SAND2014-20290C

THERMAL IGNITION OF TITANIUM/POTASSIUM PERCHLORATE PYROTECHNIC POWDERS: INCORPORATING REACTIVE CHEMICAL PROCESSES INTO PREDICTIVE IGNITION MODELS

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ABSTRACT

The reactive chemical processes that control ignition of titanium/potassium perchlorate pyrotechnic powders have been characterized and used to develop a reduced-dimensionality model to predict time to ignition in small-scale tests. Detailed and reduced chemical reaction mechanisms, developed using Simultaneous Thermogravimetry and Modulated Beam Mass Spectrometry (STMBMS), are presented, and finite-element simulations incorporating this reactive chemistry are compared with results from small-scale ignition tests. The reduced chemical reaction mechanism successfully predicts time to ignition of pressed pellets.

INTRODUCTION

Pyrotechnic powders are used in a variety of explosive devices such as thermal igniters and mechanical actuators. One common class of pyrotechnics used in weapon components consists of a metal or metal hydride fuel mixed with a perchlorate oxidizer. Titanium/potassium perchlorate (TKP) powder and titanium sub-hydride/potassium perchlorate (THKP) powder are two pyrotechnic mixtures that are frequently used in these applications.

Typical pyrotechnic explosive devices use an ignition source consisting of a wire bridge embedded in a pressed pyrotechnic powder; a power source rapidly heats the bridge wire until ignition occurs within the pressed pyrotechnic bed. Oxygen is released from the potassium perchlorate oxidizer under action of heat, which oxidizes the titanium or titanium hydride fuel, generating heat and sustaining combustion of the powder until the oxidizer and fuel are fully depleted. Several studies of the electrical and thermal sensitivity of THKP and TKP have been conducted over the years [1-3]. The ignition process has been extensively studied in previous reports [3-7].

The ability to predict and model pyrotechnic ignition thresholds is critical to Sandia’s weapon component development mission. Research and development underway include replacement and redesign of pyrotechnic components, and as part of this work, old legacy pyrotechnic materials must be recertified for use, new powders must be acquired and certified for use, and components must be designed around these materials. Predictive modeling and small-scale testing play a major role in this effort for both certification of new powders and recertification of legacy powders, and major R&D efforts are underway to develop predictive models of material performance for design of future energetic components.

The purpose of this study is to generate a reaction mechanism for ignition of TKP pyrotechnic powder that is condensed enough to be inserted into current engineering models, yet complete enough to properly reproduce the critical events in the ignition process with high fidelity. We have previously investigated the reactive chemistry involved in thermal reactions of THKP pyrotechnic powders and developed an extensive reaction mechanism for thermal ignition [8], and the work we describe here aims to reduce this full reaction manifold down to a smaller number of critical reactions for TKP. Although the work described here is centered on TKP pyrotechnics, the methodology we present is much more general, as it may be possible to apply the same methods to model thermal ignition of high explosives – a topic of considerable interest throughout the energetics community. Predictive modeling of thermal ignition of high explosives using this methodology will be investigated in future work.

EXPERIMENT

STMBMS APPARATUS

Simultaneous Thermogravimetry and Modulated Beam Mass Spectrometry (STMBMS) [9-11] was used to investigate the thermal decomposition and ignition chemistry of titanium/potassium perchlorate powder and its ingredients at small scales. References [9] – [14] describe the experimental methods and numerical algorithms used to examine and characterize the reactions of energetic materials at elevated temperatures. The basic features of a thermal decomposition experiment using the STMBMS instrument are illustrated in Figure 1. A small sample of energetic material (ingredient or mixture; 2-10 mg) is placed in an alumina reaction cell (free volume of 0.227 cm^3), which is sealed with a cap assembly containing a ceramic cup with a 30-1000μm orifice at its center. The reaction cell is heated in a controlled manner using a thermocouple and programmable thermal controller to measure and control the temperature of the cell. As the reaction cell is heated, gaseous compounds are generated due to thermal decomposition of the sample. These gases fill the free volume of the reaction cell, causing it to pressurize. The pressurized gas flows through the orifice and expands into vacuum, forming a molecular beam. The resulting molecular beam is directed into a quadrupole mass spectrometer, where the relative abundance of each constituent is measured. The reaction cell sits atop a microbalance, which records the change in mass of the sample as it is heated and undergoes sublimation/evaporation and decomposition. Together these measurements allow identification and determination of the time-and temperature-dependent rate of formation of each gaseous species that evolves from the heated sample.

