Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Bhattacharya, Shantanu , Gao, Yuanfang , Apperson, Steven , Subramaniam, Senthil , Shende, Rajesh , Gangopadhyay, Shubhra and Talantsev, Evgueni(2006) 'A Novel On-Chip Diagnostic Method to Measure Burn Rates of Energetic Materials', Journal of Energetic Materials, 24: 1, 1 — 15
To link to this Article: DOI: 10.1080/07370650500374318
URL: http://dx.doi.org/10.1080/07370650500374318

Journal of Energetic Materials, 24: 1–15, 2006

ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650500374318

Taylor & Francis
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A Novel On-Chip Diagnostic Method to Measure Burn Rates of Energetic Materials

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A novel on-chip diagnostic method has been developed to measure burn rates of energetic materials patterned on a 1 inch × 3 inch glass chip. The method is based on time-varying resistance (TVR) of a sputter-coated thin platinum (Pt) film, in which resistance of the film changes because of the propagation of ignition of the nanoenergetic material over it. The corresponding voltage differential is captured by a high-speed data acquisition system (1.25×10^6 samples/s). We have measured burn rates as high as 504 m/s for thermites of copper oxide (CuO)/aluminum (Al) and 155 m/s

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for bismuth oxide (Bi_2O_3)/Al nanoparticles using this method. We have provided an explanation for the change of resistance upon ignition, based on the microstructural characterization and energy dispersive spectroscopy.

Keywords: thermite nanoparticles, on-chip diagonosis, burn rate

Introduction

Thermites form an important subgroup of pyrotechnics. A thermite is a combination of an oxidizer and fuel that ignites and releases energy. The ignition process in thermites is a self-propagating reaction accompanying high temperatures of several thousand degrees. This necessitates the use of thermites for self-propagating high-temperature synthesis of novel materials like specialty alloys [1]. Thermites and their combination with other classes of energetic materials are applied to a range of other real-life applications such as military usage, mining, demolitions, precision cutting, explosive welding, surface treatment and hardening of materials, pulse power applications, sintering-aid, biomedical applications [2], microaerospace, satellite platforms [3], etc.

In self-propagating high-temperature synthesis (SHS), the properties such as propagation velocity of self-propagating flame or burn rate, reaction temperature, and energy release are very important. Propagation rate and burn rate often have been used interchangeably by the energetic community for nanoscale processes [4]. These properties, particularly the burn rates in powder-based SHS reactions, depend strongly on the size, impurity levels, and packing density of the constituent powders [5–7]. Size effects being the most predominant factor, nanoscaling of powders should enhance burn rates as compared to bulk micron-sized powders. This is because the former has higher surface area and lower diffusion limitations as compared to the latter. Therefore, a mixture of nanoscaled oxidizer and fuel particles is currently a major research area for SHS applications.

Burn rates of thermites can be measured in open and confined arrangements. In an earlier work [4], thermite

materials well packed inside a long square channel or Lexane tube and ignited by a CO_2 laser have been recorded by a high-speed movie camera. The burn rates are determined based on the frame speed settings in the camera system. Such a method proves to be highly expensive because of the high initial cost of a high-frame-speed camera. Another method reports an on-chip diagnosis of a highly exothermic reaction between free-standing bimetallic foils of Al and Ni [3]. The bimetallic layer is sputter coated on a silicon substrate, peeled off as freestanding foil, and ignited using a laser. The detection of the flame front is carried out by using an array of optical fibers with an expensive oscilloscope and several other optical accessories [3]. Currently there is no other information cited in the literature about on-chip measurements of burn rates for different energetic reactions.

