Thermal Conductivity Testing of Minimal Volumes of Energetic Powders†

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Abstract: *Safety constraints have traditionally presented researchers with challenges in testing the thermal conductivity of energetic powdered materials. Minimal volumes of energetic powders can now be tested with the modified transient plane source technique. The newly modified sensor design further reduces the possibility of impact, friction and electrostatic discharge (ESD) hazards. This paper will present results generated in testing ammonium perchlorate (AP).*

Keywords: *thermal conductivity, transient plane source, energetic powder, electrostatic discharge*

Introduction

Testing the thermal conductivity of most energetic powder materials is a challenge with traditional steady-state techniques, as the required large volumes of material pose undesirable safety risks or the necessary sample geometries are impractical. This often leads to estimation of thermal conductivity in predictive models rather than actual measurement. The dependence of thermal conductivity of a material undergoing an exothermic reaction on local temperature has a significant effect on the critical conditions for thermal ignition.[1] The theory of thermal ignition, whether or not consumption and diffusion of reactant is taken into account, has been commonly analyzed using the traditional grouping of dimensionless parameters suggested by Frank-Kamenetskii (1955).[2] The theory assumes that the heat generation inside a body follows an Arrhenius model:

$$q' = Q\rho A e^{-\frac{E}{RT}} \qquad (1)$$

where
Q is the heat of reaction [kJ g^{-1}]
ρ is the bulk density of the material [kg m^{-3}]
A is the pre-exponential factor [s^{-1}]
R is the universal gas constant [8.314 J mol^{-1} K^{-1}]
E is the apparent activation energy [J mol^{-1}]
T is the temperature [K]
q' is the heat generation rate per unit volume [J s^{-1} m^{-3}]

From this, Frank-Kamenetskii developed the following expression, where the non-dimensional heat generation is found:[3]

$$\frac{\rho Q A}{\lambda}\frac{EL^2}{RT_0}e^{\frac{-E}{RT_0}} = \delta \qquad (2)$$

where
λ is the thermal conductivity of the material
L is the characteristic length of the given body (the half side length for cubes).
T_0 is the ambient temperature [K]

In the present study, the modified transient plane source technique was applied to measure the thermal conductivity of an energetic material directly as an alternative to the book values that are frequently substituted in the computational models based on the aforementioned theory.

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Figure 1. *Mathis TCi Thermal Conductivity Analyzer.*

Experimental

Apparatus

The Mathis TCi™ system utilized in the study to perform the thermal conductivity measurements is shown in Figure 1.

This thermal conductivity measurement device is based on the modified transient plane source technique. It uses a one-sided, interfacial, heat reflectance sensor that applies a momentary, constant heat source to the sample. The difference between this method and traditional hot wire techniques is that the heating element is supported on a backing, which provides mechanical support, electrical insulation and thermal insulation. This modification eliminates the intrusive nature of the hot wire method and provides the capability to test smaller volumes of material as the wire is coiled as pictured in Figure 2.

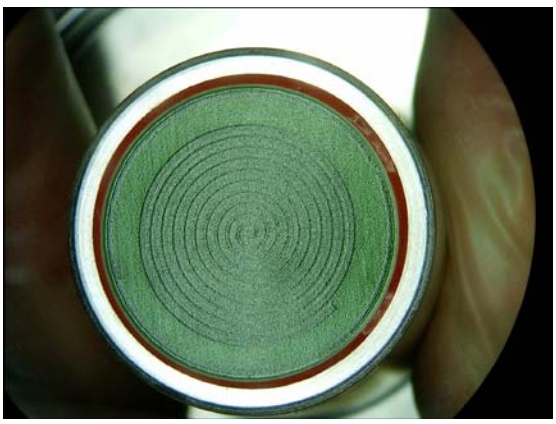

Figure 2. *Sensor face – diameter is 17 mm.*

The associated test method enables the testing of solids, liquids, powders and pastes without melting or otherwise modifying the sample to conform to the geometry of the test cell. The sample is tested by placing it in intimate contact with the heating element of the sensor for a resident amount of time of typically 1 to 3 seconds. A known current is applied to the sensor's heating element providing a small amount of heat. The heat provided results in a rise in temperature at the interface between the sensor and the sample – typically less than 2 ºC. This temperature rise at the interface induces a change in the voltage drop of the sensor element. A typical voltage data chart is displayed in Figure 3.