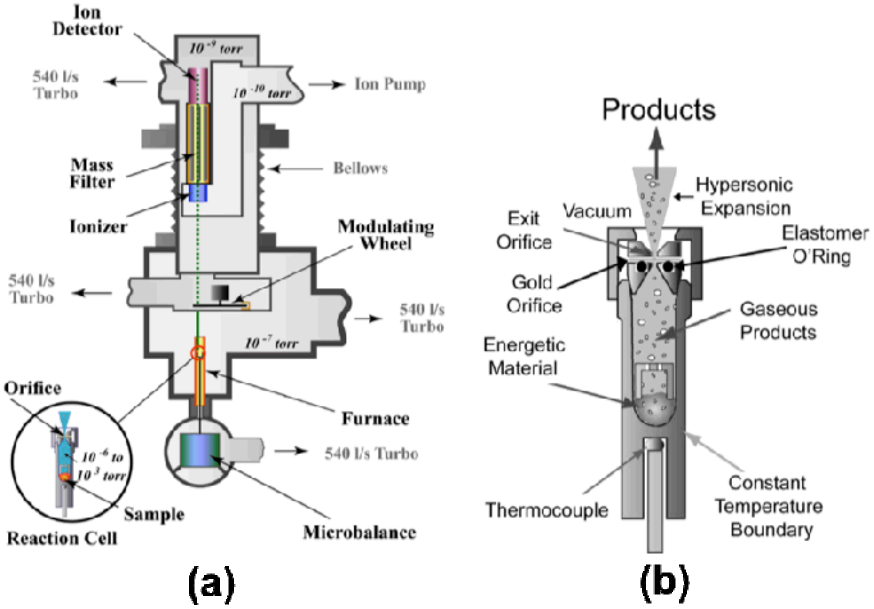


Figure 1. (a) Schematic diagram of the Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) instrument. (b) Schematic diagram of the reaction cell illustrating a typical sample configuration used in an STMBMS experiment.

The pressure of gases within the reaction cell is determined by the diameter of the orifice and the experimental conditions. The gas pressure within the cell is determined by a steady-state balance between the rate of gas formation from the sample and the rate of exhaust through the orifice. Smaller orifices will produce higher pressures for a given gas formation rate from the sample. For compounds in two-phase quasi-equilibrium, the pressure is determined by the temperature of the reaction cell and the properties of the compounds. In this case, a smaller orifice results in less of the gas exiting the reaction cell. The reaction conditions are controlled by altering the sample size, temperature, heating rate, orifice diameter and volume of the reaction cell.

PYROTECHNIC SAMPLES

Samples of titanium/potassium perchlorate pyrotechnic powder (TKP) and its constituent ingredients were received from Sandia National Laboratories, NM. The TKP powder contains, by weight, 33% titanium powder and 67% potassium perchlorate ($KClO_4$). The titanium powder has an average particle diameter of ~1 µm, and the $KClO_4$ has an average particle diameter of ~5 µm. Samples of TKP and its ingredients were used as received.

RESULTS AND DISCUSSION

The major chemical reactions that control thermal ignition of TKP pyrotechnic powder are:

$$\begin{aligned}
\mathrm{KClO_4}(s,\mathrm{rh}) &\leftrightarrow \mathrm{KClO_4}(s,\mathrm{cu}) \quad \lfloor 309^{\circ}\mathrm{C} \rfloor \\
\mathrm{KClO_4}(s) &\rightarrow \mathrm{KClO_3}(s)+\mathrm{O(g)} \\
\mathrm{KClO_3}(s) &\rightarrow \mathrm{KClO_3}(l) \quad \left[356^{\circ}\mathrm{C}\right] \\
\mathrm{KClO_4}(s)+\mathrm{KClO_3}(l) &\rightarrow \left(\mathrm{KClO_4}+\mathrm{KClO_3}\right)\left(solution\right) \\
\mathrm{KClO_3} &\rightarrow \mathrm{KCl}(s)+\tfrac{3}{2}\mathrm{O_2}(g) \\
4\mathrm{KClO_3} &\rightarrow 3\mathrm{KClO_4}+\mathrm{KCl} \\
2\mathrm{KClO_3}+\mathrm{O} &\rightarrow \mathrm{K_2O}(s)+2\mathrm{ClO_2}(g)+\mathrm{O_2}(g) \\
\mathrm{ClO_3}(g)+\mathrm{O}(g) &\rightarrow \mathrm{ClO_2}(g)+\mathrm{O_2}(g) \\
\mathrm{O}(g)+\mathrm{O}(g) &\rightarrow \mathrm{O_2}(g) \\
\mathrm{Ti}(s)+\mathrm{O_2}(g) &\rightarrow \mathrm{TiO_2}(s)
\end{aligned} \tag{1}$$