In this paper we report a novel on-chip diagnosis method for burn rate measurements in thermite reactions with oxidizer and fuel nanoparticles (see Table 1 for average particle size). Under this new method [8], a well-cleaned laboratory glass slide was sputter coated with a thin film heater and a time-varying

Table 1
Source of oxidizer and fuel nanoparticles and their physical properties

Oxidizer and fuel	Average particle size (nm)	Surface area (m^2/g)	Density (g/cm^3)	Source
CuO	9	Not available	6.30–6.49	Alfa Aesar, MA
Bi_2O_3	150	3.2–3.5	8.9	Accumet Materials Co., NY
Al (active content: 85%)	80	12.1	2.7	Nanostructured & Amorphous Materials, Inc., NM

resistance (TVR) detector, using a simplistic shadow-masking technique. The sputter-coated chip with the heater at one end and TVR at the other is coated with a uniformly thick layer of separately prepared thermite nanoparticle dispersion. The on-chip heater film is powered by a voltage supply that heats up the thermite material to its ignition point. As the ignition process is triggered, the flame propagates over the TVR film, and the resistance across this changes over a certain period of time. These change of resistance is acquired by a high-speed data acquisition (DAQ) card as a variable potential drop by means of a voltage divider circuit. This acquired time period data and a prior knowledge of the length of the TVR strip enable us to calculate burn rates of different thermite material coatings. Our DAQ card has a sampling rate of 1.25×10^6 samples/s, and at this sampling rate we can measure the flame speed with a temporal resolution of 0.8 microsec. As opposed to the high-speed digital camera method, which has a frame speed about 32,000 frames/s (corresponding to a sampling rate of 3.2×10^4 samples/s, 31.25 microsec resolution), our acquisition is much faster, and we can easily get a resolution that is almost two orders of magnitude higher than the camera method. We plan to use a DAQ card with a much higher sampling rate of 200×10^6 samples/s in our future endeavors. With this we plan to achieve a 5 ns resolution. The data acquired by a high-speed camera are limited by the response time of an associated optical sensor like a CCD, the shutter speed, and a delay due to the electronic transfer of a large amount of data [9]. This measurement method with the camera is also cumbersome because of alignment needs of the experimental setup and the requirement of a large sample amount to make a clear imaging. The novel on-chip method investigated here is reproducible, simple, rapid, and inexpensive and requires only milligram samples for testing.

Experimental Procedures

Microfabrication of a Chip

Laboratory glass slides (1 inch $\times$ 3 inch) procured from Fisher Scientific, MA, were cleaned in an Piranha solution (H_2SO_4:H_2O_2

as 3:1 v/v) and rinsed thoroughly with distilled water. These cleaned slides were dried in a gravity-fed convection oven at 110°C for 5–10 min. An aluminum foil was used as a shadow mask to expose selectively the glass chip for deposition of platinum. We cut the aluminum foil using a predesigned plastic die and wrapped the cut foil over a precleaned glass substrate in such a way that the designed pattern of the heater and TVR were exposed for metal deposition. These substrates were coated with a 130 nm platinum film using an Emitech, K-575, (UK) sputter coating system. The windows in the aluminum foil acted as openings to the sputtering process, and the remaining areas were shadowed from the platinum exposure, thus resulting in patterned substrates as shown in Figure 1(a). After sputtering, the shadow mask was unwrapped and discarded. Copper wires, 500 micrometer in diameter, were soldered as connecting leads to the heater and TVR films using a premium-grade oxide-free ultrapure soldering wire (diameter = 0.39 mm) from Digikey, MN. The chip is schematically shown in Figure 1(a).

Processing of the Thermite Nanoparticle Dispersion and Coating This on a Chip

Oxidizers such as copper oxide (CuO) and bismuth oxide (Bi_2O_3) nanoparticles were mixed with aluminum (Al)-fuel nanoparticles and dispersed in 2-propanol in a sealed bottle using an ultrasonic bath. Table 1 shows the physical properties of oxidizer and fuel nanoparticles used and their vendor details. Table 2 shows the proportions of the various components used and their time of dispersion. The postdispersion product was a slurry of oxidizer and fuel nanoparticles that was coated with a round interlocked bristle brush of size 1 on the chip running from the heater end to the TVR end. The thickness of this coating was kept around 0.5 mm with a width of around 3 mm over the whole length. This thickness was achieved by applying multiple layers of slurry one over another. We have strong evidence of confinement and subsequent increase in

