Chemical and Phase Transformations in the Systems Hydrogen-Sorbing Intermetallic Compound–Diborane

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Abstract — The reactions of the intermetallic compounds CeFe₂, CeCo₂, and λ_3 -ScFe₂ with B₂H₆ at 4.8 × 10³ Pa, 293–573 K, and various contact times were studied. CeFe₂ decomposes in the presence of diborane to give CeH_{1.9–2.2}, Ce₂Fe₁₇H_{8–10}, α -Fe, CeCo₂ decomposes into the cerium trihydride CeH_{2.7–2.8} and α -Co, whereas λ_3 -ScFe₂ forms an ScFe₂H_{0.4–0.5} hydride phase. Therewith, with CeFe₂ and CeCo₂, diborane decomposes into solid nonvolatile X-ray amorphous various-composition compounds (BH_m)_n, as well as H₂ and B₅H₉, while with λ_3 -ScFe₂, into H₂, B₄H₁₀, B₅H₉, B₅H₁₁, and (BH_m)_n.

For certain intermetallic compounds formed by rareearth metals, scandium, yttrium, etc. (A) and 3d-transition metals (B), hydrogen absorption and dissociation occur under mild conditions and fairly fast, while with different rates, according to reaction (1) [1, 2].

$$AB_n + xH_2 \xleftarrow{P_1, T_1}{\swarrow} AB_nH_x,$$
(1)
$$P_1 \ge P_2, T_2 \ge T_1; n = 1-5.$$

However, the formation of AB_nH_x hydride phases by reaction (1) is not a single possible way of reaction of an intermetallic compound with hydrogen. As shown previously, decomposition of intermetallides under the action of H₂ is more reasonable thermodynamically. Therewith, depending on the chemical nature of intermetallide and conditions (pressure and temperature), reaction (2) gives one or more X-ray amorphous products [3, 4], or results in the decomposition of the starting intermetallide into binary hydride AH_x and 3*d*-transition metal B [2] by reaction (3), or the decomposition of the intermetallide into the binary hydride and a new, B-enriched AB_mH_y hydride phase by reaction (4) [2, 4].

$$AB_n + xH_2 \xrightarrow{P, T} X$$
-ray amorphous products, (2)

$$AB_n + xH_2 \xrightarrow{P, T} AH_x + nB,$$
 (3)

$$AB_n + xH_2 \xrightarrow{P, T} AH_x + AB_mH_y, m > n.$$
 (4)

In this connection we chose as model objects $ScFe_2$, $CeCo_2$, and $CeFe_2$, whose reactions with molecular oxygen are described by reactions (1–4), and for the

hydrogenating agent, a carrier of bound and active hydrogen, diborane. The intermetallide ScFe₂ melts congruently and has two polymorphous modifications: λ_1 phase (structural type MgZn₂) formed at temperatures higher than 1473 K and λ_3 phase (MgNi₂ structural type) formed at 1873 K. In the melt with a scandium content of 36.5 at%, a Laves cubic phase λ_2 -ScFe_{1.74} (MgCu₂ structural type) was found, formed by a peritectic reaction at 1798 K [5]. The compounds CeFe₂ and CeCo₂ are formed by peritectic reactions at 1213 and 1296 K, respectively, and crystallize in the MgCu₂ structural type [5].

The aim of the present work was to study reactions of the intermetallic compounds λ_3 -ScFe₂, CeCo₂, and CeFe₂ with diborane as a carrier of chemically bound and active hydrogen.