The STMBMS experiments and analyses that led to this set of reactions are detailed and will be described in a future publication [8]. The ten reactions shown here are too numerous to incorporate into engineering codes to simulate ignition and performance of a macroscopic pyrotechnic sample. The codes can only incorporate a small number of simultaneous reactions (~2) due to the computationally expensive nature of macroscale 3D simulations. Our goal is to reduce this reaction mechanism to a minimal number that still captures the important events in the reaction sequence and the overall behavior of the material. In particular, the decomposition of the $KClO_4$ oxidizer is a multistep reaction that involves generation of oxygen, formation of $KClO_3$, liquefaction of the $KClO_3/KClO_4$ mixture followed by rapid generation of oxygen, depletion of oxygen to form KCl, and finally termination of the oxygen generation process by solidification of the reacting mixture. Given the complexity of mechanism (1), it is not immediately clear that it will be possible to reduce this scheme to a much smaller number of reactions.

Figure 2 shows an illustration of the reaction zones in a collection of TKP particles. The figure shows three basic regions where reactions occur: (1) the $KClO_4$ powder, where decomposition occurs to release oxygen, forming $KClO_3$ and ultimately KCl, K_2O, and other species as byproducts, (2) the transport region, which includes the free space and contact surface between the $KClO_4$ and Ti particles (including the growing TiO_2 oxide layer), and (3) the interior of the titanium particle where oxidation has not yet occurred. The principal reactions controlling overall behavior in each region are (1) the production of oxygen and intermediate species in the $KClO_4$ particle, (2) motion of these species across the transport region, which may involve diffusion through the oxide layer, and (3) oxidation of the titanium in the interior of the particle, which contributes to the growth of the surface oxide layer.

The simplest possible reaction mechanism that can be formulated to capture the general behavior of this system is:

$$\begin{aligned} \mathrm{KClO_4}(s) &\rightarrow \mathrm{KCl}(s) + 2\mathrm{O_2}(g) \\ \mathrm{Ti}(s) + \mathrm{O_2}(g) &\rightarrow \mathrm{TiO_2}(s) \end{aligned} \tag{2}$$

Mechanism (2) omits consideration of all species except the initial reactants (Ti, $KClO_4$), final products (KCl, TiO_2), and oxygen (O_2), which is treated as the sole reactive intermediate. This is the reduced set of reactions we will attempt to use to parameterize the system for ignition modeling. Current predictive thermal codes only address the second reaction in (2). Oxygen is assumed to evolve from the $KClO_4$ particles and form an infinite reservoir external to the titanium metal particle. This oxygen reservoir is assumed to neither fill nor deplete with time, allows for the oxygen formation process to be considered instantaneous, and no kinetics are used to describe this reaction. Oxidation of the metal particle is also considered instantaneous in the simulations. The only kinetic process incorporated is a diffusion-based rate for transport of oxygen to the titanium particle, through the TiO_2 surface coating. The description of the titanium oxidation process in the codes is far more physically realistic than the oxygen generation process, and we will therefore focus on development of a kinetic model for oxygen evolution from $KClO_4$ using STMBMS, which is uniquely suited for this purpose.

