SAND2014-20291C

Thermal Ignition of Ti/$KClO_4$ Pyrotechnic Powders:
Incorporating Reactive Chemical Processes Into Predictive Ignition Models

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JANNAF 46th CS, 34th APS, 34th EPSS, 28th PSHS Meeting
Ignition and Extinguishment of Solid Propellants
9 December 2014
Albuquerque, NM

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Energetic Materials Group at SNL/CA

- Our work is focused on understanding the reactive chemistry that drives response of energetic materials to **shock**, **impact**, **heat**, and **time** and developing models to predict that response
- Effort is focused on materials and formulations where **lack of chemical understanding is holding back R&D**
- Materials investigated are typically widely-used
- Working directly with DoD (all branches) and DOE (Sandia, LLNL)
- Progress is made by **simultaneously** developing tools and methods and investigating important applied problems – solving today's problems helps develop tomorrow's tools, and vice versa.

Understanding Reactive Processes in Energetic Materials

- **We can only predictively model what happens during steady detonation or combustion of well-studied pristine materials at their time of manufacture.**
- Predicting/understanding everything *besides* detonation and combustion is challenging:
  - Shock initiation and sensitivity (Insensitive Munitions, Component R&D)
  - Thermal ignition and sensitivity (Insensitive Munitions, Component R&D)
  - Aging
  - Designing new materials and formulations
- This is where most of energetics R&D is focused
- **Lack of understanding of chemical processes is holding up R&D in all these areas**

Pyrotechnic Component R&D at Sandia

Sandia has numerous explosive NW components based on pyrotechnic powders

- **Reliability is KEY (MUST fire when desired, NOT fire otherwise); understanding of ignition thresholds and margins critical**
- **Performance strongly affected by particle sizes, morphology, packing, surface area (hard-to-control parameters)**
- **Remanufacture of some materials difficult; hard-to-control parameters important in performance**
- **Sandia is developing codes to model ignition at component scale**

We are working with Sandia modelers and engineers to develop predictive models that can simulate performance at component level

We have unique tools to identify critical material parameters and develop reduced-dimensionality models

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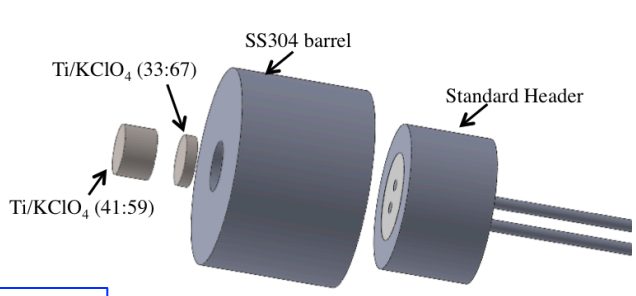
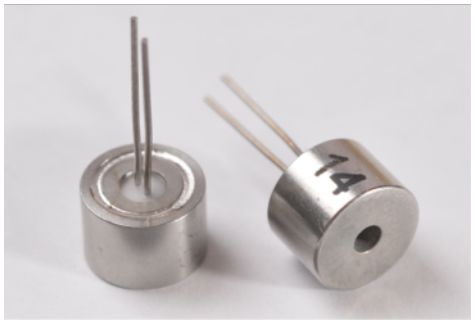
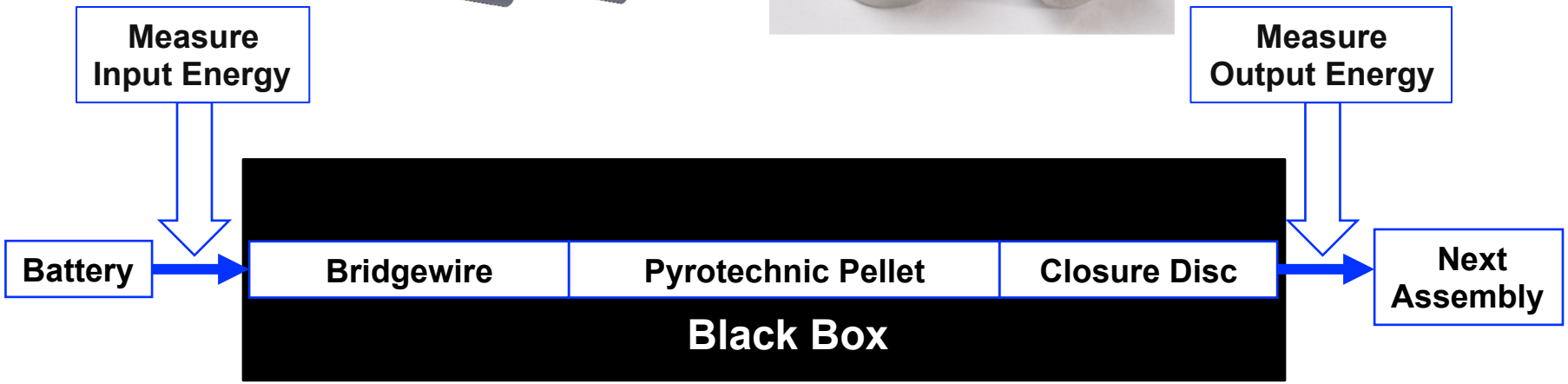
Component R&D at Sandia
Current R&D Model