As follows from the data in the table, at room temperature in the presence of CeFe2, diborane decomposes evolving hydrogen, and the intermetallide undergoes profound phase transformations involving its decomposition and formation of several crystal phases: α -Fe, CeH_r, and Ce₂Fe₁₇H_v. In all the cases studied, the crystal lattice period of CeH_x varies within 0.5578–0.5564 nm, implying formation of the hydride $CeH_{1.9-2.2}$. The $Ce_2Fe_{17}H_{1.5}$ hydride phase crystallized in the Th₂Ni₁₇ structural type (a_0 0.8651 and c_0 0.8385 nm), with the unit cell volume increased by ~6% compared with Ce_2Fe_{17} . By analogy with the $Ce_2Co_{17}H_{47}$ hydride phase whose unit cell volume is increased by 3.2% compared with Ce₂Co₁₇ [6] and assuming that the changes in the unit cell volume, related to one "absorbed" hydrogen atom $(\Delta V/H),$ for the Ce_2Fe_{17} and Ce_2Co_{17} phases should be close to each other, the y value in

Starting intermetallic compound	Reaction conditions		Reaction products	
	<i>Т</i> , К	time, h	gas phase	solid phase
CeFe ₂	293	0.5	$B_{2}H_{6}, H_{2}$	CeFe ₂
CeFe ₂	293	3.5	$B_{2}H_{6}, H_{2}$	CeFe ₂ , α -Fe
CeFe ₂	293	24	$B_{2}^{2}H_{6}^{0}, H_{2}^{2}$	α -Fe, CeH _r , CeFe ₂ ,
CeFe ₂	293	96	$B_{2}^{2}H_{6}^{0}, H_{2}^{2}$	α -Fe, CeH _x , Ce ₂ Fe ₁₇ H _y
CeFe ₂	323	4	$B_{2}^{2}H_{6}^{0}, H_{2}^{2}$	α -Fe, CeH _x , Ce ₂ Fe ₁₇ H _y
CeFe ₂	373	4	$B_{2}^{2}H_{6}^{0}, H_{2}^{2}, B_{5}H_{0}$	α -Fe, CeH _x , Ce ₂ Fe ₁₇ H _y , (BH _m) _n
CeFe ₂	423	1	$B_{2}H_{6}, H_{2}, B_{5}H_{0}$	α -Fe, CeH _x , Ce ₂ Fe ₁₇ H _y , (BH _m),
CeFe ₂	473	1		α -Fe, CeH _x , Ce ₂ Fe ₁₇ H _y , (BH _m) _n
CeC_{2}^{2}	293	144	B_2H_6 , H_2	CeCo ₂ , X-ray amorphous products ^a
$\operatorname{CeC}_{\circ 2}^{2}$	323	1	$B_{2}^{2}H_{6}^{0}, H_{2}^{2}$	CeCo ₂ , X-ray amorphous products ^a
$CeC_{\circ 2}^{2}$	373	1	$B_{2}^{2}H_{6}^{0}, H_{2}^{2}, B_{5}H_{0}$	X-ray amorphous products ^a
$CeC_{\circ 2}^{2}$	473	0.5	$B_{2}H_{6}, H_{2}, B_{5}H_{0}$	CeH ₂₇₂₈ , X-ray amorphous
2			2 0 2 5 7	products ^a
CeC _{°2}	573	1.5	_	$\operatorname{CeH}_{2,7,2,8}$, α -Co, $(\operatorname{BH}_m)_n$
ScFe ₂	293	24	$B_{2}H_{6}, H_{2}$	ScFe ₂
ScFe ₂	293	96	$B_{2}H_{6}, H_{2}$	ScFe ₂
ScFe ₂	388	7	$B_{2}H_{6}$, H_{2} , $B_{5}H_{0}$, $B_{4}H_{10}$, $B_{5}H_{11}$	$ScFe_{2}Hz$, $ScFe_{2}$, $(BH_{m})_{n}$
ScFe ₂	423	2	$B_{2}H_{6}, H_{2}, B_{5}H_{0}, B_{4}H_{10}$	$ScFe_2H_z$, $ScFe_2$, $(BH_m)_n$
ScFe ₂	473	0.5	$B_{2}H_{6}, H_{2}, B_{5}H_{0}$	$ScFe_2H_z$, $(BH_m)_n$
2		l l		

Conditions and results of the reactions of $CeFe_2$, $CeCo_2$, and $ScFe_2$ with B_2H_6 at the initial pressure $P 4.8 \times 10^3$ Pa in the static mode

^a Solid nonvolatile X-ray amorphous products containing hydrogen and no boron (according to chemical and IR spectral analysis).

