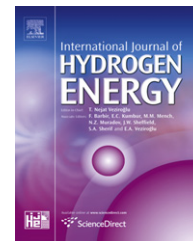


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## Ultraviolet activation of thermal decomposition of $\alpha$ -alane

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### ABSTRACT

We investigated activation of thermal dehydriding of  $\alpha$ -AlH<sub>3</sub> crystal by preliminary irradiation by ultraviolet light using thermal desorption spectroscopy, barometry, and cathode luminescence methods. It is shown that hydrogen vacancies appear due to irradiation; they serve as points where metal nuclei probably appear, so dehydriding becomes significantly faster. Possible explanation of transformation of hydrogen vacancies to metal phase nuclei is suggested: new vacancies are more likely to appear near the first one compared to remote places. Using density functional theory method we calculated the electronic structure of stoichiometric  $\alpha$ -AlH<sub>3</sub> and  $\alpha$ -AlH<sub>3</sub> with a hydrogen atom removed from a regular lattice site with a vacancy in place of it. It is suggested that an appearance of a new vacancy near the first vacancy needs less energy compared to the first one. From cathode luminescence data we see that appearance of vacancies can also be activated thermally. The model of hydrogen desorption from  $\alpha$ -AlH<sub>3</sub> activated by UV light is suggested and kinetic parameters of desorption are evaluated.

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## 1. Introduction

Aluminum hydride (alane) contains much hydrogen (up to 10% by weight corresponding to 148 g/L). Therefore, it is considered as a possible hydrogen carrier in hydrogen-fueled vehicles. Equilibrium pressure for this hydride is extremely high (about 10 GPa), so control over the desorbing gas flux is possible via changing the temperature of the material [1]. This needs detailed description of the kinetics. It seems reasonable to reduce the temperature of intensive hydrogen desorption by a few dozens of degrees. Numerous attempts of reducing this temperature were mostly based on mechanochemical activation, i.e. by milling in ball mills with catalysts added (see e.g. [2]). Review [3] contains references to attempts to improve

the kinetics of alane. It concludes that partial desorption of hydrogen and formation of metal nuclei facilitate further dehydriding.

In [4] we show that for temperature range 70–120 °C long incubation period (from dozens of minutes to hours or even days, depending on the temperature) precedes quick hydrogen desorption from alane. After some hydrogen desorbs, nuclei of metal aluminum appear. Hydrogen desorption from metal is much faster than from ion-covalent hydride. Therefore first metal nuclei serve as channels of easier dehydriding. Hydrogen appearing at the hydride-metal boundary, diffuses in metal to the nuclei-gas boundary and desorbs to gas rather quickly. Hence, the volume of the non-metal hydride phase decreases and that of the metal phase

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grows. In other words, nuclei grow and displace hydride. Also, velocity of hydride-metal phase boundary is evaluated in [4,5].

Incubation delays hydrogen desorption from alane in case decomposition is isothermal; in case of linear heating desorption starts at higher temperature. Undoubtedly, methods of influencing on the incubation processes, reducing their duration, and lowering temperature of quick hydrogen desorption, are of interest. However, incubation has not been described in detail so far.

A popular opinion is that the surface of hydride is covered by the passivation layer (e.g. oxide) that prevents hydrogen desorption. High temperature destroys the layer and desorption starts. This opinion seems reasonable for active hydrides with metal type of bonding. In case of ion-covalent bonding (as in the considered case) the material itself seems to be extremely passive with respect to hydrogen desorption. A layer, e.g. oxide, can exist, but hydrides with certain ionic contribution into chemical bonding, including alane, are significantly less oxidizable compared to metals. Besides, hydrogen itself serves as oxidant in aluminum hydride, “pulling” a part of charge to itself [6].

The calculations of the total and partial densities of electronic states (DOS, PDOS) of  $\alpha$ -AlH<sub>3</sub> [7] show that this crystal is a semiconductor, and the DOS near the top of the valence band is dominated by the hydrogen states. Consequently, it makes possible a throw of electrons to the conduction band mostly from the hydrogen states. Basing on this fact, we have suggested [4] that such throws of electrons engender two factors that activate desorption:

- neutral hydrogen atoms able to recombine to molecules appear;
- concentration of free electrons grow, improving catalytic activity of the material.