Pyrotechnic Components: Building a Predictive Capability







This is how energetic component R&D has traditionally been done

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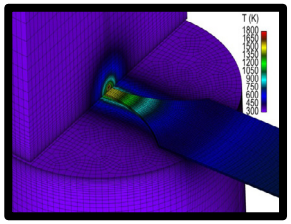
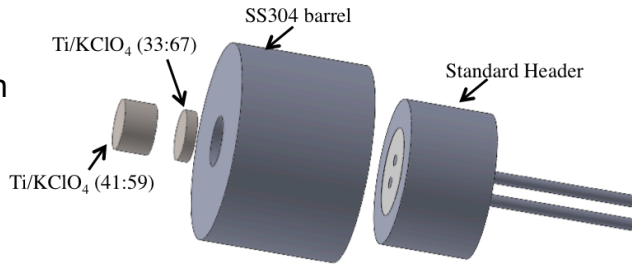
Component R&D at Sandia

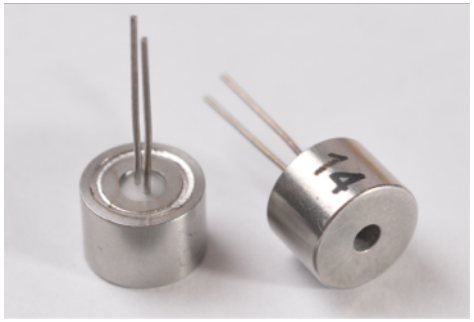
New R&D Model

This is the R&D model we are moving towards

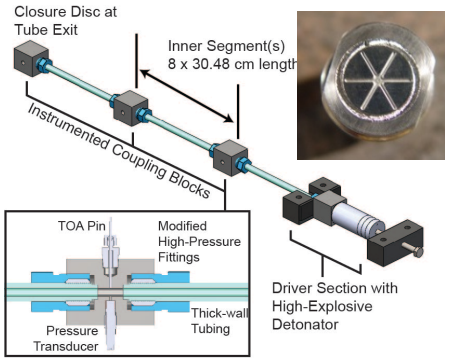
INPUT: Model Ignition Temperature





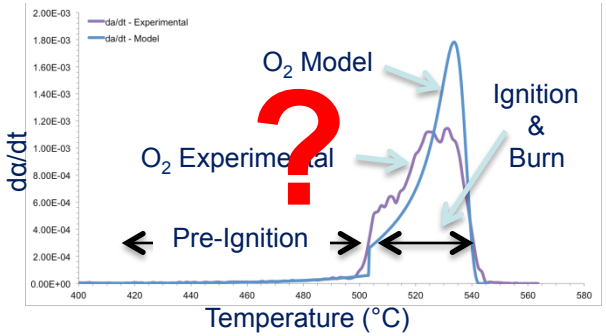


OUTPUT: Model Closure Disk Mechanics

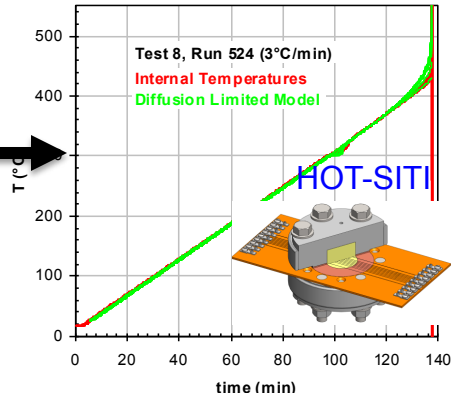


Inside the Black Box

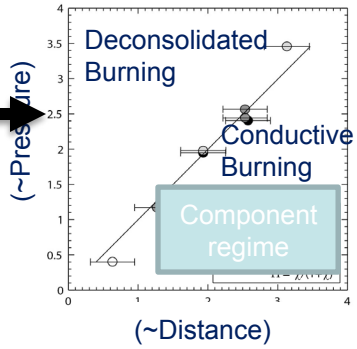
Reactive Chemistry



Pre-Ignition: Empirical Diffusion-Limited Model



Global Conductive-to-Convective Transition in Pyrotechnics



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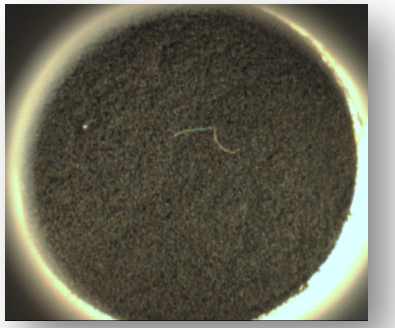
Pyrotechnic Ignition

In this work we developed a reduced reaction model for thermal ignition of pyrotechnics

$Ti / KClO_4$ $TiH_{1.65} / KClO_4$



$TiH_{1.65} / KClO_4$
Powder

- Titanium particle size: 1 micron; Perchlorate particle size: 5 microns
- $TiH_{1.65}$ is made by de-hydriding TiH_2 by heating; developed as compromise between under-sensitive TiH_2 and more sensitive Ti
- Used in igniters and actuators

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Pyrotechnic Reaction Mechanism

Phase Changes:

1. $KClO_4(s, rh) \Leftrightarrow KClO_4(s, cu)$ {~309°C}
2. $KClO_4(s, cu) \Leftrightarrow KClO_4(l)$ {~525°C}
3. $KClO_3(s) \Leftrightarrow KClO_3(l)$ {~356°C}
4. $KCl(s) \Leftrightarrow KCl(l)$ {770°C}

Reactions:

1. $KClO_4(s, rh) \rightarrow KClO_3(s) + 1/2O_2(g)$ {or O}
2. $KClO_4(s, cu) \rightarrow KClO_3(s) + 1/2O_2(g)$ {or O}
3. $KClO_4(s, cu) \rightarrow KClO_3(l) + 1/2O_2(g)$ {or O}
4. $KClO_3(s) \rightarrow KCl(s) + 3/2O_2(g)$ {or O}
5. $KClO_3(l) \rightarrow KCl(s) + 3/2O_2(g)$ {or O}
6. $4KClO_3(s) \rightarrow 3KClO_4(s, rh) + KCl(s)$ {<309°C}
7. $4KClO_3(s) \rightarrow 3KClO_4(s, cu) + KCl(s)$ {309°C< T < 356°C}
8. $4KClO_3(l) \rightarrow 3KClO_4(s, cu) + KCl(s)$ {> 356°C}
9. $KClO_3(s,l) \Leftrightarrow KClO_3(g)$
10. $KCl(s) \Leftrightarrow KCl(g)$

