Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 452 (2007) 28–30
thermochimica acta
www.elsevier.com/locate/tca

Thermal conductivity of ammonia borane complex and its composites with aluminum powder

Nahid Mohajeri *, Ali T-Raissi, Karthikeyan K. Ramasamy

Florida Solar Energy Center, University of Central Florida, 1679 Clearlake Road, Cocoa, FL 32922-5703, United States

Received 20 April 2006; received in revised form 10 October 2006; accepted 11 October 2006
Available online 26 October 2006

Abstract

The thermal conductivity of ammonia borane (AB) complex, in the temperature range of 300–420 K, was measured experimentally using ASTM method E 1225. At 300 K, the thermal conductivity of pure AB was found to be approximately 15 W/m-K. A composite pellet prepared by mixing 10 wt% aluminum powder with AB had a thermal conductivity that was a factor of 4 higher than that of pure AB complex. The extent of the pyrolytic weight loss for AB/Al composite and pure AB complex was 25.4% and 33.9%, respectively—indicating comparatively lower levels of volatile species evolved as impurities (e.g. monomeric aminoborane, borazine, diborane, etc.) in the product hydrogen.

Keywords: Ammonia borane; Thermal conductivity; Hydrogen storage

1. Introduction

Amine borane complexes with the empirical formula $B_xN_xH_y$ are being investigated as the high capacity hydrogen storage materials. Ammonia borane (BH_3NH_3), the simplest of amine borane complexes with material hydrogen content of 19.6 wt% and a volumetric energy density of about 2.74 kWh/L versus 2.36 kWh/L for liquid hydrogen is considered to be one of the most promising hydrogen storage materials, to date [1,2]. Hydrogen is released via thermolysis and thus, its thermochemical and thermophysical properties are of great interest from the point of view of hydrogen storage system design and engineering of a suitable field deployable device. Furthermore, it has been shown that the heating rate affects the product slate from thermolysis of ammonia borane (AB). The extent of volatile products evolved as impurities in the H_2 increases as the heating rate is increased.

Among these impurities are monomeric aminoborane BH_2NH_2, borazine, and diborane. Formation of these impurities is undesirable if the AB complex were to become a viable hydrogen carrier especially for the proton exchange membrane fuel cell (PEMFC) applications. The thermochemical properties of pure AB complex and some of its decomposition products are known and some data on its thermophysical properties are also available [3–5]. However, no data can be found on the thermal conductivity of AB and its pyrolysis products.

Here, we report experimental data for the apparent thermal conductivity of AB complex and composites formed by mixing fine aluminum powder with AB in the temperature range of 300–420 K.

2. Experimental

2.1. General procedure

Ammonia borane complex was purchased from Aldrich and used as received. Aluminum powder, 0.1 micron, spherical, was purchased from Alfa Aesar and was handled inside a glove box. The AB complex was mixed and grinded with aluminum powder with a 10:1 mass ratio inside the glove box.

Thermogravimetric (TG) analysis was performed using a Perkin-Elmer, Diamond TG/DTA in argon flow at a heating rate of 10 °C/min.

Fig. 1 depicts the arrangement used for the measurement of the thermal conductivity of the as received AB. Two coaxial cylindrical bars were machined using aluminum 6061-T6 stock (thermal conductivity of 180 W/m-K). Both pieces had an outside diameter of 0.378 in. and were 0.181 in. long. They were used as the reference blocks for the measurement of heat flux

* Corresponding author. Tel.: +1 321 638 1525; fax: +1 321 504 3438.
E-mail address: nmohajeri@fsec.ucf.edu (N. Mohajeri).

0040-6031/$ – see front matter
doi:10.1016/j.tca.2006.10.012

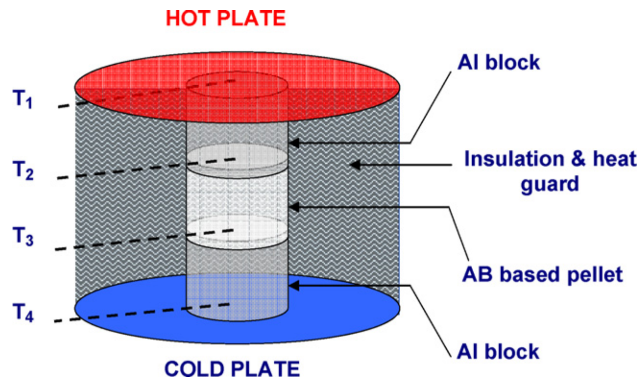

Fig. 1. Setup for measuring thermal conductivity of AB complex.

