International Journal of Heat and Mass Transfer 79 (2014) 676–688

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Determination of thermal diffusivity, conductivity, and energy release from the internal temperature profiles of energetic materials ☆

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ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form 15 August 2014
Accepted 22 August 2014

Keywords:
Thermal diffusivity
Thermal conductivity
Energetic material

ABSTRACT

A novel data processing technique has been developed to obtain thermal diffusivity, conductivity, and reaction heat release for energetic materials from Sandia Instrumented Thermal Ignition (SITI) experiments heated with a linear ramp temperature boundary condition. The method is based on the equivalence of the temperature responses of: (a) ramped temperature boundary condition with no internal heat generation and (b) uniform heat generation (that is, with a negative value) with constant temperature boundary conditions; which is true regardless of the spatial domain. For the specific case analyzed herein (the SITI apparatus), the midplane temperature profile is well represented by a quadratic expression in the radial coordinate for both ramped boundary temperature and uniform heat generation responses. Internal temperature data from temperature ramped SITI experiments with various pyrotechnics, propellants, and explosives were analyzed. Quadratic fits to the temperature profile data were made and the associated fitting coefficients were converted to yield thermal diffusivity directly. Thermal conductivity was then determined from thermal diffusivity, given knowledge of the material's specific heat capacity and density. Finally, because of the equivalence of the cases (a) and (b) above, their individual contributions to a combined temperature profile can be easily separated, thereby yielding internal heat generation as well. This technique allows for measurements of properties for pressed and powdered materials over a range of densities and temperatures. The technique is demonstrated using pyrotechnic materials ($KClO_4$ and $Ti/KClO_4$), a composite solid propellant (herein referred to as "Propellant A", a class 1.3 AP-HTPB-aluminum propellant) and an explosive (PBX 9502).

1. Introduction

The thermal properties of energetic materials play important roles in their behavior under thermal loading. In order to accurately predict behavior of energetic components, devices and systems, it is essential that one have accurate material property values—particularly for properties to which the material behavior is highly sensitive. For example, models of pyrotechnic materials have shown the pyrotechnic thermal conductivity to significantly impact the time to ignition for hot wire devices [1].

There are a variety of techniques which have been used to determine thermal diffusivity and conductivity—a cursory examination of the American Society for Testing and Materials (now ASTM International) website [2] lists dozens of standard procedures for measuring thermal conductivity of materials of various types—some of which would be inappropriate for use with energetic materials. However, our purpose here is not to provide an exhaustive list of available methods and to enumerate their various advantages and disadvantages, but rather to suggest a new way to derive this information from tests on energetic materials conducted with the various versions of the Sandia Instrumented Thermal Ignition (SITI) apparatus—tests which are already being conducted for other reasons. It is expected that by careful analysis of the experiments, additional material property information can be gleaned from these tests.

Other approaches including inverse methods [3] and optimization techniques [4] have been applied to SITI to obtain information on material properties and/or energy release. One difference here is that the approach to be presented does not require the use of a computational model for data processing. Once the initial geometric scaling factor has been established, the data can be processed directly. This work therefore represents a data analysis technique, rather than a modeling and simulation technique.

☆ Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This work was performed under internal funding.

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http://dx.doi.org/10.1016/j.ijheatmasstransfer.2014.08.059
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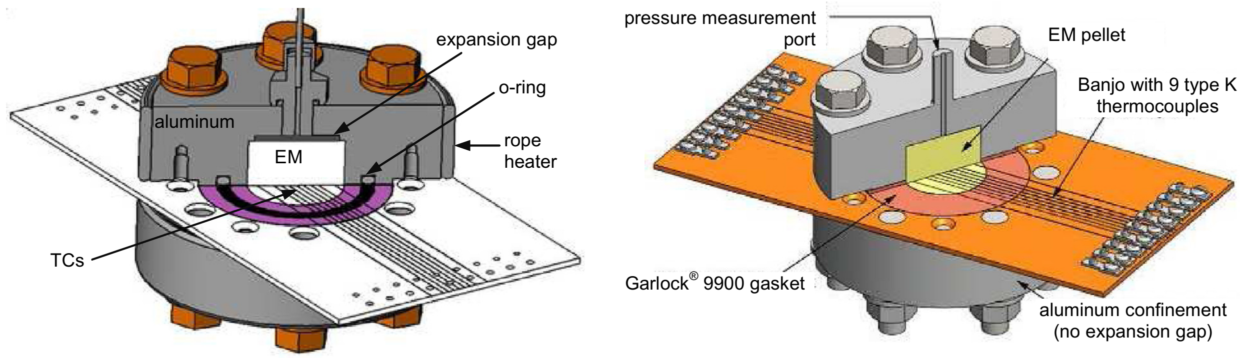

Fig. 1. Cutaway of SITI devices. Left: original SITI; Right: HOT-SITI.