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Pyrotechnic Reaction Mechanism
(Continued)

- 11. $2O \rightarrow O_2(g)$
- 12. $KClO_x(s) \rightarrow KClO_y(s) + O$
- 13. $2KClO_3 + O \rightarrow K_2O + 2ClO_2 + O_2(g)$
- 14. $2KClO_4 + O \rightarrow K_2O + 2ClO_4$
- 15. $TiH_x(s) \Leftrightarrow Ti(s) + H_2(g)$
- 16. $Ti(s) + 2O \rightarrow TiO_2(s)$
- 17. $Ti(s) + O_2(g) \rightarrow TiO_2(s)$
- 18. $H_2(g) + O \rightarrow H_2O(g)$
- 19. $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$

Reaction mechanism is far too complicated for practical engineering model - need to distill down to a small number of reactions

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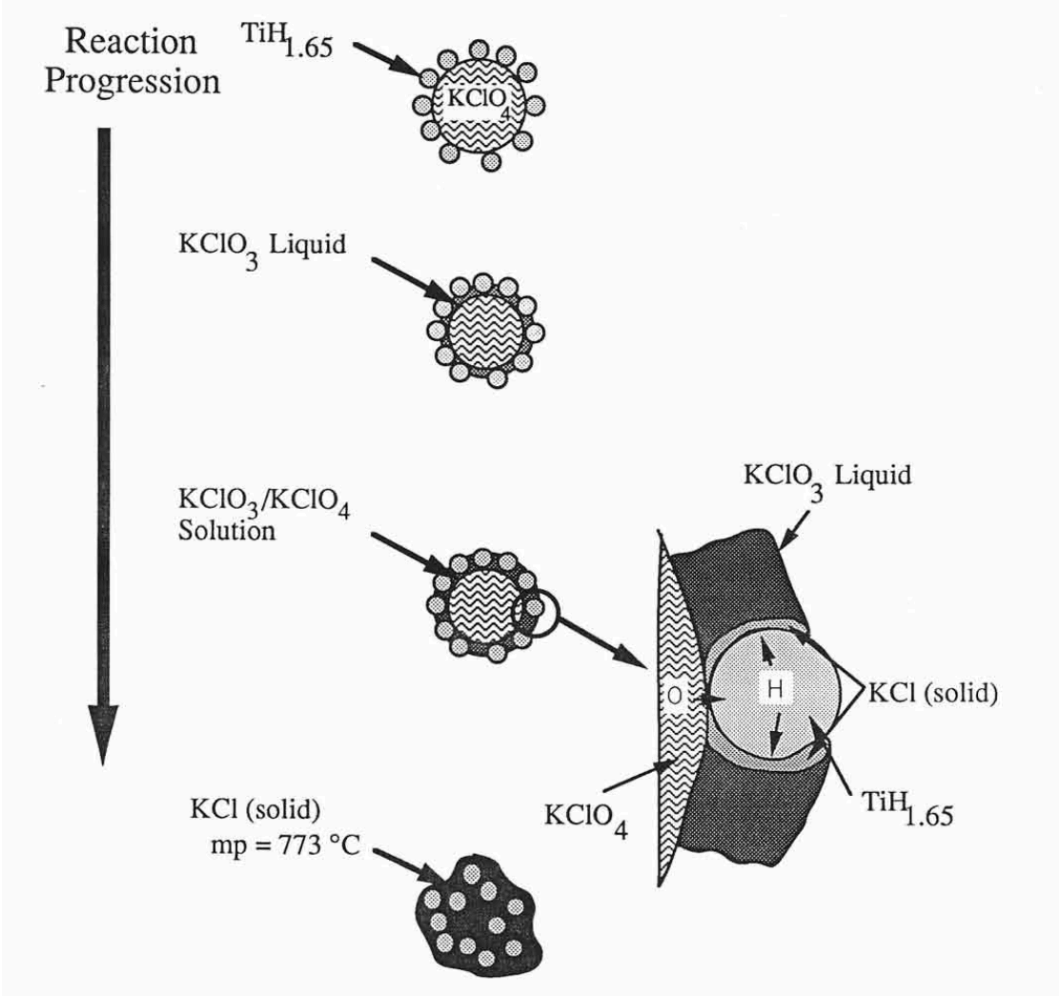
Pyrotechnic Ignition



Take a step back – what are most important species to capture correctly?

Start with oxygen generation mechanism.

Oxygen generation is a complex process that involves many species and multiple phases