Study of thermal and photo activation of dehydriding of alane in [4] showed that reasons of active hydrogen desorption are more complex than thermal excitation of electrons to the conduction band. The band gap values of  $\alpha$ -AlH<sub>3</sub> obtained in various calculations differ significantly. The value of 3.54 eV, calculated in [7] using the many-body perturbation theory (the GW method) [8–10] seems the most reliable. Throw of electrons through this band gap is possible by the ultraviolet (UV) radiation.

The aim of this work was to use the UV-radiation of alane to study details of incubation and as a method of direct activation of dehydriding. Influence of UV on alane was studied in [11–13]. The authors of these papers obtained much data showing that UV light indeed accelerates the hydrogen desorption, but did not give any admissible interpretation of this effect.

In our research we compared hydrogen desorption kinetics of the original alane and UV-radiated alane. Also we compared thermal and UV activation and showed that metal phase nuclei (that help quick desorption) appear from hydrogen vacancies. We also show that kinetics of alane decomposition is improved not only due to reducing the incubation stage, but also due to change of morphology of metal phase growth.

## 2. Samples and experiment

We used alane made by means of wet chemistry [14]. Dehydriding kinetics was studied using thermal desorption spectroscopy (TDS) and barometry. Samples were heated in the autoclave of small volume. Amount of desorbed hydrogen was measured via pressure change in the vessel of calibrated volume. The temperature of the vessel was measured by the semiconductor temperature sensor. Then the data were converted to the reacted fraction (RF). If hydrogen desorption was less than 100% after long degassing, dehydriding was forced by higher temperature: 180/200 °C. In order to improve heat contact between alane powder and walls of the autoclave, it was filled with hydrogen with pressure 30/50 Torr (4/6 kPa). Experiment is described in more detail in [15].

Thermal desorption was studied in experiments of two types: with linear heating and under constant temperature. In the last case temperatures were from 80 to 120 °C with the step 10 °C, needed temperature was obtained after about 20 min. Alane powder was irradiated by the UV light on the vibrating table in atmosphere at the room temperature. Mercury lamp was used. Exposure duration was 6.5 h. For the CL method we used the scanning electron microscope Zeiss SUPRA 40VP equipped with the system of cathode luminescence registration Gatan MonoCL3+. CL spectra were registered in the range 250–800 nm in the mode of continuous scanning of the sample's surface by the electron beam. Width of the scanned area was 30  $\mu$ m. A line was scanned during 1.67 s. Distance between two lines was 293 nm. A point at the spectrum was registered during 2 s. Spectral resolution was 2 nm. Energy of electrons that excite luminescence was 20 keV. The beam current was 2.8 nA. SEM micro photos were made using the same equipment in Interdisciplinary Resource Center for Nanotechnology of Saint-Petersburg State University.

## 3. Geometric and electronic structure of the $\alpha$ -AlH<sub>3</sub> crystal

In this work we study the  $\alpha$ -modification of AlH<sub>3</sub>, which is the most stable polymorph of AlH<sub>3</sub> at ambient conditions [16,17] and crystallizes in the lattice with space group R-3c ( $D_{3d}^5$ ). The hexagonal unit cell (UC) of  $\alpha$ -AlH<sub>3</sub> with lattice parameters  $a = 4.449$  Å,  $c = 11.804$  Å [16] contains six formula units AlH<sub>3</sub>. A detailed description of the geometric structure can be found in [3,16]. As already mentioned, hydrogen in the crystal  $\alpha$ -AlH<sub>3</sub> acts as an oxidant in the sense that hydrogen atom in crystal has some negative charge. We calculate this charge using density functional theory (DFT) method with the exchange-correlation (XC) functional of GGA-type (Generalized Gradient Approximation), namely the PBE XC functional [18]. We used the pseudopotential density functional code CASTEP [19,20] (with the Materials Studio graphical user interface [21]), which employs a plane wave (PW) basis set for valence electrons, the atomic core being incorporated by ultra-soft pseudopotentials [22].

Population analysis, including the calculation of Mulliken atomic charges and bond overlap populations between two

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