(Q') through AB samples. The AB pellets (0.378 in. OD and three different thicknesses: 0.181 in., 0.261 in., and 0.223 in.) were placed between the two aluminum cylinders. Temperature measurements were made using four T-type thermocouples.

3. Results and discussion

The rate of conductive heat transfer (Q') depends upon the temperature difference ($T_{HOT}-T_{COLD}$), distance (d), and the thermal conductivity of the material (κ) as follows:

$$Q' = \frac{\kappa(T_{Hot} - T_{Cold})}{d}$$

Apparent thermal conductivity was measured using the steady state method according to ASTM E 1225. A test sample is inserted under load between two similar specimens of known material thermal conductivity. A steady state temperature gradient is established in the test stack and heat losses minimized using a longitudinal heat guard subject to approximately the same temperature gradient. Under steady-state conditions, the thermal conductivity of the target specimen can be derived in terms of the temperature gradients in the respective specimens and the thermal conductivity of the reference material.

Fig. 2 depicts the measured thermal conductivity of the AB pellet having a thickness of 0.181 in., as heated in the temperature range of 300–420 K. At room temperature, thermal conductivity of the palletized AB was calculated to be approximately 15 W/m-K, comparable to that of dielectric materials such as alumina (κ = 30 W/m-K) and calcium oxide (κ = 16 W/m-K) [6]. The apparent thermal conductivity increases as the pellet undergoes decomposition process at higher temperatures, i.e. mixture of AB and decomposition products.

Table 1
Thermal conductivity of AB complex with different pellet thickness

Pellet thickness (in.)	Temperature (K)	Measured *k* (W/m-K)	Calculated *k* (W/m-K) based on Fig. 2
0.261	333	25.6	20.5
0.223	337	26.9	21.3

The experimental error for these thermal conductivity measurements was determined by using two additional pellet thicknesses of 0.223 in. and 0.261 in. Table 1 depicts the measured values of the thermal conductivity of AB for the 0.223 in. and 0.261 in. pellets. Corresponding values of κ for AB pellets having a thickness of 0.223 in. and 0.261 in. calculated using Fig. 2 data are also given in Table 1.

In an effort to increase the thermal conductivity of AB complex, we prepared AB composites by mixing fine aluminum powder with ammonia borane. The apparent thermal conductivity of the composite AB/Al material increases by a factor of 4 over that of pure AB when 10 wt% of aluminum powder is added to AB material. This is shown in Fig. 3 depicting the thermal conductivity of pure AB and AB-Al (10:1) composite in the temperature range of 300–420 K.

Finally, we conducted TG analysis of the AB/Al composites in order to measure the effect of Al addition on the dehydrogenation of AB complex. Typical results are shown in Fig. 4. It can be seen that blending Al powder with AB complex results in a reduction in the overall AB mass loss from 33.9% to 25.4%. It appears that the addition of aluminum powder to AB pellets improves the thermal conductivity of the material and the difference in mass loss may be attributed to the reduced levels

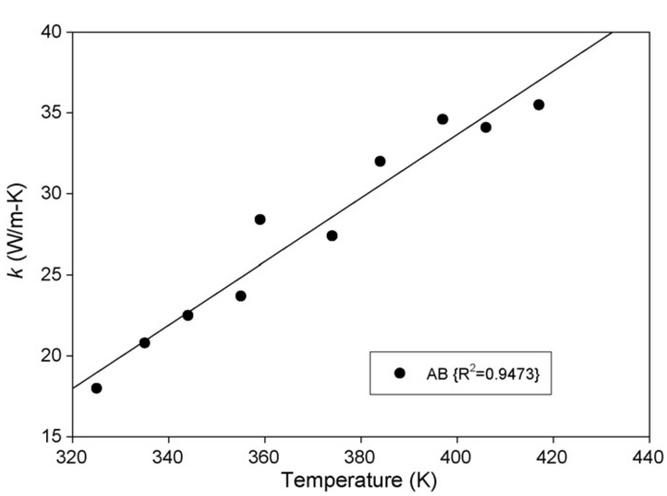

Fig. 2. Thermal conductivity of AB complex as a function of temperature.

