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The *P,T*-State Diagram and Solid Phase Synthesis of Aluminium Hydride

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The *P,T*-diagram for aluminium hydride obtained at pressures 0.5−6.5 GPa and temperatures 100−700 °C indicates that the decomposition of AlH_3 is reversed at high pressures and the compound can be prepared from the elements at pressures above 2.5 GPa. However, synthesis of AlH_3 via the solid-state exchange reactions of $LiAlH_4$ or LiH with $AlCl_3$ under quasi-hydrostatic conditions is more advantageous. The synthetic *P,T*-conditions are limited by two straight lines that correspond to the decomposition of AlH_3 into elements and the phase transition α-$LiAlH_4$ → β-$LiAlH_4$. Similar reaction of α−$LiAlH_4$ with aluminium chloride does not occur at all, while reactions with α- and β-Li_3AlH_6 lead to complete decomposition of the starting compounds. The reaction of $AlCl_3$ with LiH to give AlH_3 proceeds only at $P > 5.6$ GPa and $T > 550$ °C. Only the most compact α (hexagonal) modification of AlH_3 is formed under the *P,T*-conditions studied.

Introduction

Covalent electronodeficient beryllium, aluminium and gallium hydrides are the most interesting and at the same time hardly available compounds in the series of binary nontransition metal hydrides. This is mostly due to the thermodynamic instability of the compounds ($\Delta G°_f[BeH_2] = 3.68$, $\Delta G°_f[AlH_3] = 11.11$ kcal mol^{-1})[1,2] which accounts for many previous unsuccessful attempts to prepare these compounds from elements under the conditions used for the synthesis of alkaline or alkaline earth metal hydrides (the *P,T*-conditions). Al, Be and Ga hydrides were obtained by multistep indirect routes associated with pyrolysis of beryllium organometallic derivatives,[3−5] dissociation of ether from $AlH_3 \cdot nEt_2O$,[6] or exchange reactions between $(H_2GaCl)_2$ and lithium gallohydride.[7] The products thus obtained are insoluble inorganic polymers $\{BeH_2\}_n$ and $\{AlH_3\}_n$[8,9] or dimers $\{GaH_3\}_2$[10] in which metals form a complicated system of M−H−M bridges. Crystalline Al and Be hydrides decompose into elements were slowly and are rather stable under ambient conditions. The compounds are, however, destroyed very rapidly even on mild heating. An increase in the hydrogen pressure in the systems MH_m−H_2 increases the stability. It has been shown[11] that eq 1 is completely shifted to the left at pressures ca. 2 GPa.

$$AlH_3(s) \rightarrow Al(s) + {}^3/_2H_2(g) \qquad (1)$$

Our goal was to find the exact *P,T*-conditions of equilibrium dissociation of AlH_3 and to evaluate the conditions for its synthesis both from the elements and by exchange reactions in the absence of donor solvents. To achieve this, we have studied the *P,T*-state diagrams of $\{AlH_3\}_n$ under the quasi hydrostatic pressures 0.5−6 GPa in the temperature range 20−700 °C. The main problem of investigation under such conditions is to determine the temperature and pressure in a high-pressure cell. We have solved it by modification of the differential thermal analysis such that it became possible to obtain data up to 8 GPa and 1000 °C. This was achieved by using tin as the internal standard which allowed an increase in the precision of obtaining the *P,T*-parameters.

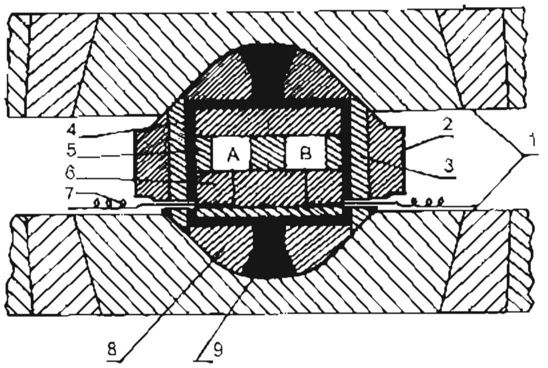

Figure 1. Construction of the high-pressure device: 1 − Bridgman anvils (WC); 2 − ring from lithographic stone (d_{inter} = 18 mm, d_{exter} = 30 mm); 3 − container from lithographic stone (d_{inter} = 12 mm, d_{exter} = 18 mm); 4 − grafite heaters with caps (d_{inter} = 10 mm); 5 − holder with a sample (A) and standard (Al_2O_3) from NaCl (B); 6 − thermocouple unit from NaCl; 7 − thermocouples (d = 3 mm); 8 − thermoisolators from lithographic stone; 9 − graphite leads.

