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Thermal properties characterization of sodium alanates

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Abstract

High energy density hydrogen storage is a critical technology requirement in a hydrogen-based energy infrastructure. Although there are no current storage methods that meet desired energy density goals for vehicular hydrogen storage, complex metal hydride based systems are among the most promising. These materials form compounds with hydrogen under appropriate conditions and release hydrogen by thermal decomposition. The complex hydride, sodium alanate, is particularly useful due to its favorable reversibility. Thermal properties characterization of sodium alanate has been performed at Sandia National Laboratories to gain a detailed understanding of how complex hydrides will behave in a storage system. Thermal properties were investigated using the thermal probe method (ASTM D5334). Custom test hardware was designed and built to accommodate the complex decomposition and recombination of sodium alanate. Thermal conductivity and thermal wall resistance were determined by utilizing analytical and numerical data analysis methods. The thermal conductivity of sodium alanate was found to vary by more than 90% with changes in phase composition and hydrogen gas pressures between 1 and 100 atm. The quality of thermal contact between the alanate and the vessel wall was characterized numerically for various pressures and phase compositions. The contact resistance is high for all states, indicating poor contact between the material and the vessel wall.

Keywords: Hydrogen; Hydrides; Energy storage materials; Heat conduction; Thermal analysis

1. Introduction

Efficient hydrogen storage is one of the primary challenges facing the integration of hydrogen into an energy infrastructure. Complex hydride systems have been proposed by many researchers as a high energy density hydrogen storage solution [1]. Sodium aluminum tetra-hydride ($NaAlH_4$) is a complex hydride historically used as a reducing agent, which was found to reversibly release and accept hydrogen in a two-step phase change process in 1997. This discovery of compound destabilization by titanium doping made sodium alanates ($NaAlH_4$, Na_3AlH_6) promising materials for hydrogen storage systems [2,3]. However, before sodium alanate hydrogen storage systems can be designed and optimized, engineering properties and the physical behavior of the alanates must be characterized. This effort enables accurate thermal modeling and optimization of gravimetric and volumetric storage densities.

This complex hydride absorbs and releases hydrogen in a two-step decomposition and recombination reaction shown in Eq. (1)

$$NaAlH_4 \leftrightarrow \tfrac{1}{3}Na_3AlH_6 + \tfrac{2}{3}Al + H_2 \leftrightarrow NaH + Al + \tfrac{3}{2}H_2 \quad (1)$$

The thermodynamics of these reactions are well characterized [4,5] and require significant heat management in a storage system environment. The thermal properties of the storage material, especially the thermal conductivity, will dramatically influence the hydride based hydrogen storage bed design and performance [6].

Only limited engineering properties work has been previously reported for sodium alanate. In 2003, Sandrock and Thomas reported a value (0.2 W/m K) for thermal conductivity during sorption of hydrogen [7]. United Technologies Research Center reported a thermal conductivity range of 0.35–0.50 W/m K and a wall resistance of 500 W/m^2 K for non-catalyzed (non-reversible) alanate powder [8]. The property variation on relevant bed operating conditions was not

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explored. This work describes the thermal properties of the sodium alanates as a function of cycle, composition, hydrogen gas pressure, and temperature.

2. Thermal properties measurement method

The Thermal Probe Method was chosen based on ASTM D 5334 and Blackwell [9,10]. Others have used this method to measure low conductivity materials as well as packed beds [11,12]. This method is attractive due to the transient nature of the measurement. Because large long-term temperature gradients are not required, this method is especially well suited for the measurement of low conductivity materials. Furthermore, physical changes such as thermally induced decomposition and hydrogen desorption are minimized due to the relatively short measurement time and small sample temperature increase. The rate that heat can be moved through the alanate (thermal conductivity) is calculated from the transient temperature of a constant power heat source, this will be referred to as the "probe".

The apparatus was designed using numeric methods. The system is capable of measuring apparent thermal conductivities up to 3 W/m K for measurement times between 100 and 1000 s with <10% error due to the analytic curve fit. Higher conductivities can be measured numerical analysis methods are used for data analysis. The probe consists of a nichrome heating element and a temperature measurement element encased in a stainless steel sheath. The design detail of the probe is shown in Fig. 1.