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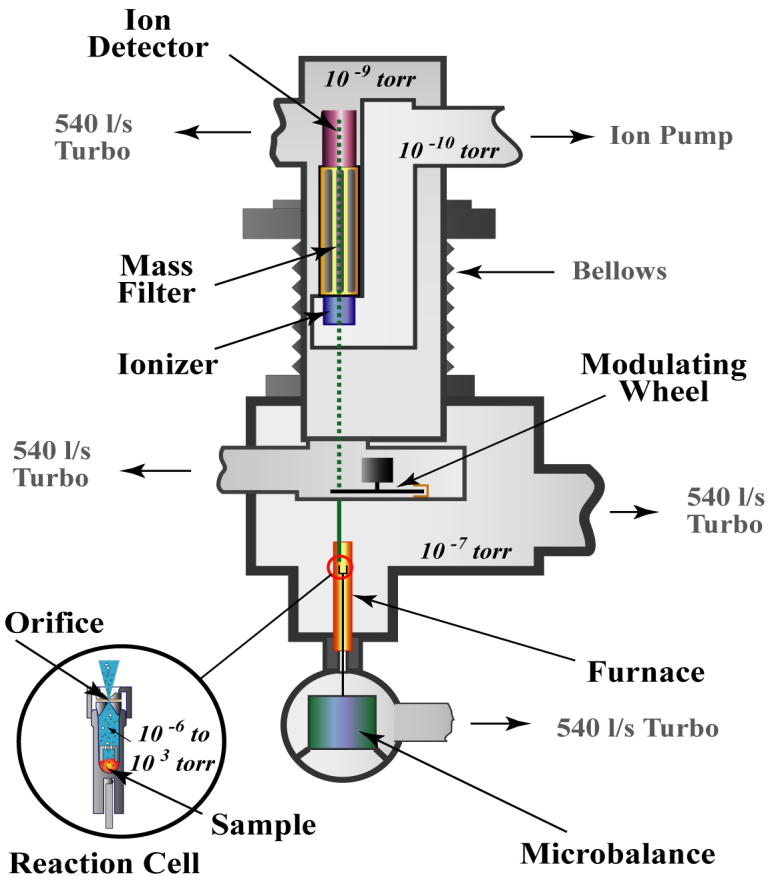
STMBMS Experiments Probe the Reaction Processes Controlling Ignition of Pyrotechnics

- **STMBMS experiments**
  - Samples placed in reaction cell with 10-1000 um orifice (low or high confinement)
  - Samples heated from 25°C up to 600°C at 1-5°C/min
  - Gaseous products are ionized in ionizer, generating molecular ions and ion fragments
  - Quadrupole mass spectrometer records individual ion signals as function of time
  - Microbalance simultaneously records mass loss (2 µg mass accuracy)
  - Using both mass spectrometry and microbalance data, quantitative measurements can be made of species emitted from sample.
  - Total experiment time ~1-10 hours
- **Results allow us to directly determine:**
  - Which species evolve from sample
  - What time/temperature they evolve
  - Rate of evolution
  - Total amount of evolved gas
- **Data are used to develop a reaction mechanism**

Schematic of STMBMS



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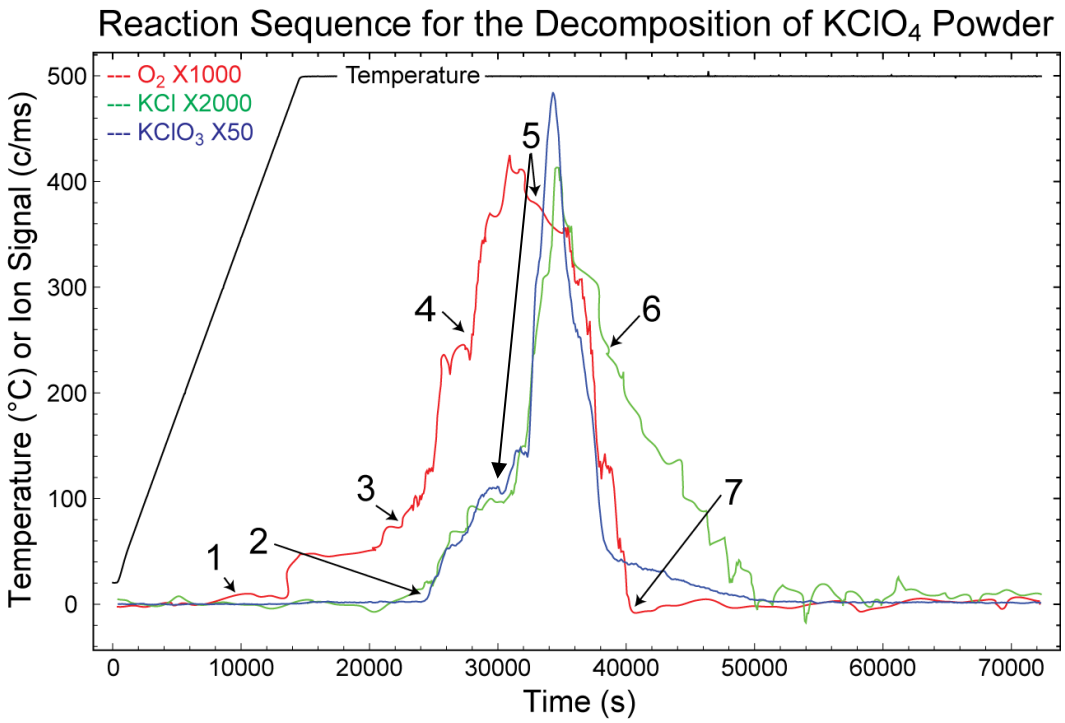
Oxygen Generation Process in $KClO_4$ Oxidizer