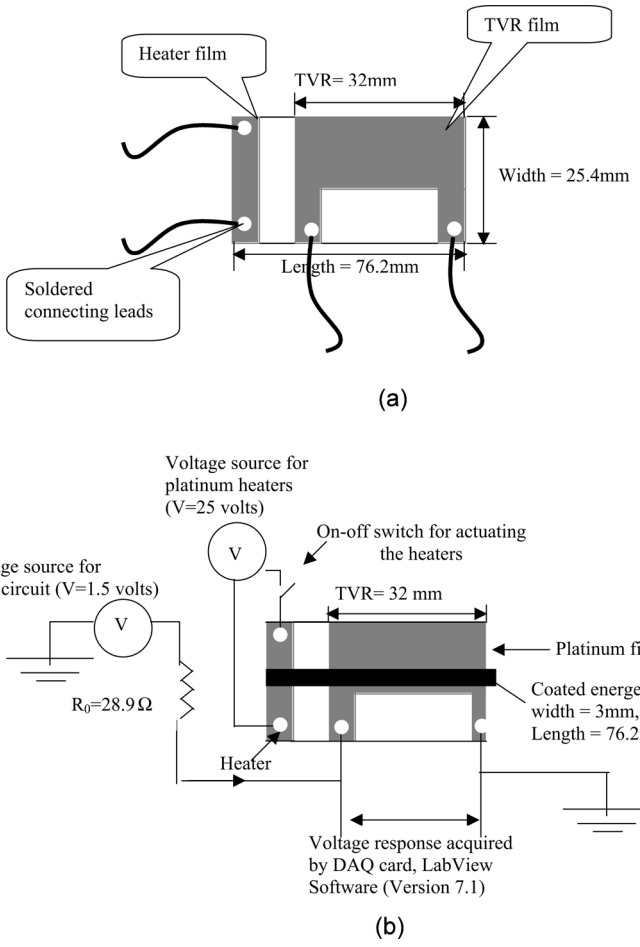


Figure 1. (a) Schematic of platinum sputtered chip with heater and TVR and soldered connecting leads; (b) Schematic of voltage divider circuit used for on-chip burn rate measurement.

the burn rates due to this multiple layering. We plan to study these mechanics in detail as a part of our future endeavors. The coated chip was dried in an oven at 90°C for 10 min to remove all the solvent.

Table 2
Composition of mixtures of oxidizer and fuel nanoparticles and dispersion time

Nanoenergetics (oxidizer/ fuel)	Oxidizer/ fuel ratio (Φ)[a]	Weight of oxidizer, (g)	Weight of fuel, (g)	Volume of 2-propanol (ml)	Dispersion time (hr)
CuO/Al	1.65	1.0	0.37	5.0	6–8
Bi_2O_3/Al	3.70	0.7	0.3	2.5	6–8

[a]Φ is oxidizer to fuel ratio based on reaction stoichiometry [4].

Experimental Setup and Measurement of Burn Rate

A voltage divider circuit as shown in Figure 1(b) was used to measure the voltage drop across TVR detector film. The TVR on-chip, coated with energetics, was connected serially with another resistor to form a voltage divider circuit. Current of 2–3 A was supplied to the heater when the ignition switch was toggled. The excitation voltage applied on the detection circuit was 1.5 V. A data acquisition (DAQ) card (PCI-MIO-16E-1) with a sampling rate of 1.25×10^6 samples/s from National Instruments Inc., TX, was used to acquire the voltage drop data with the help of the LabView software (version 7.1, National Instruments Inc). The data acquisition was started around 1 s before the heater was powered. The ignition usually occurred within the first second, and data acquisition was continued over 5 s to enable the system to monitor the whole burning process. After triggering ignition, the flame propagation caused the resistance across the TVR film to change. This was acquired as a change in voltage response across the TVR film. As our data acquisition system was continuously monitoring the voltage response during the whole burning process, there was no instrumentation delay factor in our measurements. The time period corresponding to the change in voltage response was extracted out of the entire 5 s data using Microcal Origin data processing software from Origin Lab Corp., MA. The time period and the fixed length of the TVR film (32 mm) enabled us to determine the burn rates.