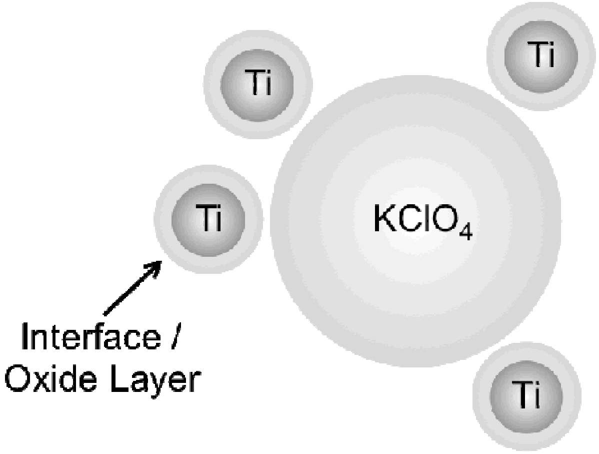
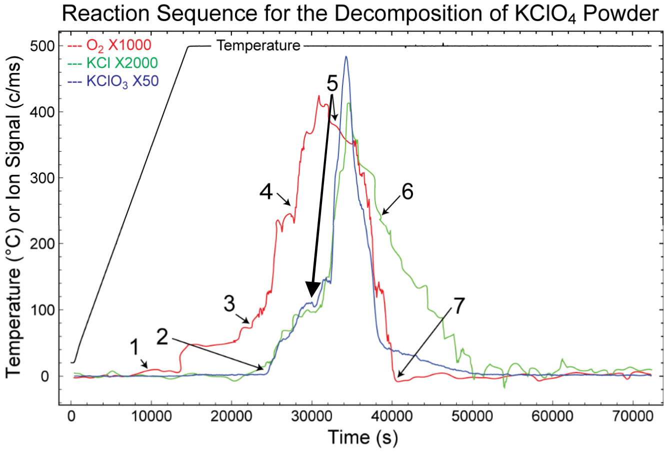


Figure 2. Illustration of the reaction zones in a reacting TKP powder. Shown are $KClO_4$ particles and oxidizing titanium metal particles, which have a growing layer of TiO_2 at their surface.

Figure 3 shows species that are evolved during isothermal decomposition of $KClO_4$ oxidizer at 500°C as measured using STMBMS. The figure shows that the oxygen release process is not constant, but evolves through a series of phases. In the first phase, the material slowly evolves oxygen. $KClO_3$ then forms and subsequently liquefies. Upon liquefaction of $KClO_3$, oxygen is rapidly released. When oxygen becomes significantly depleted, KCl forms and the material solidifies, terminating oxygen release and halting the reaction process.



Oxygen release process:

1. Oxygen loss from $KClO_4$ (slow)
2. Formation of $KClO_3$
3. Liquefaction
4. Rapid release of O_2
5. Depletion of O_2, formation of KCl
6. Solidification
7. Termination of oxygen release

Figure 3. Reaction sequence for thermal decomposition of $KClO_4$ and generation of oxygen.

To parameterize this process, we will develop a differential equation describing the time and temperature dependence of the rate of reaction to the extent of reaction α. We write this differential equation as

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \qquad (3)$$

In this notation, *α* is the "extent of reaction" (or progress variable), *f*(*α*) is the condensed-phase reaction model, which describes the dependence of the kinetics on the spatial aspects of the problem (particle sizes, diffusion, etc.), and *k*(*T*) is the kinetic model, which describes the dependence of the rate of reaction on temperature *T*. For this system, we will employ a Prout-Tompkins condensed-phase reaction model:

$$f(\alpha) = C\alpha^x(1-\alpha)^y \qquad (4)$$

and an Arrhenius kinetic model:

$$k(T) = A\exp\left(-E_a/RT\right). \qquad (5)$$

The final form of the model is

$$\frac{d\alpha}{dt} = C\alpha^x(1-\alpha)^y A\exp\left(-E_a/RT\right). \qquad (6)$$

Figure 4 shows the isothermal rate of oxygen release (dO_2/dt) for a TKP powder mixture (magenta dots) and the result of a fit to the data using the constants C = 1.95e-4, x = 0.93, y = 0.60 (green line). Integrating the rate of oxygen release gives the concentration of oxygen as a function of time $[O_2(t)]$ and the total oxygen evolved $O_{2,tot}$; normalizing $[O_2(t)]$ to $O_{2,tot}$ defines the progress variable α, which is shown in Figure 5.