Generation of oxygen by $KClO_4$ is a key process that controls ignition



Oxygen release process: Illustrated on Figure to Left

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

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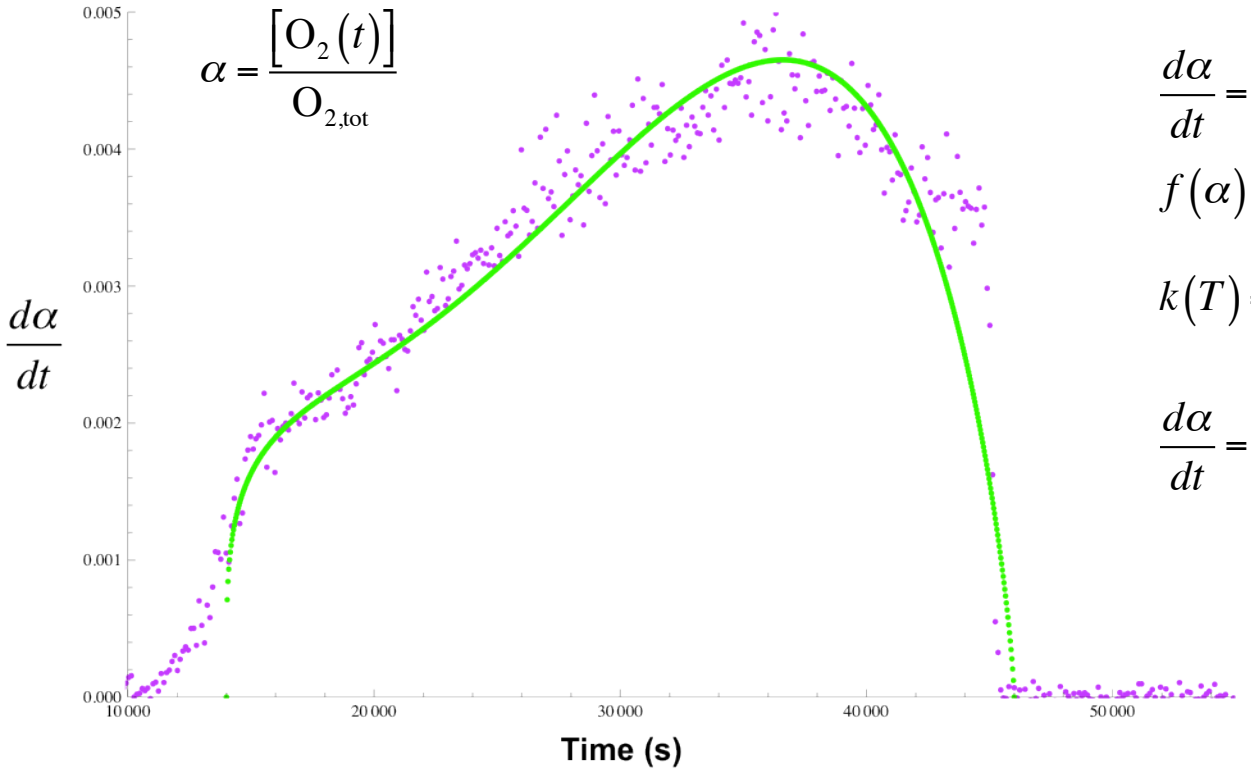
Oxygen Release Process in $KClO_4$ Oxidizer

Oxygen generation process is parameterized by fitting measured rate of release of O_2 to a condensed-phase reaction model



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

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

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

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

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

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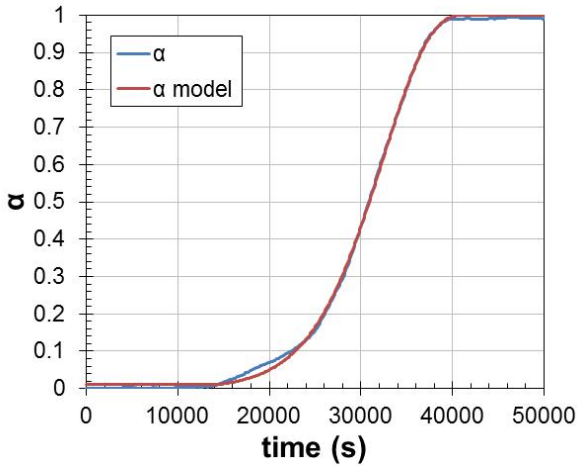
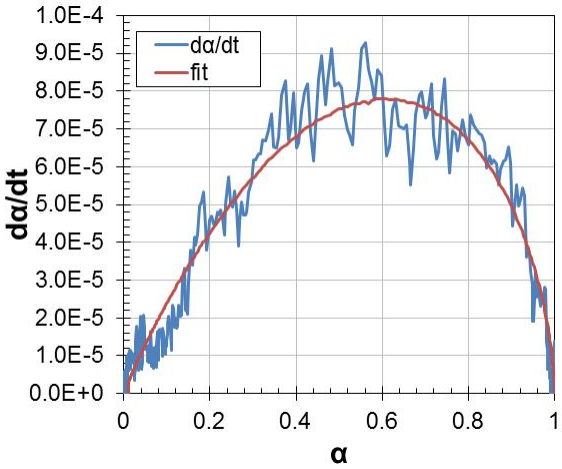
Reduced Model for Ti/$KClO_4$ Ignition

$$\alpha = \frac{[O_2(t)]}{O_{2,tot}}$$





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).

Fit using constants: C = 1.95e-4, *β*=0.93, *γ*=0.60, α_o= 0.01, A=7.5e17, E_a=63 kcal/mol

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

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Reduced Model for Ti/$KClO_4$ Ignition

To model ignition of TKP powder, we combined our measured KClO4 oxygen generation kinetics with one-step oxidation of Ti:

$KClO_4(s) \rightarrow KCl(s) + O_2(g)$ (R1)

$Ti(s) + O_2(g) \rightarrow TiO_2(s)$ (R2)

5 Species: $KClO_4(s)$, $KCl(s)$, $O_2(g)$, $Ti(s)$, $TiO_2(s)$

Define progress variables associated with reactions:

$$\alpha_1 = \left[KClO_4(s)\right]_0 - \left[KClO_4(s)\right] / \left[KClO_4(s)\right]_0 \qquad \alpha_2 = \left[Ti(s)\right]_0 - \left[Ti(s)\right] / \left[Ti(s)\right]_0$$