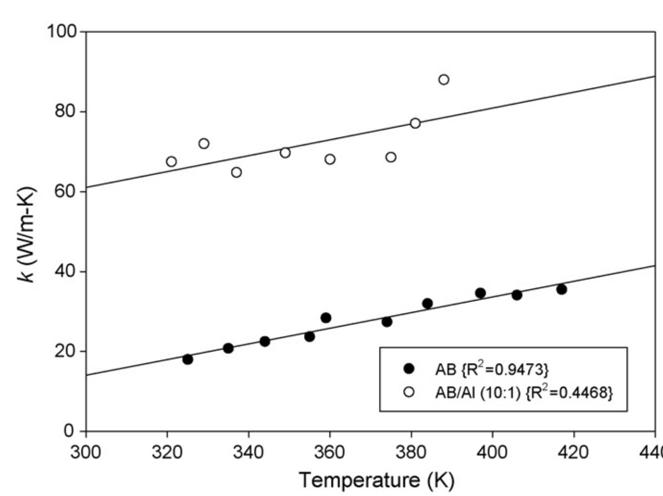

Fig. 3. Thermal conductivity of AB complex and AB-Al (10:1) composite as a function of temperature.

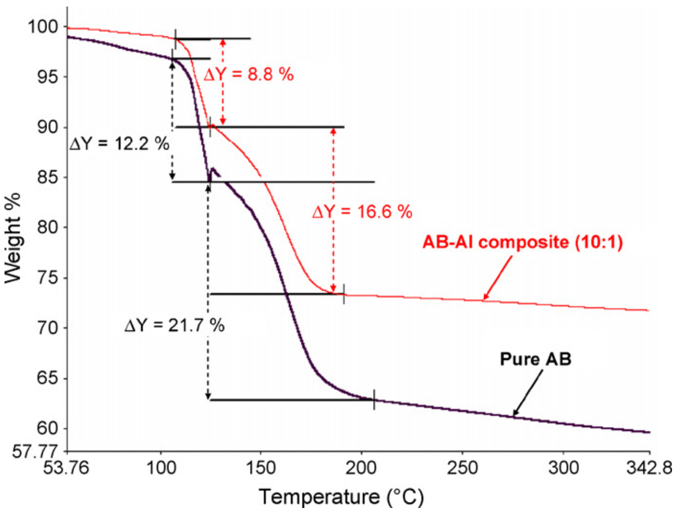

Fig. 4. TG analysis of pure AB and AB/Al (10:1) composite.

of undesirable thermolysis products released, e.g. borazine, BH2NH2, diborane, etc.

4. Conclusions

The thermal conductivity of AB complex, in the temperature range of 300–420 K, was measured experimentally using ASTM method E 1225. At 300 K, the thermal conductivity of pure AB is approximately 15 W/m-K.

A composite pellet prepared by mixing 10% by weight aluminum powder with AB complex had a thermal conductivity that was a factor of 4 higher than that of pure AB. Weight loss due to pyrolysis of AB/Al composite was significantly less than that of the pure AB complex indicating comparatively lower levels of volatile species formed as impurities (e.g. monomeric aminoborane, borazine, diborane, etc.) in the hydrogen generated.

Acknowledgement

This work was supported by a grant from the National Aeronautics and Space Administration (NASA) through Glenn Research Center under contract No. NAG3-2751.

References

[1] A. T-Raissi, Proc. U. S. DOE Hydrogen Program Review, (2002), and references therein.
[2] N. Mohajeri, A. T-Raissi, Mater. Res. Soc. Symp. Proc.,Warrendale, PA, 884E (2005) GG1.4.
[3] G. Wolf, J.C. van Miltenburg, U. Wolf, Thermochim. Acta 317 (1998) 111.
[4] G. Wolf, J. Baumann, F. Baitalow, F.P. Hoffmann, Thermochim. Acta 343 (2000) 19.
[5] F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-RÖβler, G. Leitner, Thermochim. Acta 391 (2002) 159.
[6] D.R. Lide, Handbook of Chemistry and Physics, CRC Press, 1995.