Microstructural Characterization and Energy Dispersive Spectroscopy

The chip coated with CuO/Al after the ignition was characterized using a scanning electron microscopy (SEM) (Hitachi S-4700) system. During ignition, the products of a thermite reaction can react with platinum film to form an alloy because of the localized high temperature. To verify this, a portion of the TVR film part of the chip was imaged with SEM immediately after the burn process. An adjacent portion from the same chip was cleaned with Piranha solution to dissolve metallic impurities and sonicated for 2 min to remove the surface debris, and finally rinsed with distilled water and dried at 80–90°C for 10 min. After this cleaning step, the leftover residues again were characterized by SEM, and energy-dispersive spectrometry (EDS) was performed on the microstructure using beam energy of 4.6 keV in an Armray 1600 SEM system.

Results and Discussion

A CuO/Al energetic nanoparticle mixture was tested by the on-chip ignition method [8] as described in the previous section. After triggering ignition, as the flame propagated across the TVR detector film, the corresponding voltage drop across this film was acquired by a DAQ card using LabView software. The useful part of these data indicating the voltage change was extracted and replotted using Microlocal Origin, as can be seen in Figure 2. It was observed that the voltage increased from 0.674 to 0.69 V over a time period of 63 μs and remained constant after this. The velocity was calculated by assuming the temporal response of the DAQ card to be same as the time taken by the flame actually to propagate over the TVR detector film with a fixed length of 31.8 mm. The burn rate was calculated to be 504 m/s. Several measurements were obtained using the same CuO/Al nanoparticles mixture to study the repeatability of this new diagnosis technique. Table 3 summarizes these measurements for CuO/Al and Bi_2O_3/Al energetic mixtures. The average burn rate of the CuO/Al nanoparticle mixture was found to be 442 ± 55.4 m/s, which

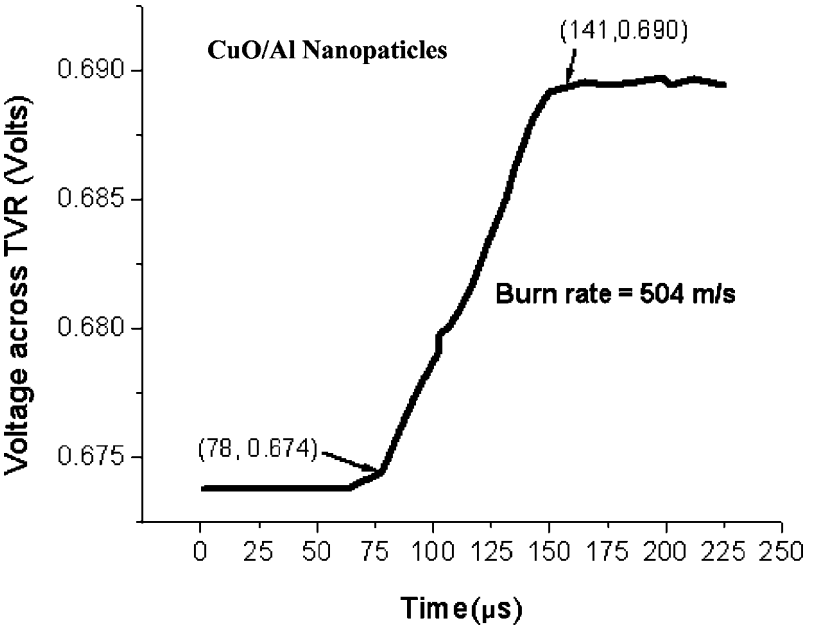


Figure 2. Voltage drop across TVR detector vs. time acquired by DAQ card using LabView software for CuO/Al nanoparticle mixture during on-chip ignition and propagation.