Define rate expressions for progress variables; the first is our $KClO_4$ rate expression. The second is based on diffusion-limited process of Ti with an O_2 concentration dependence (shrinking core/ thickening shell model w/ spherical particles)

$$\frac{d\alpha_1}{dt} = f_1(\alpha_1) k_1(t) = C_1 \alpha_1^x (1-\alpha_1)^{y_1} A_1 \exp\left(-E_{a,1} / RT\right)$$

$$\frac{d\alpha_2}{dt} = \left[O_2(t)\right] f_2(\alpha_2) k_2(t) = \left[O_2(t)\right] C_2 (1/\alpha_2)^{y_2} A_2 \exp\left(-E_{a,2} / RT\right)$$

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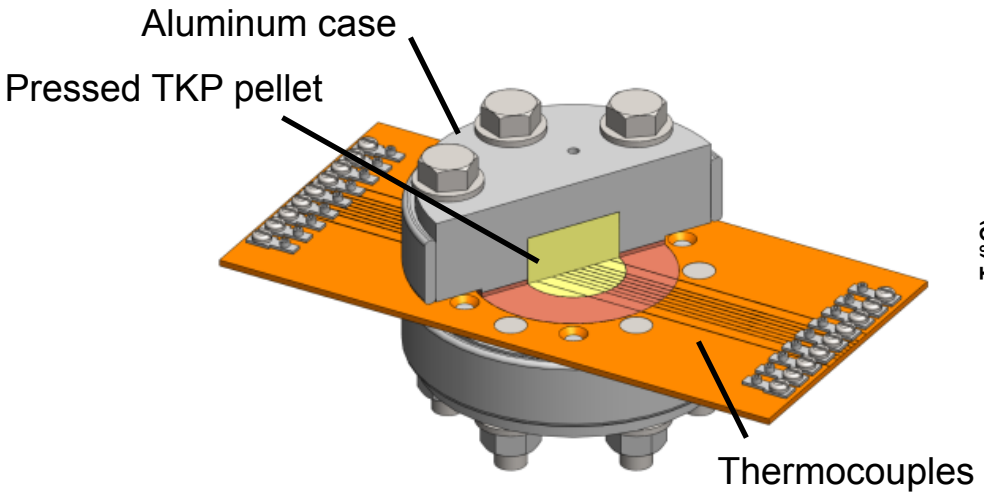
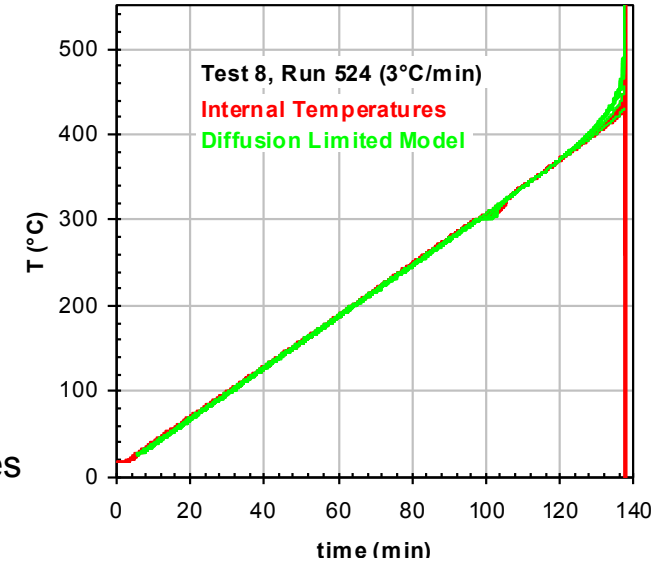
Modeling Small-Scale Ignition Data

SITI (Sandia Instrumented Thermal Ignition) test provides data on thermal response of EMs





Aluminum casing is heated from outside
Thermal gradient develops in EM
EM reacts with varying degrees of violence
Time to ignition is measured (runaway observed followed by termination of TC conductivity)

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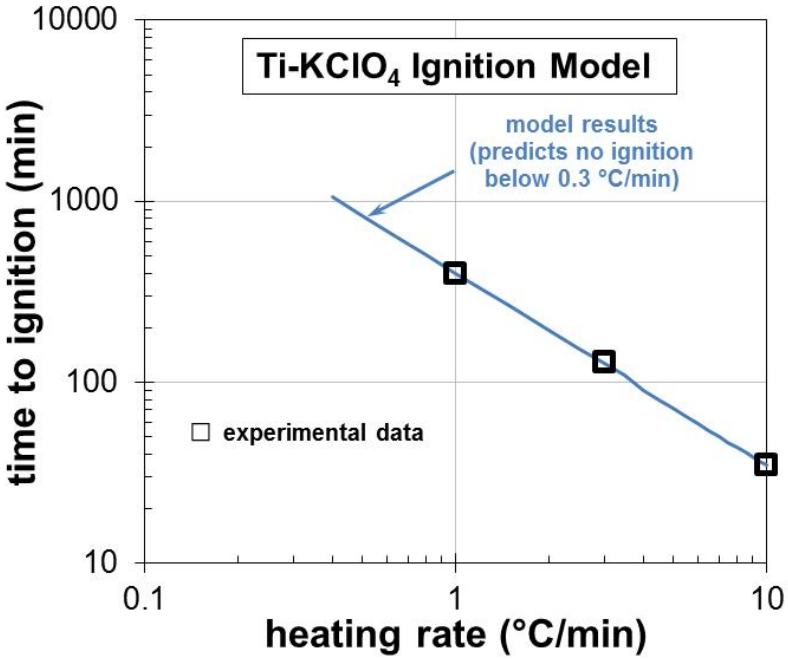
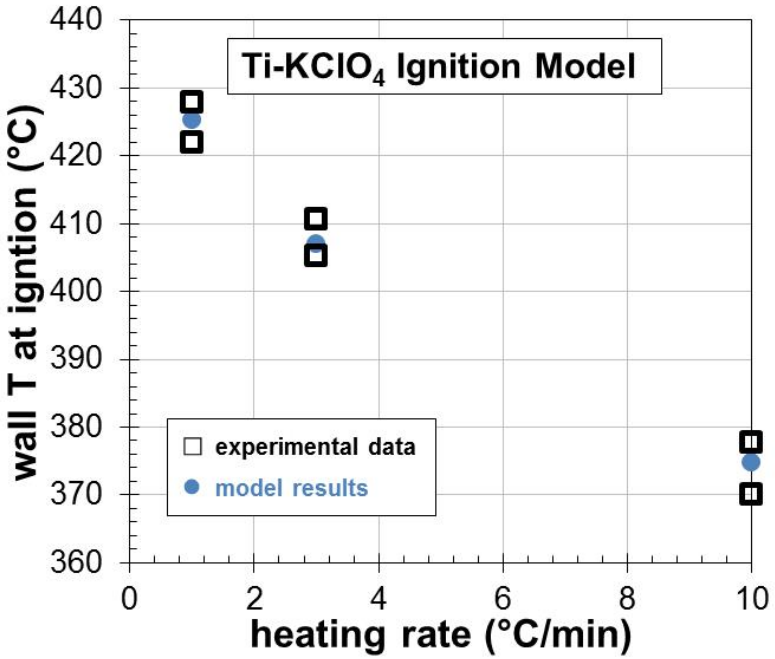
Modeling HOT-SITI Data