Since the rate of temperature rise at the heating element is inversely proportional to the thermal conductivity of the material, this material property can be determined by measuring the rate of voltage rise when a constant current is applied.[4] Voltage increase can be correlated with thermal conductivity through a calibration with reference

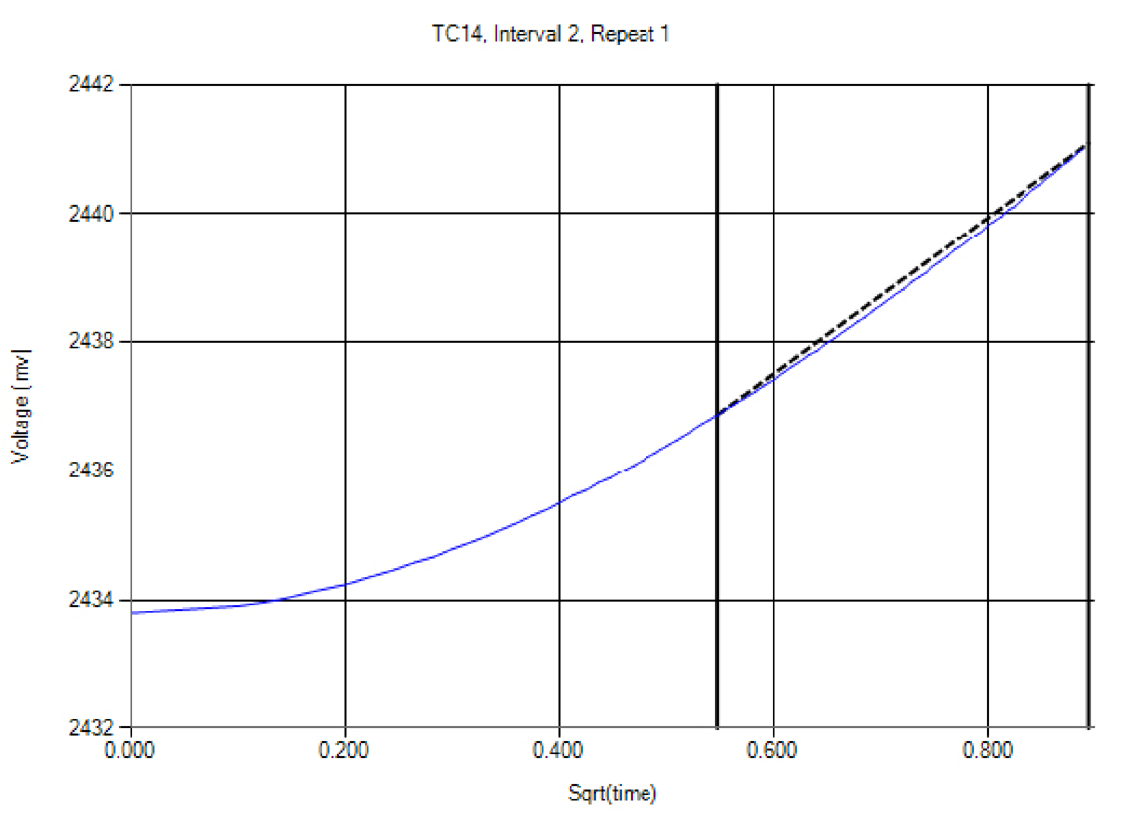

Figure 3. *Voltage data chart.*

Figure 4. *TCi small-volume test cell.*

Table 1 *Test results – ammonium perchlorate [relative standard deviation (RSD)].*

Test	Thermal conductivity/ W m^{-1} K^{-1}	Average/W m^{-1} K^{-1}, $N = 4$	RSD (%), $N = 4$	Average/W m^{-1} K^{-1}, $N = 3$	RSD (%), $N = 3$
1	0.127086 0.127641 0.127866 0.127969	0.1276	0.31%		
2	0.130499 0.128595 0.128970 0.129272	0.1293	0.64%	0.1288	0.75%
3	0.129295 0.129967 0.128839 0.129063	0.1293	0.38%		

materials having known thermal conductivity. From this calibration, the conductivity of unknown materials can be determined.[5] The more thermally insulative the material is, the steeper the voltage rise. Additional work was needed to configure the sensor to accommodate US Navy energetics needs.

Many energetic powders are sensitive to initiation via impact, friction or electrostatic discharge (ESD).

A specially designed sensor test cell was constructed to minimize the effect of these hazards. The test cell was designed such that it can be rigidly attached to the sensor while diminishing the possibility of powder going into screw holes which are potential impact and friction hazards. Further, the sensor head design also allowed grounding leads to the test cell, cap, and sensor so that ESD effects could be minimized.

