data for reaction products [14]. Thus, it is reasonable to assume that the LaSi sample studied by Bohmhammel and Henneberg [14] also underwent disproportionation. It should also be noted that Henneberg was the author or coauthor of both reports [13, 14].

CONCLUSIONS

At a hydrogen pressure of ≤ 250 MPa and room temperature, the synthesized silicides sorb an insignificant amount of hydrogen. Raising the reaction temperature leads to disproportionation of the silicides into a binary rare-earth hydride and RSi₂ disilicide.

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