Model correctly predicts time-to-ignition in small scale tests

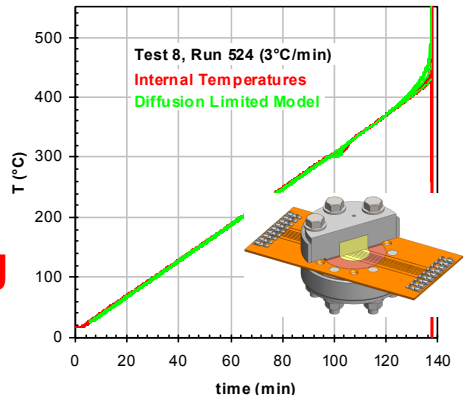
Time to Ignition



Wall Temperature at Ignition



Finite-element model of SITI
Aluminum casing is heated (thermal source), heats EM
Heat transport from case plus reactions in each finite element
Each element has extent of reactions, and this is followed.



Our chemistry is now in a code predicting small scale testing

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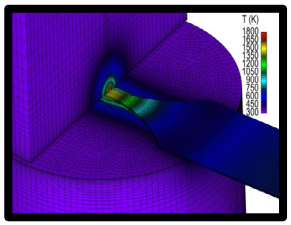
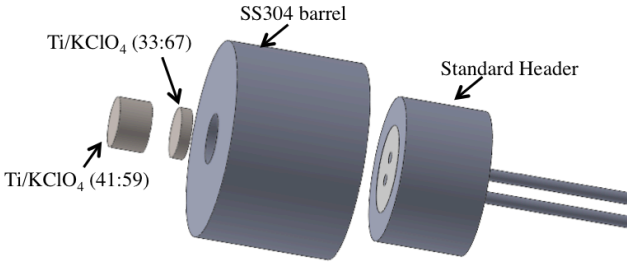
Component R&D at Sandia