Table 3
Burn rate of CuO/Al and Bi_2O_3/Al nanoparticle mixture measured by on-chip method

Oxidizer/fuel	Trial no.	Burn rate (m/s)	Average burn rate (m/s)
CuO/Al	I	504	442 ± 55.4
	II	355	
	III	469	
Bi_2O_3/Al	I	137	147 ± 6.5
	II	149	
	III	155	

is comparable to the value reported earlier in the literature by using a high-speed camera imaging method [10]. We have further investigated the effect of various TVR lengths (25, 35, and 50 mm, respectively) on burn rate measurements, and our observations seem to show consistency. The calculated velocities have been found to be independent of the TVR length. Currently this measurement method is used regularly to obtain burn rates of other synthesized nanoscale energetic materials in our laboratory.

In the on-chip method investigated here, we used an electrical source to ignite the CuO/Al nanoparticle mixture on a chip by resistive heating. This electrical source basically provides a thermal impulse to the energetics to trigger the thermite reaction:

$$3CuO + 2Al \longrightarrow 3Cu + Al_2O_3 + \Delta H,$$

where ΔH is the heat of the thermite reaction. In particular the heat release of 604 kJ/mol of Al and reaction temperature of 3794 K [11] is associated with the above reaction. At such a high temperature, the products of thermite reaction easily can react further with platinum TVR film to form an alloy. We investigated the possibility of this alloying process by studying the microstructures and analyzing the composition of the postreaction TVR film by energy dispersive X-ray microanalysis.

The scanning electron microscopic (SEM) image of the products of the reaction on the platinum film after completion of the burning process is shown in Figure 3. We can observe the platinum film, the glass substrate, and the debris from the thermite reaction on the surface of the TVR film. The particle debris are found to contain products of a thermite reaction (Cu and Al_2O_3) and presumably some unknown alloys. The microstructure revealed bigger particles of about 2 μm size with fibers or whiskers on the surface, smaller particles of about 50–100 nm size, and a brighter interface layer of a few nm thickness between the platinum and particle debris.

Here we would like to hypothesize that platinum film undergoes an alloy formation with the products of thermite

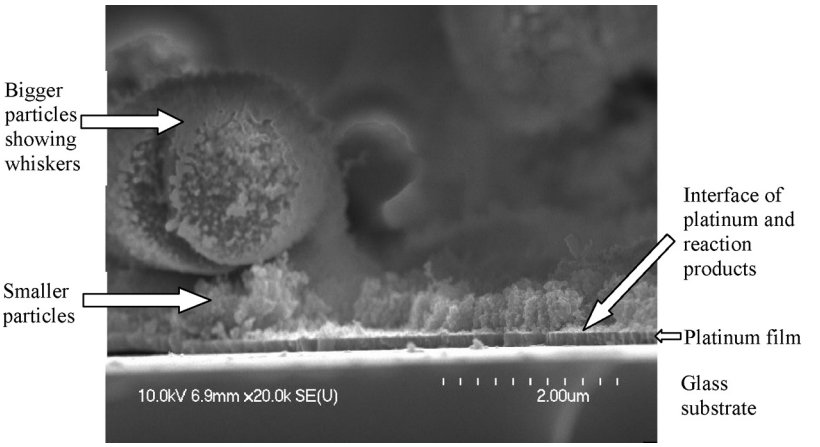
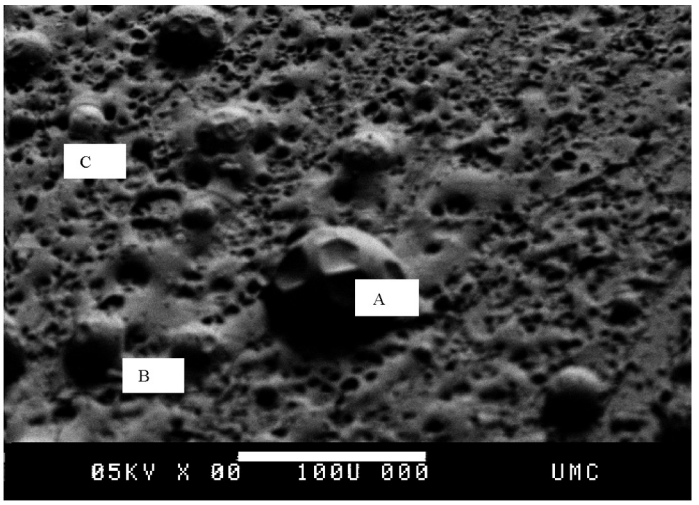


