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A MEMS-based microthermal analysis of explosive materials

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ABSTRACT

An upgraded microcalorimeter comprising a MEMS-based thermal conductivity vacuum gauge with a ~1.3 mV/K thermopile sensor and a thin Si_3N_x film heater was constructed. The improved features relative to a previous design are linear rise of the temperature with time and rapid heating of up to ~500 °C/s. The device was used for thermal analysis of micrometer-size particles of the explosives TNT, RDX and PETN by measuring temperature changes while heating the film heater. The TNT thermogram features a single exotherm that is well separated from the endotherm. The area and position of the melting and decomposition peaks in the RDX thermogram are proportional to the particle mass. The observed heats of melting agree with known thermodynamic data. The observed heat of deflagration is less than 1% of the calculated value, because a large fraction of the heated sample was sputtered from the heater and most of the heat was lost to the surrounding. Monitoring the air temperature above the heater with an ultrathin thermocouple yielded identifiable thermograms in accord with the surface thermograms. Such contactless sensing above the heater can detect the decomposition of micrometer-size particles and offers potential for the development of an inexpensive, simple to use field explosive detector.

1. Introduction

Over the years, several technologies were proposed for trace detection of explosive materials. The most widely spread of them: colorimetric analysis, chemiluminiscence and ion mobility spectrometry were reviewed in previous papers [1–3]. Recently, mass spectrometry techniques are also showing significant progress toward real-time field operation. Wilson et al. demonstrated real time detection of triacetonetriperoxide (TATP) using selected ion flow tube mass spectrometer (SIFT/MS) [4]. Their work demonstrates the advantages of MS analysis being fast sensitive technique that provides accurate identification of the target material. The above technologies track specific chemical properties of explosives.

However, for routine inspection, for example, in public transportation facilities, there is still a need for a fast, simple to use and inexpensive portable explosive detector. Recently, Lee and Bromberg utilized the thermal response of the suspected materials to develop a universal explosive detection system to screen passengers in airports [5]. Their setup incorporated a sampling unit, heater and IR camera that measured the heat flux while heating the sample. They obtained a unique signature that can be used to distinguish explosive materials from potential clutter materials [5]. Zuck et al. have recently shown feasibility to obtain thermal analysis profile (thermogram) of the suspected material, using a low cost MEMS device [1]. Their microcalorimeter was based on a MEMS-based pressure gauge and comprised a thin film heater and a solid-state thermopile temperature sensor for thermal analysis of micrometer-scale particles [6,7]. Staymates and Gillen suggested a similar heater device, though larger in dimensions, for imaging of thermal desorption phenomena [8].

In the microcalorimeter described by Zuck et al. [1], the examined particles are heated to a higher temperature than their initiation temperature, while monitoring the temperature change in the sample. The thermal analysis output (thermogram) depicts the changes in heat flux as a function of the sample temperature. A negative peak in the thermogram (endotherm) is caused by endothermic processes, such as heat absorption and melting. The involved amounts of heat are defined in terms of heat capacity and heat of crystallization, respectively. A positive peak (exotherm) originates from heat release from the sample, due to exothermic processes, such as combustion and detonation, characterized by heat of combustion and heat of detonation, respectively. When the specific heat of melting (C_{melt}) and the mass of the particle (m) are known, the absorbed heat of melting Q_{melt} is given by Eq. (1):

$$Q_{\text{melt}} = C_{\text{melt}} \cdot m \tag{1}$$

Similarly, the heat of combustion of the sample of is given by:

$$Q_{\text{combustion}} = C_{\text{combustion}} \cdot m \tag{2}$$

The areas of endotherm and exotherm in the thermogram represent the heat which is absorbed or released, respectively, from the system. From the known sample mass and specific heat of

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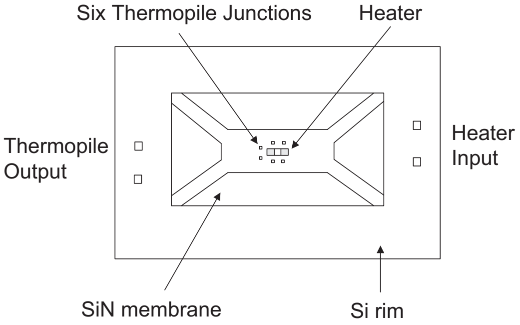

Fig. 1. Scheme of the thermal conductivity gauge sensor. Two such units were incorporated in the setup (see text).

melting, the area of the endotherm can be directly related to the amount of heat that was absorbed in the system. Explosion in the form of either detonation or deflagration (high-rate combustion) is common to all types of explosives under heating and distinguishes them from non-explosive materials. However, in heated micro-sized explosive particles, deflagration rather than detonation occurs. Nevertheless, in thermal analysis, the heating rate can be designed such that each of the common explosive will yield a characteristic pattern of peaks in the thermogram.

The present paper describes further characterization of thermal processes in micro-sized explosive particles. The results are compared to reported thermodynamic data: heat of melting and deflagration/detonation. Heat changes are measured on the membrane surface and in the surrounding. The results further elucidate a process of rapid heating of minute explosive particles under non-adiabatic conditions. It is suggested that such microthermal analysis can provide a basis for future developments of portable devices for the detection and identification of explosives.