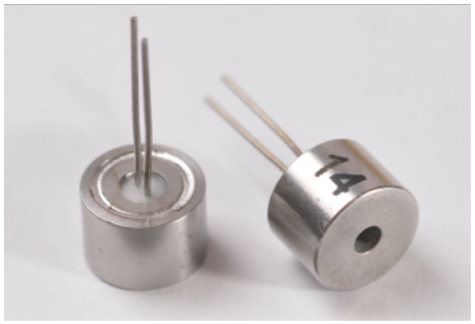
New R&D Model

This is the R&D model we are moving towards

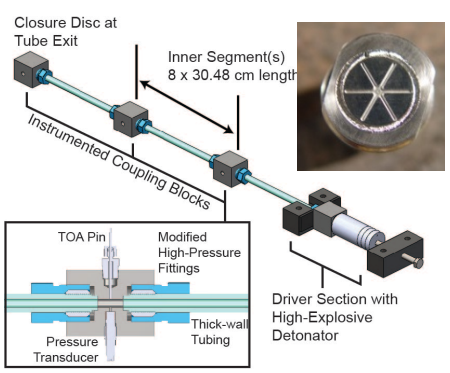
INPUT: Model Ignition Temperature





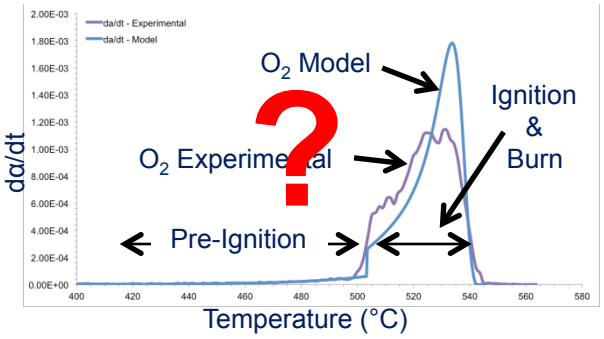


OUTPUT: Model Closure Disk Mechanics

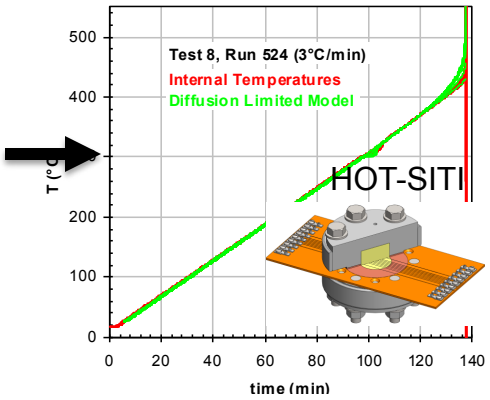


Inside the Black Box

Reactive Chemistry



Pre-Ignition: Empirical Diffusion-Limited Model



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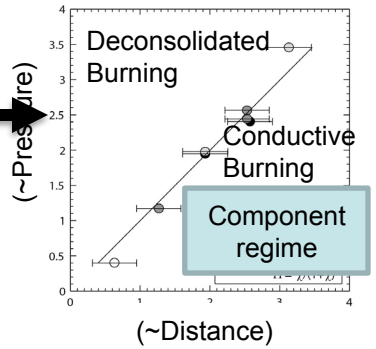

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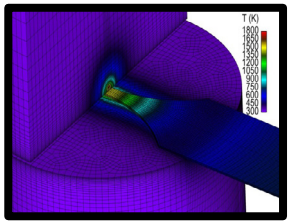

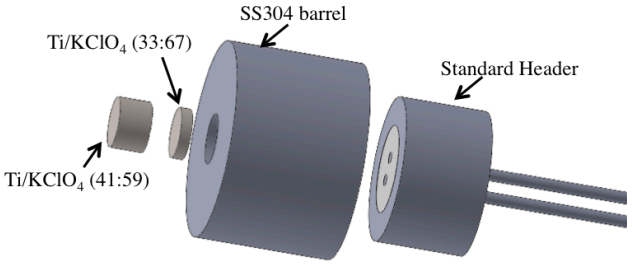

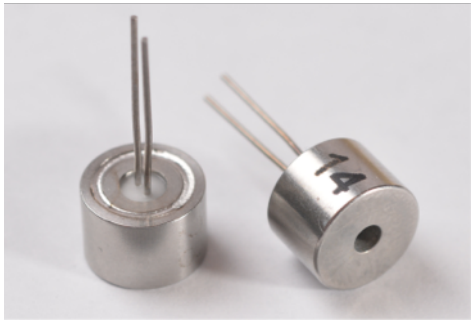

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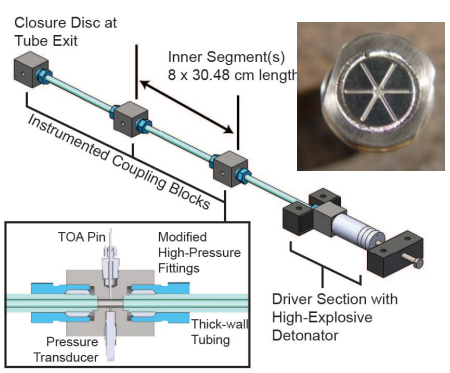

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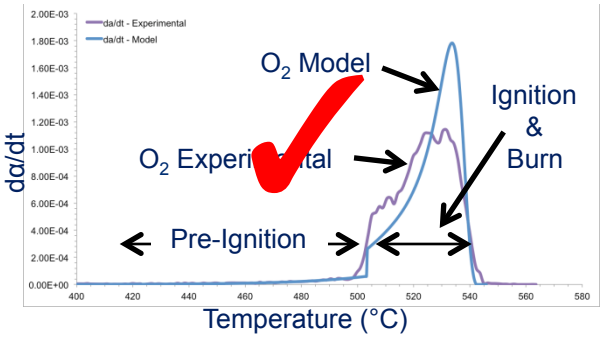

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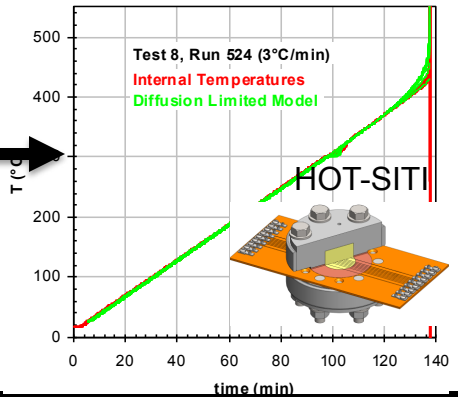

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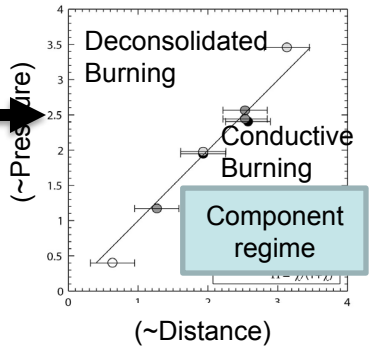

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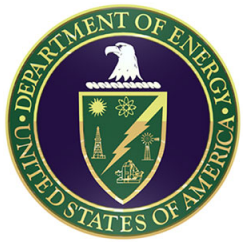
Conclusions and Future Directions

- We have parameterized the reactive processes controlling thermal ignition of pyrotechnic powders used in Sandia explosive components
- Developed reduced reaction mechanism that is scientifically correct yet small enough for input into engineering model
- Model correctly predicts time-to-ignition in small scale tests
- Same methodology will be applied to HE to predict cookoff and reactive burn in small scale tests of explosives (J. Steill)
- We are now developing rapid heating capabilities for the STMBMS to be used in rapid (<< second) ignition experiments similar to conditions in components

Questions?



Thank you to:

US DoD/DOE Joint Munitions Program
Leanna Minier (SNL/NM)