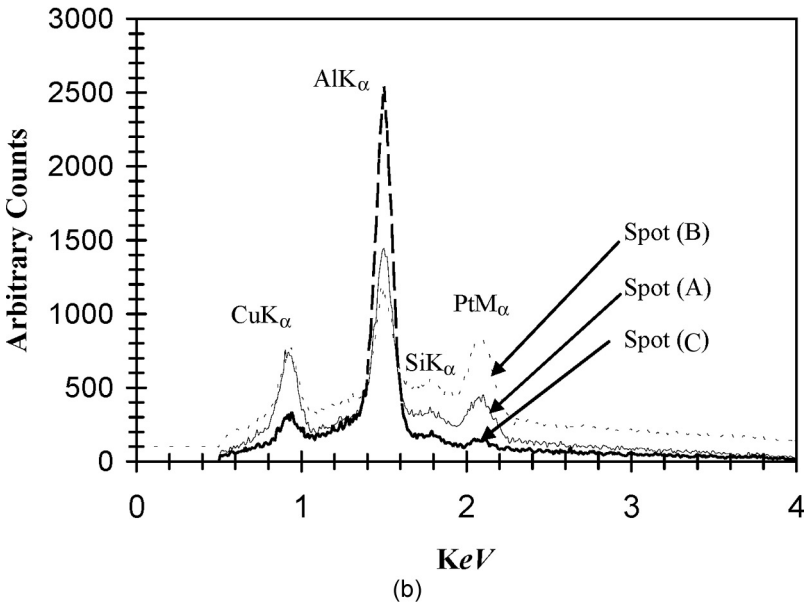
Figure 3. SEM image of on-chip thermite reaction products of CuO/Al nanoparticle mixture ignited using an electrical source.

reaction, causing the change in resistance. To verify this hypothesis we characterized the surface again by SEM and EDS analysis. We began with removal of most of the debris using a Piranha cleaning step, as mentioned earlier in the experimental section, to expose the surface of the platinum TVR film. After these cleaning steps, a microstructural characterization was performed, and the SEM image obtained is shown in Figure 4(b). We observed the surface to be heterogeneous with large and small particles and relatively flat surfaces.

We focused an electron beam at different spots on the surface indicated in Figure 4(a) to acquire basic compositional information. The EDS spectra obtained for the spot (A) large particle, (B) flat surfaces, and (C) small particles are shown in Figure 4(b). From the EDS spectra, it can be seen that the composition of spot (B) is most evenly distributed for the three metals Pt, Cu, and Al, while we can observe a smaller Pt peak at spot (A) and a still smaller Pt peak at spot (C). The three peaks in all EDS spectra can be identified as Al K_α, Cu L_α, and Pt M_α lines, which indicate the possibility of the presence of an alloy containing Al, Cu, and Pt with a wide concentration



(a)



(b)

Figure 4. (a) SEM image of on-chip thermite reaction products of CuO/Al nanoparticle mixture cleaned with Piranha solution and by ultrasonication; (b) EDS spectra of surface taken at three different spots.

distribution. As we were using a very low-beam energy of 4.6 keV, the interaction depth of this electron beam in the sample is estimated to be less than 300 nm (from a Monte Carlo simulation). We interpret from this that it is impossible for the electron beam to reach the sputter-coated Pt layer under the micron-sized particles on the surface. Thus, we would like to conclude that the Pt M_α lines in the EDS spectra came from platinum alloyed with the thermite reaction products by the localized heat of thermite reaction. This alloying resulted in a change in resistance of the TVR film during the burning process. The other possible reasons could be structural changes in platinum on heating, conduction/convection and sudden cooling, and oxide formation.