Experimental Section

The *P,T*-state diagrams were obtained on a device consisting of a hydraulic press (2000 ton), two Bridgman anvils, and a high-pressure apparatus of the "lens"-type made of lithographic stone.[12,13] A principial diagram of the apparatus is shown in Figure 1.

A cylinder-shaped individual sample or a mixture with Al_2O_3 as standard (diameter 4 mm, height 3 mm) was placed into brass "glass-in-glass" capsules, sealed in a press-form, installed into the specially designed holder made from NaCl and equipped with a thermocouple,

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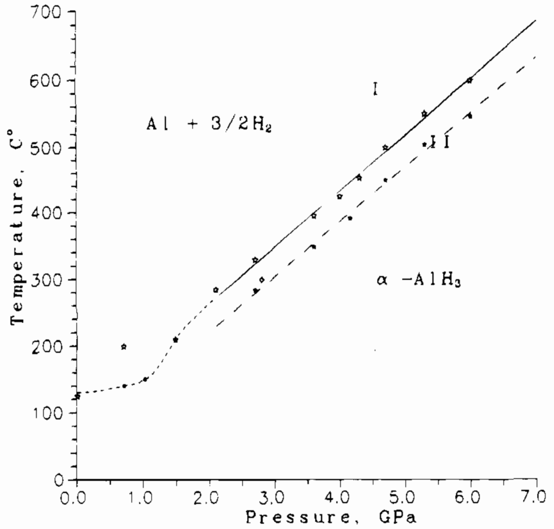

Figure 2. P,T-state diagram of aluminium hydride (I – heating; II – cooling).

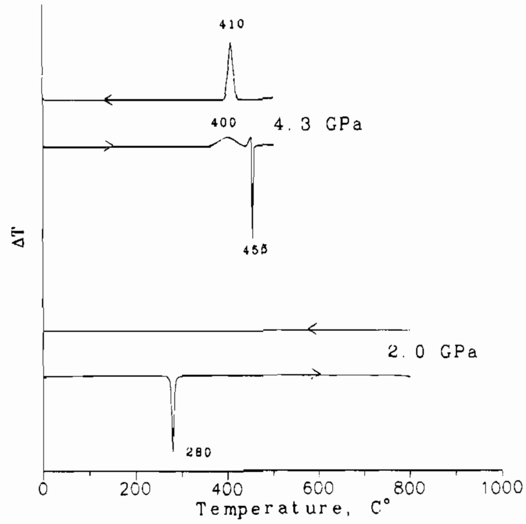

Figure 3. Typical heating and cooling thermograms of α-AlH_3 (→ – heating; ← – cooling).

and then heated at a constant rate of 10 deg min^{-1}. Heat effects were recorded after amplification by an H-308 XY-recorder. All operations on assembling and separating the capsule were carried out in a box filled with dry nitrogen.

Calibration of the home-assembled set showed that the axial and radial temperature gradients measured by thermocouples did not exceed 0.1–1 °C/1 mm 100 °C and 0.5–1 °C/1 mm 100 °C, respectively. The pressure inside the camera was determined by observing the melting temperature of a small piece of tin placed close to the reference thermocouple. The pressure in the camera was determined from the melting point of tin as described in ref 14. The pressure in the camera was thus determined with uncertainty lower than 0.1 GPa in the ternary point. It decreased to 0.05 GPa at higher and lower pressures. The error in determining the temperature was within 3–5 °C.

Samples of α- and γ-AlH_3 were prepared as described elsewhere.[6] An X-ray powder analysis was performed after release of pressure on a DRON-2 diffractometer (Cu Kα irradiation).