The measurement bed was instrumented with 12 radially and axially distributed thermocouples to compare the measured temperature field with the model. The measured alanate sample volume was 219 cc. A solid model of the resulting apparatus design is shown in Fig. 2. The radial and axial thermocouples were later modified to minimize their influence on the thermal field. This allowed for the measurement of samples with higher conductivities and facilitated the accurate measurement of the thermal resistance between the hydride materials and the vessel wall.

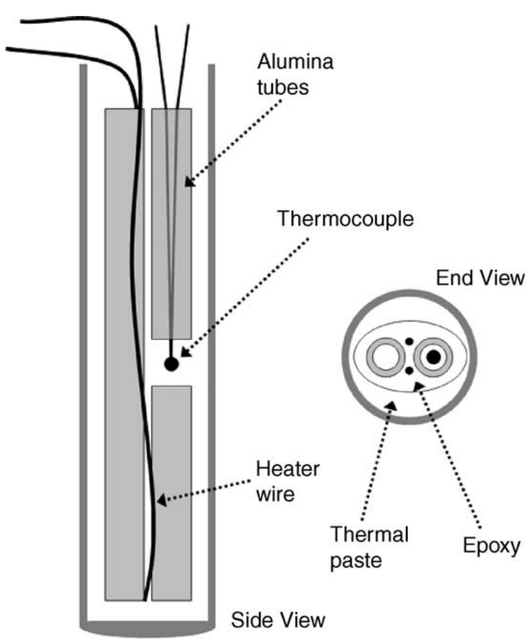

Fig. 1. Transient thermal probe assembly consists of a thermocouple and heating element encased in a stainless steel sheath. Details of construction are included in the appendix (picture not to scale).

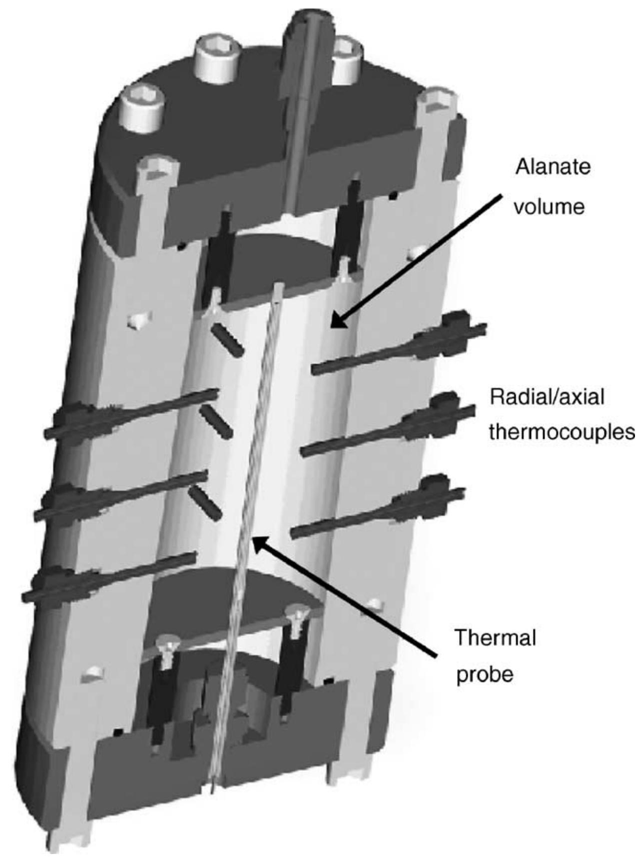

Fig. 2. Solid model of thermal properties analysis chamber. Built to withstand pressure and temperature required for hydrogen absorption and desorption.

The measurements were conducted with the bed near room temperature to minimize the influence of hydrogen absorption or desorption. To analyze heat transport within the material, an appropriate constant current is applied to the probe heater producing a constant power input to the bed. The heater power required depends on the thermal conductivity of the sample.

2.1. Analytic thermal probe solution

The experimental probe temperature within the alanate is fit by the one-dimensional heat transfer solution described by Carslaw and Jaeger [13] and simplified by Blackwell as follows:

$$T(t) = A\ \ln(t) + B + C\frac{\ln(t)}{t} + D\frac{1}{t} \qquad (2)$$