Ce₂Fe₁₇H_y can be estimated at 8–10. The crystal lattice period of α -Fe in all experiments was the same (a_0 0.2865), which is nicely consistent with published data (a_0 0.2866 nm [7]). At reaction temperatures increased to 373–423 K, along with H₂ and B₂H₆, in the gas phase we found ~5% of B₅H₉, whereas in solid products, up to 10% of nonvolatile variable-composition boranes (BH_m)_n.

The intermetallide $CeCo_2$ reacts with B_2H_6 at an appreciably lower rate than with CeFe₂. At 293–323 K, among solid reaction products, some unreacted CeCo₂ is present along with X-ray amorphous hydrogen-containing compounds, while diborane decomposes with H_2 evolution. At 373–473 K, in the gas phase we found, along with hydrogen and diborane, $\sim 2\%$ of B₅H₀, and among solid product, along with X-ray amorphous nonvolatile variable-composition boron- and hydrogen-containing products, a cerium hydride with the crystal lattice period a_0 varying within 0.5546–0.5542 nm, which suggests the formula CeH_{2.7-2.8}. At 573 K, diborane decomposes completely, and among solid products we found, along with cerium trihydride and boron- and hydrogen-containing X-ray amorphous compounds, α -Co which crystallized in the hexagonal syngony with the lattice periods a_0 0.2505 and c_0 0.4074 nm. The latter values are in close agreement with published data (a_0 0.2507 and c_0 0.4070 nm [8]).

Unlike CeFe₂ and CeCo₂, which decompose or pass into the X-ray amorphous state at moderate temperatures under the action of both molecular hydrogen and diborane (carrier of bound H₂), ScFe₂ reacts with B₂H₆ at 388–473 K to form a hydride phase with the crystal lattice periods a_0 0.5030– 0.5040 and c_0 1.640–1.653 nm, implying the formula ScFe₂N_{0.4-0.5}. In this temperature range in the gas phase, along with diborane and H₂, the higher boranes B₄H₁₀, B₅H₉, and B₅H₁₁ are present, whose total concetration decreases with increasing temperature, while certain boranes, such as B₄H₁₀ and B₅H₁₁, do not form at 473 K.

For a more detailed study of thermolysis of B_2H_6 on ScFe₂N hydride phases we prepared the hydride phase ScFe₂H_{2.7} with the crystal lattice periods a_0 0.5257 and c_0 1.7039 nm, which agrees well with published data (a_0 0.5255 and c_0 1.7040 nm [9]). Since on contact of B_2H_6 with λ_3 -ScFe₂ at 293–473 K in static conditions the gas phase always contains hydrogen, then thermolysis of diborane in the presence of ScFe₂N_{2.7} we performed with equimolaramounts of B_2H_6 and H_2 in dynamic conditions at a contact time of 30 s, an initial pressure of the gas mixture of 0.15 MPa, and a temperature of 398 K. At a 20% conversion of B_2H_6 , in the gas phase we found 60% of B_4H_{10} , 5% of B_5H_{11} , and 25% of B_5H_9 and in the solid phase, along with the hydride phase on the basis of λ_3 -ScFe₂, about 10% of nonvolatile variable-composition boranes (BH_m)_n.

The IR spectra of solid X-ray amorphous reaction products of diborane with CeFe₂, CeCo₂, and ScFe₂ lack absorption bands characteristic of bridging B–H vibrations (1915 and 1602 cm⁻¹) and contains absorption bands due to skeletal stretching vibrations (980 and 1080 cm⁻¹), as well as absorption bands at 2700– 2750 cm⁻¹ due to terminal B–H vibrations. These findings led us to conclude that the solid nonvolatile boron- and hydrogen-containing compounds comprise polymeric chains including B_nH_m fragments.

Thus, the considered reactions of intermetallic compounds with diborane follow the same regularities reactions of the same compounds with molecular hydrogen and can be represented by reactions (1)–(4).