Results and Discussion

As seen in Figure 2, the P,T-state diagram of aluminium hydride is rather simple. The solid line corresponds to the decomposition of α-AlH_3 on heating and the broken line corresponds to its synthesis on cooling. Thermograms of α-AlH_3 at pressures 0.5–2.0 GPa are characterized by one irreversible endothermal effect, Figure 3, which is due to decomposition of AlH_3 into elements. If the pressure is increased up to ca. 2.5 GPa, a broad ($\Delta = 100-120$ °C), poorly resolved exothermal effect appears, Figure 3, which is then becomes endothermal. The latter is also due to decomposition of AlH_3 into elements, but equilibrium 1 is shifted to the left at pressures higher 2.5 GPa. If the samples then cooled, the corresponding thermal effect associated with the synthesis of α-AlH_3 is observed and the powder diffractogram of the product contains lines typical of α-AlH_3. As seen in Figure 2, the thermal hysteresis for the forward and backward reactions does not exceed 50 °C at pressures 2.5–6.0 GPa. The pressure required for the synthesis of AlH_3 from the elements can probably be as low as 1.7–2.0 GPa. However, the reaction rate may be lower than the rate of diffusion of hydrogen through the cell walls of the apparatus under these conditions. The yield of the hydride might not thus be that high.

It should be pointed out that the thermograms give no evidence for the presence of AlH_3 modifications other than α-AlH_3 in the pressure range 0.5–6.5 GPa. This means that in the pressure range 1–2 GPa γ-AlH_3 easily and irreversibly transforms into α-AlH_3 even at 50–80 °C. This is really remarkable since the crystallization from solution gives at least five different phases.[6]

The nature of a weak exothermal effect that precedes the decomposition of α-AlH_3 at pressures higher than 2.5 GPa is unclear, Figure 3. Other regimes of the thermal treatment (short or prolong annealing, gradual variation of temperature or "quenching") provided only α-AlH_3 according to the powder diffraction data. It might be assumed that at pressures higher than 2.5 GPa polymeric crystalline aluminium hydride becomes amorphous before the decomposition due to partial cleavage of the M–H–M bridges.

On addition of 1–3% LiH to BeH_2, the formation of the crystalline phases (α- and β-BeH_2) occurs under milder P,T-conditions.[15] There is no similar effect, however, in the case of α-AlH_3 and the P,T-diagram of AlH_3 does not change (i.e. there are no new modifications). At higher concentrations of LiH, additional reflexes appear on the diffractograms ascribed to tetrahydridoaluminate.[16] This is indicative of a reaction between LiH and AlH_3. However, this process proceeds rather slowly at fair temperatures (200–400 °C, 3–5 GPa), since it involves the cleavage of bridging H–Al–H bonds. At higher temperatures AlH_3 decomposes into elements.

The P,T-state diagram suggests that the synthesis of AlH_3 from the elements becomes feasible in the temperature range 280–300 °C at pressures higher than 2.5 GPa. This is in agreement with the data of Baranovski, et al.[11] Two important observations should, however, be taken into account. First, hydrogen reacts with a fine nonoxidized Al powder obtained by thermal decomposition of AlH_3. If Al powders obtained by conventional routines and, therefore, have oxidized surface are used, the synthesis must probably be carried out under more vigorous conditions. Second, a leakage of H_2 through the walls of the high-pressure cell due to diffusion is inversely dependent on the time of keeping the sample under the P,T-conditions above the curve of AlH_3 decomposition; i.e. the longer high-temperature exposure, the lower is the yield of the hydride.

All these complications vanish by synthesis of aluminium hydride via the Schlesinger exchange reactions starting from

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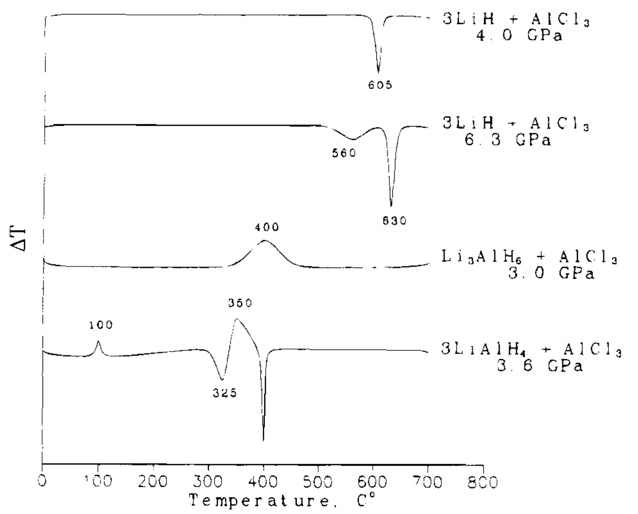

Figure 4. Typical heating thermograms of mixtures used for the Schlesinger exchange reactions.