The original SITI device [5] has been used to investigate the behavior of over 30 different energetic materials (EMs) including explosives, propellants, and pyrotechnics. In these tests, two 1″ (2.54 cm) diameter by 0.5″ (1.27 cm) high cylindrical samples of an EM are enclosed within aluminum confinement. Nine thermocouples (TCs) are laid horizontally in a grid between the two EM samples. O-rings maintain a hermetic seal with Kapton® sheets to electrically isolate the TC wires. A feedback-controlled rope heater wrapped around the outside surface of the confinement provides heating to the device.

Modifications to SITI were made to accommodate the higher temperatures required to study inorganic pyrotechnic materials. These modifications include the use of a flat gasket made of Garlock® 9900 for sealing, the application of screw-mounted TCs on the exterior, and a simplification of the interior cavity shape (expansion gap was removed). The resulting apparatus became known as High Operating Temperature SITI (HOT-SITI). Fig. 1 shows a cutaway illustration of the SITI and HOT-SITI devices.

To date, HOT-SITI has been used with several different pyrotechnics or pyrotechnic ingredients, including $TiH_{1.65}$–$KClO_4$ (THKP), Ti–$KClO_4$ powder (41% Ti, 59% $KClO_4$ aka TKP output), and pure $KClO_4$. In all of these tests, the powdered samples were pressed to form monolithic pellets, typically with about 18–20% porosity. Details of tests of the HOT-SITI apparatus are described elsewhere [6,1]. Here we will demonstrate some analysis techniques using test data for TKP output material and $KClO_4$.

2. Background

In a fully enclosed device such as HOT-SITI, the temperature profile produced in the interior is determined (if internal self-heating from reactions can be ignored) by heating the exterior. With its high thermal conductivity, the aluminum confinement provides a near isothermal boundary condition. By varying the amount of heat supplied to the aluminum, various temperature histories can be produced. The typical mode of operation in SITI experiments has been a fast (∼10 °C/min) ramp to a set temperature, followed by a constant temperature soak. During the soak period, chemical reactions within the interior of the energetic material proceed and self-heating occurs—eventually leading to a thermal runaway ignition event. The ramp-and-hold profile allows the energy release from reactions to be studied in considerable detail (because the responses of the interior TCs become separated temporally), which has led to improved thermal decomposition reaction models [3].

However, the same ramp-and-hold heating profiles are inadequate for inorganic pyrotechnic materials. Because of the diffusion-limited reaction behavior of two-component pyrotechnics, a ramp-and-hold profile tends to not produce a full ignition event but rather a thermal excursion which eventually self-quenches as condensed phase reaction products form a passivation barrier between the oxidizer and fuel particles [1,3]. As a consequence, most of the HOT-SITI tests with pyrotechnic materials have been performed with a temperature ramp profile—temperature is continually increased in a linear fashion until an ignition event occurs.

During the course of analyzing the temperature profiles for the ramped HOT-SITI tests, it was observed that the spatial variations (i.e. T as a function of r at the device mid-plane) were all very similar in shape—near perfect quadratic profiles in r. While the "depth" of the profile would differ based on heating rate, each produced a quadratic profile (see examples in Fig. 2). It was hoped that this information would be useful to obtain relevant material parameters from the test data. After some careful analysis, we discovered that thermal diffusivity and reaction heat release can be obtained. The process of doing so is the subject of this paper.

3. Mathematical basis for analysis

It can be easily demonstrated[1] that the spatial temperature profile produced in an arbitrary-shaped object by a ramped boundary condition and zero volumetric source is *exactly the same* as the profile produced by a constant, uniform volumetric source term of appropriate value in the same object with constant Dirichlet boundary conditions. While this can be proven in the general case for a linear system, here we focus on a specific geometry of interest—a finite solid cylinder reminiscent of SITI. We obtain analytic solutions for the cylindrical geometry by methods in heat transfer texts [7–9].

Here we begin by considering the initial boundary value problem for the temperature in a finite cylinder defined over the radial region $0 \leqslant r \leqslant R$ and axial region $-L \leqslant z \leqslant L$, as shown in Fig. 3. The governing equation is defined by Eq. (1) subject to its initial condition, boundary conditions and source term for the cases of interest (Table 1). In Eq. (1), α is the thermal diffusivity [m^2/s], λ is thermal conductivity [W/m-K], and Q is a volumetric source term [W/m^3].

$$\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} + \frac{Q}{\lambda} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \quad (1)$$

The full analytic solution for the profile shape from a temperature ramped finite cylinder (case a) is given here as Eq. (2a). The corresponding solution for the constant source, zero boundary condition (case b) is given in Eq. (2b).

[1] An interesting exercise is to use a finite element code to model an arbitrary geometry initially at $T = T_0$ in which the entire exterior surface is subjected to a temperature ramp boundary condition rising at heating rate, H [units of K/s], and the entire interior has a constant volumetric source term of value $Q = \rho C_p H$. For constant density and specific heat, the temperature profile of the entire geometry will remain spatially uniform over time; the temperature at every location precisely given by $T = T_0 + Ht$. This choice of volumetric heat source exactly counteracts the profile that would normally result from a change in boundary temperature.