EXPERIMENTAL

The intermetallic compounds CeFe₂, CeCo₂, and ScFe₂ were prepared by alloying metal charge (purity, %: cerium 99.71, scandium 99.84%, cobalt 99.99%, and iron 99.96) on a copper water-cooled floor of an arc furnace with a nonconsumable tungsten electrode under a high-purity nitrogen pressure of ~0.2 MPa. The deviation of resulting from preset compositions was no more than 0.05 wt %. For homogeneous alloys the samples were realloyed three times. Homogenizing annealing was performed at 973 K for 400 h in evacuated quartz ampules with subsequent quenching in ice water. To prevent reaction of alloys with quartz they were wrapped in a molybdenum foil. As a residual oxygen getter we placed in the ampules titanium turnings. By neutron activation data, the oxygen contents of the samples were no more than $2.8 \times 10^{-2}\%$.

CeFe₂ and CeSo₂ were proved to have the MgCu₂ structure (a_0 0.7288 and 0.7155 nm, respectively). ScFe₂ crystallized in the MgNi₂ structural type with the lattice periods a_0 0.4970 and c_0 1.630 nm, nicely consistent with published data [5].

X-ray analysis of starting alloys and their reaction products was performed on a complex comprising an ADP-1 diffractometer (CrK_{α} radiation) and a control computer. The crystal lattice periods were determined with an accuracy of no more than 0.0002 nm for starting alloys and 0.0004 nm for reaction products.

The gas mixtures containing hydrogen and boranes were analyzed on an LKhM-8MD chromatograph with a thermal conductivity detector on a column (length 1 m, diameter 0.003 m) packed with tricresyl phosphate (30 wt%) on Celite 545, rate of carrier gas (He, Ar) 30 ml/min.

The IR spectra of the gas and solid phases were obtained on a UR-20 spectrometer at $400-3600 \text{ cm}^{-1}$ in cells with KBr windows.

Hydrogen and boron were determined by standard procedures. Hydrogen was determined by burning a sample in oxygen in a device for semimicroanalysis and boron, by potentiometric titration with alkali of mannitolboric acid after binding metals with Trilon B.

Diborane was prepared by the Schlezinger procedure from boron trifluoride etherate and NaBH₄ in diglyme (B₂H₆ was prepared by L.A. Gavrilova). Pure grade boron trifluoride etherate was purified by distillation at 333 K directly before use. Sodium borohydride (purity > 99.0%) was prepared by crystallization of technical product from 1 N NaOH and dried in a vacuum of 1.33×10^{-1} Pa of 393 K.

The reactions of intermetallic compounds with diborane were studied in a laboratory device equipped with gas samplers and capable of operating both at reduced and increased pressures. All preliminary works, including sampling of solid products, were performed under argon.

REFERENCES

- Kuijpers, F.A., *Philips Res. Repts. Suppl.*, 1973, vol. 22, no. 2, p. 1.
- Semenenko, K.N. and Burnasheva, V.V., Vestn. Mosk. Gos. Univ., Ser. 2: Khim., 1977, vol. 18, no. 5, p. 618.
- 3. Irodova, A.V., Parshin, P.P., Shilov, A.L., and Bellissan, R., *Poverkhnost'*, 1997, no. 12, p. 36.
- 4. Burnasheva, V.V. and Semenenko, K.N., Zh. Obshch. Khim., 1986, vol. 56, no. 9, p. 1921.
- 5. Gladyshevskii, E.I. and Bodak, O.I., *Kristallokhimiya intermetallicheskikh soedinenii redkozemel'nykh metallov* (Crystal Chemistry of Intermetallic Compounds of Rare-Earth Metals), Lvov: Vysshaya Shkola, 1982.
- Semenenko, K.N., Burnashena, V.V., Fokin, V.N., Fokina, E.E., and Troitskaya, S.L., *Zh. Obshch. Khim.*, 1983, vol. 53, no. 7, p. 1443.
- 7. X-Ray Powder Date File, ASTM, 1997, Cards 6-0696.
- 8. X-Ray Powder Date File, ASTM, 1997, Cards 5-0727.
- Burnasheva, V.V., Ivanov, A.V., Yartys', V.A., and Semenenko, K.N., *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1981, vol. 17, no. 6, p. 980.