binary or complex alkali metal hydrides (eqs 2–4). We expected that stabilization of AlH_3 by high pressure will be at least as effective as that by donor solvents. However, although the "classical" stabilization of the monomeric molecule AlH_3 occurs due to formation of the $AlH_3 \cdot L$ solvates ($L = Et_2O, NR_3$, THF), the formation of spatial polymer with bridging Al–H–Al bonds is responsible for the stabilization in the case of solid-state reactions of nonsolvated reagents. It is clear that the successful realization of solid-state reactions 2–4 is possible when the temperature at a fixed pressure is lower than the temperature of decomposition of AlH_3 via eq 1.

$$3LiAlH_4(s) + 3AlCl_3(s) \xrightarrow{P,T} 4AlH_3(s) + 3LiCl(s) \quad (2)$$

$$Li_3AlH_6(s) + 3AlCl_3(s) \xrightarrow{P,T} 2AlH_3(s) + 3LiCl(s) \quad (3)$$

$$3LiH(s) + AlCl_3(s) \xrightarrow{P,T} AlH_3(s) + 3LiCl(s) \quad (4)$$

Consider the thermogram of $3LiAlH_4 + AlCl_3$ mixture at 3.6 GPa as an example. As shown in Figure 4, there are four thermal effects. The first, as in the case of pure $LiAlH_4$,[16] should be attributed to interaction of $LiAlH_4$ with products of its partial hydrolysis or oxidation. Since these admixtures do not exceed 0.5% in fresh prepared $LiAlH_4$,[17] we assume that the first effect does not influence the course of the major pathway. Therefore, it is not indicated in Figure 5. The second endothermal effect (325 °C) is due to the phase transition α-$LiAlH_4 \rightarrow \beta$-$LiAlH_4$. Its *P*,*T*-conditions are shown by line I in Figure 5 and are identical to those for pure tetrahydridoaluminate.[16] Exchange reaction 2 occurs only after this phase transition. Third exothermal effect corresponds to reaction 2 and has a maximum at 350 °C, but α-AlH_3 formed decomposes into elements at 400 °C (the fourth heat effect). Attention should be paid to a profile of curve III in Figure 5 which defines the *P*,*T*-conditions of reaction 2. It is a superposition of two curves which cross line II showing the thermobaric conditions of synthesis and decomposition of AlH_3. Above this curve, the reaction between $LiAlH_4$ and $AlCl_3$ proceeds via eq 5. As a result, the area of *P*,*T*-conditions suitable for synthesis of AlH_3 via reaction 2 becomes limited, Figure 5.

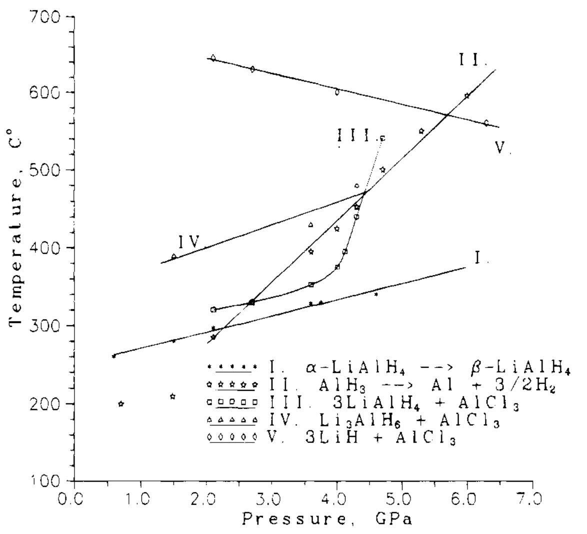

Figure 5. *P*,*T*-conditions for synthesis of α-AlH_3 via the exchange reactions.

$$3LiAlH_4(s) + AlCl_3(s) \xrightarrow{P,T} 4Al(s) + 6H_2(g) + 3LiCl(s) \quad (5)$$

The heating thermogram of the mixture α-$Li_3AlH_6 + AlCl_3$ is characterized by one exothermal effect due to reaction 6 in the whole pressure range, Figure 4. Attempts to carry out the interaction between α-Li_3AlH_6 and $AlCl_3$ according to eq 3 were unsuccessful. This was not however surprising, since curve IV which defines the *P*,*T*-conditions for the interaction between α-Li_3AlH_6 and $AlCl_3$, Figure 5, is above the curve of AlH decay in the pressure range studied (1.5–4.0 GPa). The hydride β-Li_3AlH_6 is not involved in reactions 3 and 6, because it is formed at higher temperatures.[16]

$$\alpha\text{-}Li_3AlH_6(s) + AlCl_3(s) \xrightarrow{P,T} 2Al(s)^s + 3H_2(g) + 3LiCl(s) \quad (6)$$