2. Experimental

The experimental setup used in this work is similar to the one described in previous study [1]. A brief description of this setup and the highlights of the changes made in the present work are given below. The heater and temperature sensor elements of a thermal conductivity pressure gauge on a chip served as microcalorimeter for the thermal analysis. The pressure gauge (see scheme in Fig. 1 consists of a silicon rim that surrounds a silicon-nitride membrane and is of dimensions 2.50 × 3.33 mm and 0.3 mm thickness. The membrane dimensions are 1.5 × 2 mm and 0.5 μm thickness. A thicker silicon mesa underneath the membrane is connected to the four corners of the silicon rim. A poly-Si thin-film heater is located in the center of the membrane. The heater is surrounded by six serially connected thin-film Si/Al hot junctions, which together form a temperature-sensitive thermopile around the center of the membrane with an effective sensitive area of about 200 by 200 μm. The cold junctions of the thermopile are located on the silicon rim. The thermopile sensitivity is approximately 1.3 mV/K [6]. The microcalorimeter device was placed on a Signatone hybrid probe station under the objective of an Olympus Model SZ-STB1 stereo microscope equipped with a digital video camera. A sample of the examined powder was layered as a heap on the microcalorimeter rim. A particle was randomly picked up by touching the heap with the tip of a short flexible fiber. The fiber was gently guided to place the particle in the center of the heater (±10 μm) within the field of view of the microscope. The optical monitoring of the sample also enabled us to correlate thermal peaks with visual physical changes such as melting and explosion. The particle dimensions were estimated by microscopy from the known dimensions of the heater. A regular symmetric particle shape (sphere, cube or parallelepiped) was assumed. A voltage ramp was supplied to the heater and the temperature change of the loaded membrane was monitored. Comparing the thermogram of an empty membrane (“reference”) to a thermogram obtained when the membrane is loaded with a sample particle provides information about the thermochemical properties of the material.

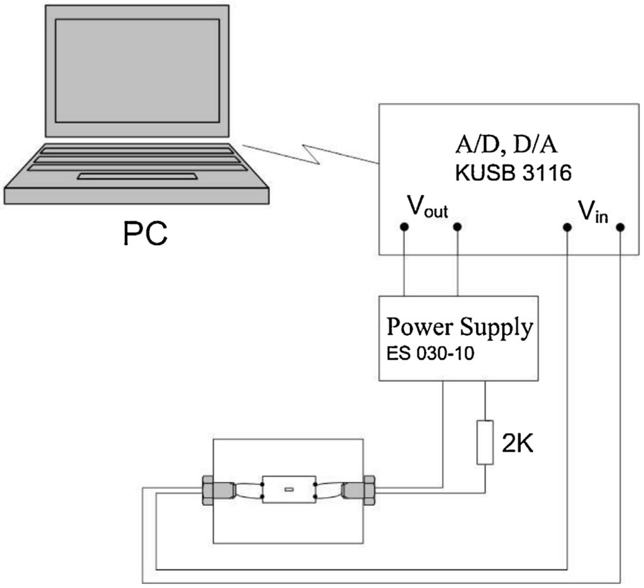

Fig. 2. Scheme of the upgraded micro-calorimeter setup. The D/A subunit of the data acquisition module controls the power supply. Data from the thermopile are processed by the A/D subunit (for simplicity, one of the two identical thermopiles is shown). The programming voltage supply and the data acquisition are software-triggered. The 2 KΩ resistor in series with the heater serves to minimize the effect of changes in the heater resistivity with temperature (see text).

Two identical sensors, for the sample and reference, respectively, are mounted and wire-bonded to a Kyocera LCC-68 Leadless Chip Carrier (68 pins, 25 × 25 mm). From the voltage difference between the sample and reference thermopiles, the net heat flow at any temperature can be derived. The microcalorimeter is housed in an aluminum chamber of dimensions 80 × 60 × 30 mm. The chamber is open to the atmosphere.

The control and data acquisition system of the previous design [1] was upgraded to provide higher heating rates, higher sampling rates and a linear rise of the temperature with time. A 0–15 VDC voltage is supplied to the heaters by a remotely controlled power supply (ES-030-10, Delta Elektronika BV, the Netherlands). A 16-bit A/D-D/A data acquisition module (KUSB-3116, Keithley Instruments, USA) provides a programmed 0-5VDC analog signal, which is wired to the power supply. The same board is used to record the thermopile voltage change. All control and data acquisition operations are performed by means of an in-house written CEC Testpoint® application. The software enables tailoring of control voltage to vary the time dependence of the heater voltage and temperature as needed. A scheme of the experimental set-up is shown in Fig. 2.

Typically, the supplied voltage rise (0–15 V within 1 s) in the upgraded setup yielded heating rates of up to 500 °C/s, compared to the rate of 300 °C/s obtained with our previous setup [1]. The upgraded setup enables higher sampling rates, which provide the opportunity to accurately study fast processes. Another improvement in the new setup is the feasibility of a linear temperature rise with time. Basically, the temperature (T) of the heater is proportional to the square of the voltage (V) supplied to the heater. In our previous setup, V was proportional to the time (t), hence T was proportional to t^2. However, a linear temperature rise would facilitate