The grounding wire could then be attached to the building's grounding system. Figure 4 shows the sensor head without the attached grounding leads.

Materials

Ammonium perchlorate (NH_4ClO_4) was used as received with a nominal particle size of 200 μm. The salt is a common energetic component in US Navy weapons systems.

Methods

The small-volume test cell pictured in Figure 4 is filled with approximately 3/8 teaspoon (1.9 ml) of ammonium perchlorate. Care is taken to avoid compaction of the powder prior to placing the test cell cap.

An accuracy check was performed on the instrument prior to running any tests on a standard reference material and confirmed the instrument was performing well within the stated accuracy specification of 5%.

Results

A summary of the results is provided in Table 1 and graphically in Figure 5. For all measurements, the instrument demonstrated a precision better than 1%.

Accuracy test

An accuracy check was performed on the instrument prior to running any tests on a standard reference material and confirmed the

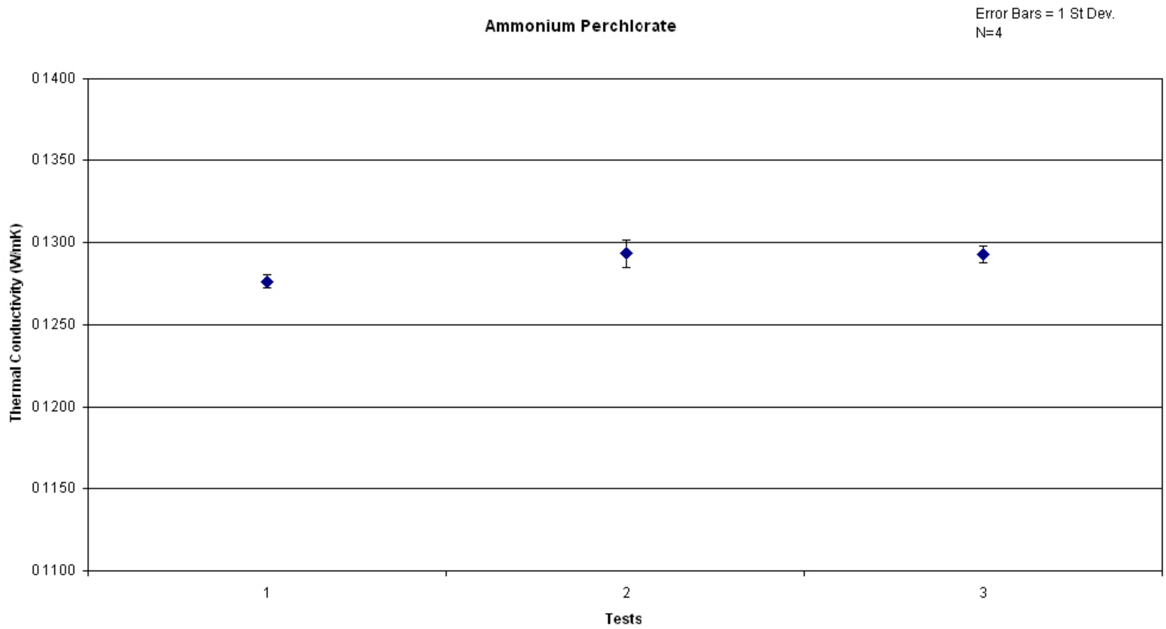

Figure 5. *Results of AP Analyses.*

instrument was performing well within the stated accuracy specification of 5%. The accuracy of the measurements conducted under specific environmental conditions can be examined by measuring calibration materials with externally certified thermal conductivity values under such specific environmental conditions. In comparing the observed measurements of the materials with the known thermal conductivity values of the materials, the accuracy of the measurements for unknown samples can be evaluated. In this study, PDMS (DiMethyl PolySiloxane silicone fluid) was used as the calibration standard to assess the accuracy of the measurements carried out in this study. The results are listed in Table 2.

Conclusions

The thermal conductivity of a volume of approximately 3/8 teaspoon of ammonium perchlorate was measured with an accuracy of better than 2.5%. Further studies are recommended to investigate the relationship between particle size, moisture content, and packing density on the thermal conductivity.

Table 2. *Accuracy test results vs. certified values.*

Sample	Measured k/W m^{-1} K^{-1}	Average of measured k/W m^{-1} K^{-1}	RSD (%)	Real k/W m^{-1} K^{-1}	Accuracy (%)
PDMS	0.162194 0.162951 0.162945 0.163008 0.163226	0.162865	0.24%	0.159	2.43%