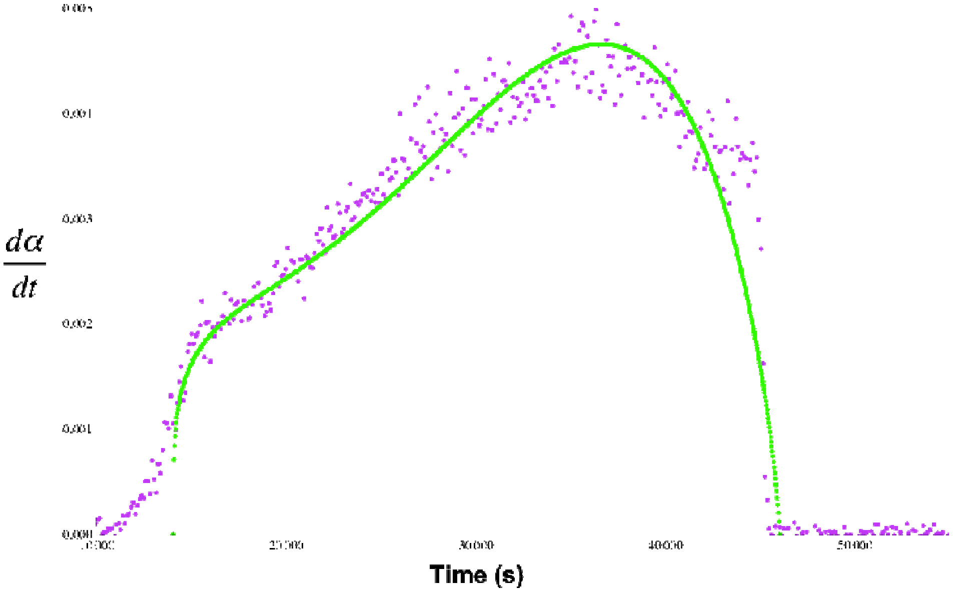


Figure 4. Comparison of fitted reaction model (green) with rate of release of oxygen derived from STMBMS experiments (magenta).

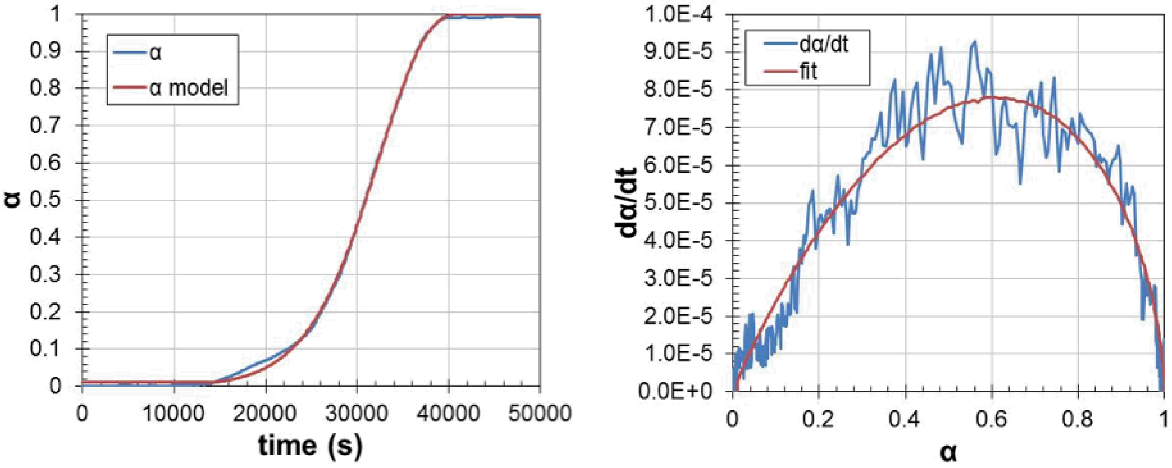


Figure 5. Comparison of measured extent of reaction *α* and measured rate of reaction d*α*/dt derived from STMBMS experiments (blue lines) with fit (red lines).

The temperature dependence of the reaction is determined by a similar procedure using an experiment with a slow heating ramp, using the measured activation energy for $KClO_4$ decomposition in the presence of TiO_2 (E_a = 63 kcal/mol [15]) yields A = 7.5e17 and fully determines the fit model of Equation (6). The quality of the fit appears to indicate that the model described by Eq. (6) adequately represents the experimental data.