The other energetics Bi_2O_3/Al nanoparticle mixture also was tested using our novel on-chip method [8]. The results obtained are shown in Figure 5. It is observed that the potential across the TVR film increased from 0.36 to 0.39 V in 166 μs, which gives the burn rate of 138 m/s. This proves that Bi_2O_3/Al has a lesser burn rate in comparison to CuO/Al thermites. Repeatability of the measurements was confirmed on the Bi_2O_3/Al nanoparticle mixture. In these experiments, burn rates were found to be 147 and 155 m/s. Table 3 summarizes the burn rates for Bi_2O_3/Al nanoparticle mixture.

The on-chip method investigated here is rapid and inexpensive and uses a few milligram quantities of energetic materials to measure the burn rate. The instrumentation involved is very simple and easy to set up.

Conclusions

A novel on-chip method has been developed to measure the burn rates of energetic materials. Burn rate measurements were carried out for thermite materials CuO/Al and Bi_2O_3/Al nanoparticle mixtures. Results indicated the respective burn rates to be 504 and 155 m/s. The measurements were repeated several times, and the error bars for the burn rate were 12.5% for CuO/Al and less than 5% for Bi_2O_3/Al, respectively. The microstructure and EDS analysis of on-chip ignition products

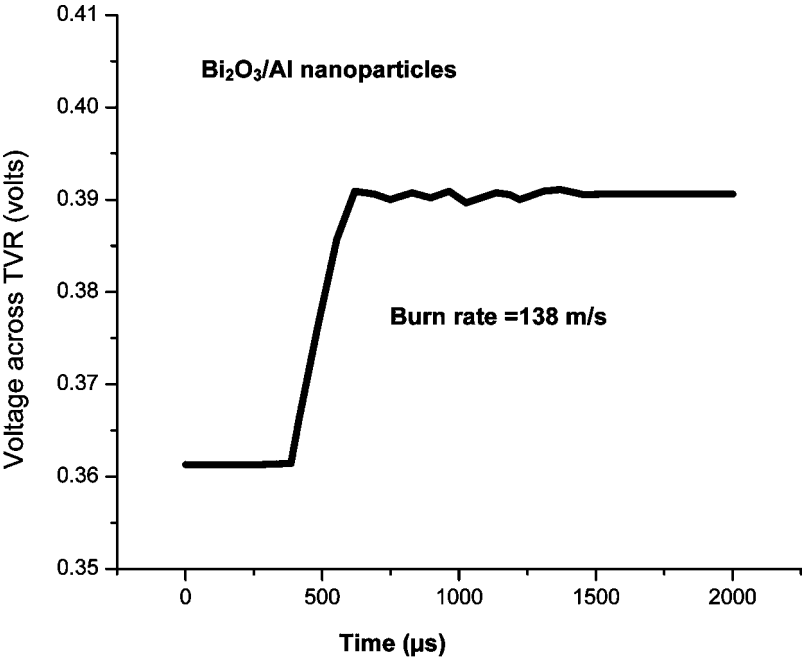


Figure 5. Voltage drop across TVR detector vs. time acquired by DAQ card using LabView software for Bi_2O_3/Al nanoparticle mixture during on-chip ignition and propagation.

of the CuO/Al nanoparticle mixture suggest the presence of an alloy containing Cu, Al, and Pt. This indicates one of the main reasons for the change in the resistance of TVR platinum film during flame propagation. This method is simple, rapid, and inexpensive and requires a few milligram quantities for testing the burn rates. These attributes make this on-chip method an elegant approach to exploring testing of other classes of energetic materials.

Acknowledgements

The authors gratefully acknowledge the fruitful discussions with Professor K. Gangopadhyay, Electrical and Computer Engineering

Department, University of Missouri, Columbia and the financial support from the National Science Foundation.

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