The heating thermograms of $3LiH + AlCl_3$ at pressures lower 5.6 GPa have one endothermal effect because of reaction 7, Figure 4. At higher pressures, two thermal effects are observed. The first corresponds to the synthesis of AlH_3 via eq 4 and the second is due to its decomposition into elements. The latter is reversible, in agreement with the *P*,*T*-state diagram of α-AlH_3. Therefore, in this case, AlH_3 is formed in the range of *P*,*T*-conditions between lines I and II as well, Figure 5.

$$3LiH(s) + AlCl_3(s) \xrightarrow{P,T} Al(s) + {}^3/_2H_2(g) + 3LiCl(s) \quad (7)$$

The formation of AlH_3 in donor solvents occurs by successive substitution of halide ligands in AlX_3 by hydride via the intermediates $AlH_{3-n}X_n \cdot L$ (X = Hal; $n = 0$–2; $L = Et_2O$, THF, NR_3, etc.).[18,19] No chloroalanes were found in the case of the solid state reactions. Chloroalanes also cannot be prepared via reactions 8–11.

$$LiAlH_4(s) + AlCl_3(s) \overset{P,T}{\not\rightarrow} 2AlH_2Cl(s) + LiCl(s) \quad (8)$$

$$LiAlH_4(s) + 2AlCl_3(s) \overset{P,T}{\not\rightarrow} 4AlHCl_2(s) + LiCl(s) \quad (9)$$

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$$AlH_3(s) + 2AlCl_3(s) \overset{P,T}{\nrightarrow} 3AlHCl_2(s) \qquad (10)$$

$$2AlH_3(s) + AlCl_3(s) \nrightarrow 3AlH_2Cl(s) \qquad (11)$$

All the data show the principal difference between the Schlesinger reactions in solution and in the solid state under high pressure. As seen in Figure 5, the formation of AlH$_3$ from LiAlH$_4$ and AlCl$_3$ is only observed after generation of β-LiAlH$_4$ (line I). Unfortunately, the structure of this compound has not been solved directly. It was mentioned[16,20] however, that the structure is unusual in the series of related alkali metal tetrahydridoaluminates, i.e. aluminium has strongly distorted octahedral rather than tetrahedral environment. Since the main building blok of α-AlH$_3$ is the {AlH$_6$} octahedron,[9] it can be assumed that the interaction between β-LiAlH$_4$ and AlCl$_3$ under the high pressure proceeds via the substitution of Li$^+$ by Al^{3+} (arising from AlCl$_3$) which enters the hydride octahedron β-LiAlH$_4$ rather than by substitution of hydrido for chloro ligands. α-Li$_3$AlH$_6$ differs from β-LiAlH$_4$ in its stoichiometry and regular arrangement of the {AlH$_6$} octahedron. These are probably two reasons that make impossible the preparation of AlH$_3$ by the solid state reaction 3 in the pressure range studied (P < 4 GPa). One cannot, however, exclude that the reaction 3 may occur at higher pressures. This suggestion finds a support in both the location of line IV which will cross Line II at P > 4.5 GPa and the formation of AlH$_3$ at P > 5.6 GPa via eq 4. In the latter case, β-LiAlH$_4$ might be an intermediate which interacts further with AlCl$_3$. Direct substitution of chloro-ligands by hydrido-ligands in reaction 4 is also possible at P > 5.6 GPa as suggested by different features of reaction 2 in solution and the solid phase.

In conclusion, we have shown that thermodynamically unstable AlH$_3$ can be prepared under high pressure either directly from the elements or by the solid-state Schlesinger exchange reactions. The hexagonal modification of AlH$_3$ (ϱ = 1.47 g/cm^3) was formed in both cases. This fact shows that α-AlH$_3$ is the most "stable" phase at the pressures and temperatures studied in comparison with other known modifications of aluminium hydride. However, this does not imply that other modifications of aluminium hydride are not available at pressures higher than 6.5 GPa or by other routes.

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