The ultimate test of this reduced reaction model is successful predictive modeling of an ignition event in a macroscopic sample. This reduced reaction model has been used [16] to predict time to ignition of TKP powder as measured in small-scale tests [17, 18]. These simulations combine the reduced dimensionality reaction mechanism above with a shrinking-core/thickening-shell model for oxidation of the titanium particles in a two-part model described by the equations:

$$\begin{aligned} \frac{d\alpha_1}{dt} &= f_1(\alpha_1)k_1(t) = C_1\alpha_1^x(1-\alpha_1)^{y_1}A_1\exp\left(-E_{a,1}/RT\right) \\ \frac{d\alpha_2}{dt} &= \left[\mathrm{O}_2(t)\right]f_2(\alpha_2)k_2(t) = \left[\mathrm{O}_2(t)\right]C_2(1/\alpha_2)^{y_2}A_2\exp\left(-E_{a,2}/RT\right) \end{aligned} \quad . \tag{7}$$

This two-part reaction model is used in a finite-element code to calculate the ignition time of a pressed TKP sample heated in an aluminum case. The results are shown in Figure 6. The excellent fit of the time to ignition and internal temperatures to the experimental data indicates that the reaction model of Equation (7) is fully adequate to describe the physics of ignition, and the reaction model for oxygen evolution in Equation (6) is fully adequate to describe the oxygen generation process. Thus, the reduced reaction mechanism described by Eq. (2) is adequate to describe the oxygen release process for thermal ignition under these conditions.

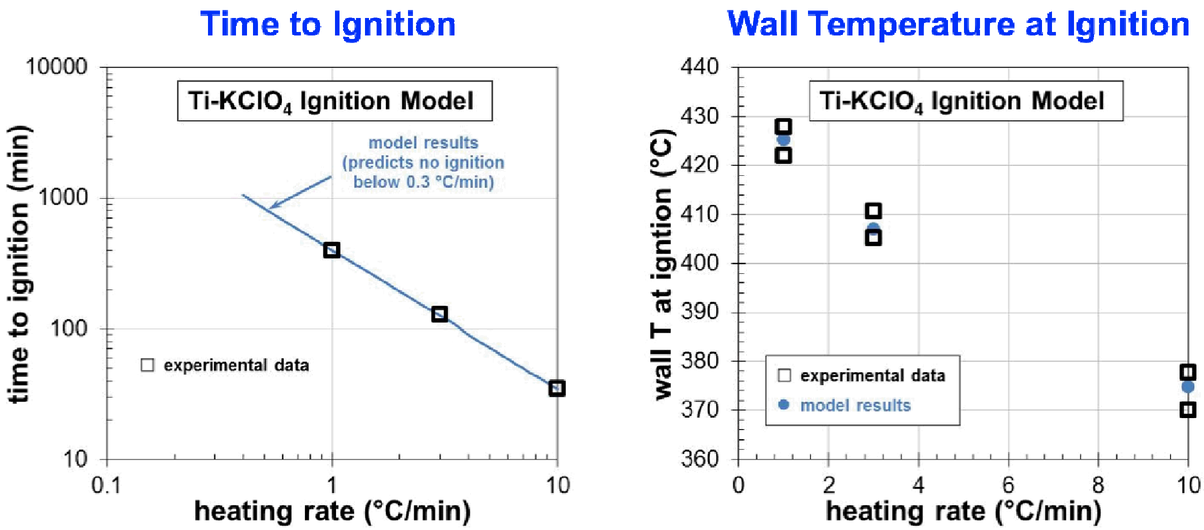


Figure 6. Comparison of finite-element model (combining oxygen generation model developed here with shrinking-core/thickening shell model for Ti oxidation) with experimental data from small-scale time-to-ignition testing of TKP powder [18]. The finite element model shows excellent agreement with experimental data, indicating that the reduced reaction model for oxygen generation is adequate for ignition modeling under these conditions.

SUMMARY AND CONCLUSIONS

We have characterized the reactive processes that control ignition of titanium/potassium perchlorate (TKP) pyrotechnic powder, and developed a reduced dimension reaction model for thermal ignition of TKP. Ignition of these materials involves at least ten major chemical reactions. From these 10+ reactions we developed a two-step model for ignition that describes the time and temperature dependence of the ignition process. This reduced dimensionality model is sufficiently small to be incorporated into component engineering codes, and has been successfully used in finite element codes to predict time-to-ignition of pyrotechnic powders in small-scale ignition tests, increasing their predictive capability.

Future work will expand these results to enable predictive modeling of pyrotechnics at higher temperatures, pressures, and heating rates, and applying similar methodology to thermal ignition of high explosives, which is of broad interest within the energetics community.

ACKNOWLEDGMENTS

The authors would like to thank Marcia Cooper, Ryan Marinis, and Leanna Minier of Sandia National Laboratories, New Mexico, for frequent helpful discussions and guidance. We also acknowledge Deneille Weise-Smith and Aaron Highley of Sandia National Laboratories, California, for technical support.

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