Experimental observation of reaction propagation in 3D-printed biocidal energetic materials to improve performance and reliability

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Energetic materials: a *(very)* brief overview *(Intro)*

Propellants / pyrotechnics / explosives capitalize on the conversion of stored chemical energy to kinetic energy.

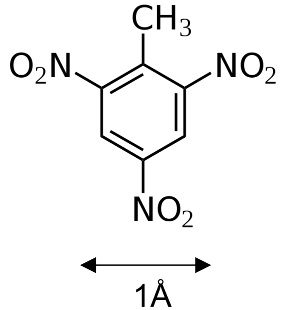
Temperature and **burn velocity** are critical parameters for propellant combustion.

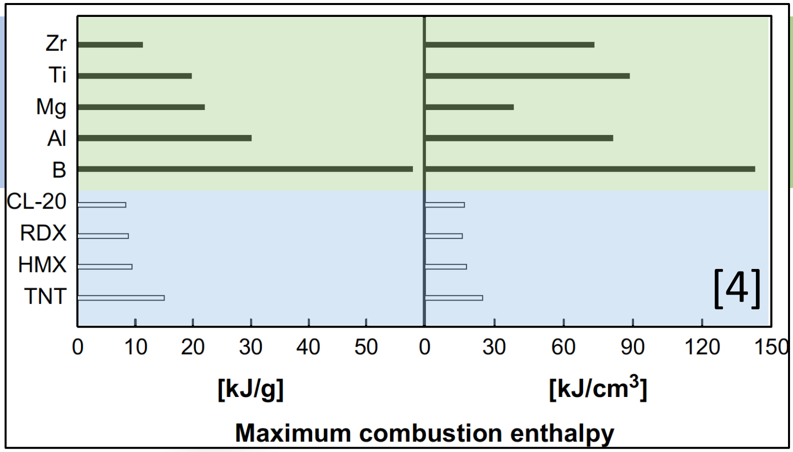
Temperature dependent on thermodynamic properties of starting/final products, stoichiometry, degree of completion.

Burn velocity dependent on reaction rate ($\dot{\omega}$), thermal conductivity (α), and degree of mixing. $v = \sqrt{\alpha \cdot \dot{\omega}}$

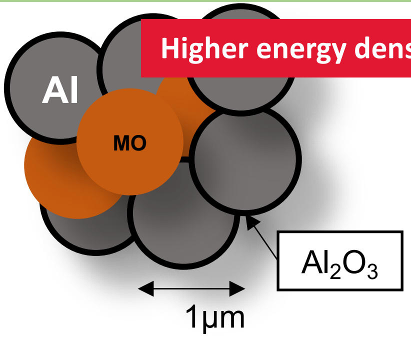
Shorter diffusion distance / faster energy release

Monomolecular CHNO:
Atomic scale mixing
Not stoichiometric





Heterogeneous composites:
Large diffusion distance
Stoichiometric

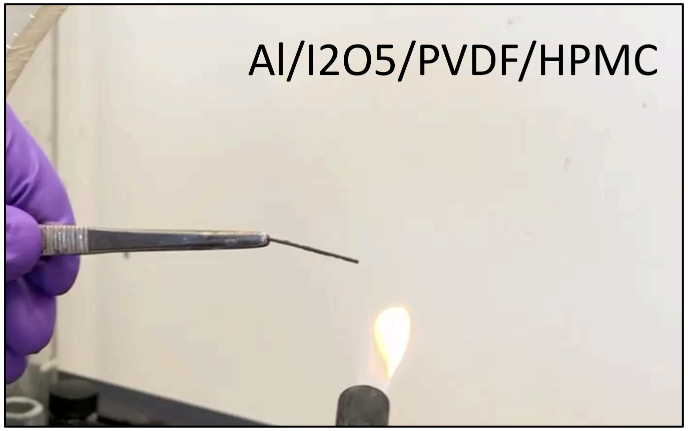


[1] D.D. Dlott, Mater. Sci. Technol. **22**, 463 (2006).
[2] S.H. Fischer and M.C. Grubelich, (1998).
[3] V.E. Zarko and A.A. Gromov, *Energetic Nanomaterials: Synthesis, Characterization, and Application* (Elsevier, 2016).
[4] E.L. Driezen, Prog. Energ. Combust. Sci. 35 (2009) 141.

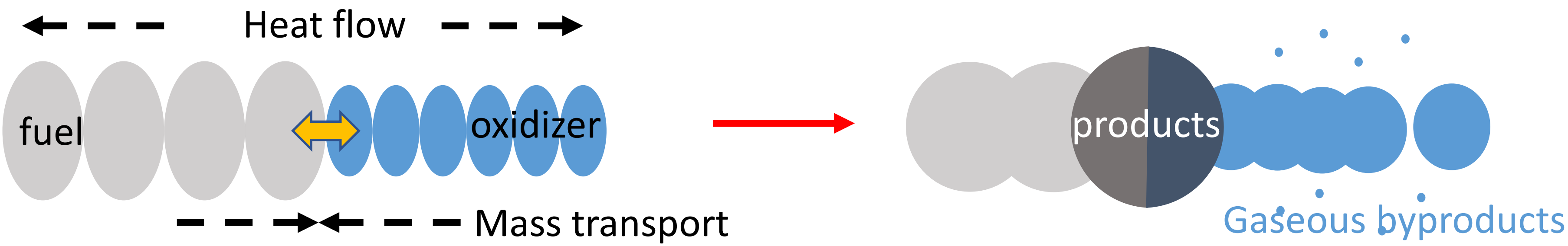
Biocides & nanoenergetic materials

Biocidal additives – especially those containing **Iodine and Silver** - into energetic materials offer a fast, effective method for **elimination of biological threats** (notably bacterial/fungal spores).

Iodine	I_2 crystals	High I_2 release, heat sink, not an oxidizer [5]
	I_2O_5	Powerful oxidizer, superior gas generation [6]
	$Ca(IO_3)_2$	Long term storability, less powerful oxidizer [7]
Silver	Ag_2O	Poor oxidizer [8]
	$AgFeO_2$	Powerful oxidizer, expensive to manufacture [8]



Reactive sintering results in loss of structure and incomplete reactions for nanothermites and is a well-documented deficiency in thermites because of incomplete conversion [9,10].



Typically happens in materials that have little gas generation

[5] H. Wang, J.B. DeLisio, G. Jian, W. Zhou, M.R. Zachariah, Combust. Flame **162** (2015) 2823.
[6] T. Wu X. Wang, J.B. DeLisio, H. Wang, M.R. Zachariah, Combust. Flame **191** (2018) 335.
[7] H. Wang, D.J. Kline, M.C. Rehwoldt, M.R. Zachariah, Prop. Explos. Pyrotech. **43**, 10 (2018) 977.
[8] T. Wu, M.R. Zachariah, RSC Adv. **9** (2019) 1831.
[9] K. Sullivan, N. Piekel, C. Wu, S. Chowdhury, S. Kelly, T. Hufnagel, K. Fezzaa, M.R. Zachariah, Combust. Flam. **159** (2012) 2.
[10] H. Wang*, D.J. Kline*, & M.R. Zachariah, Nat. Commun.**10** (2019) 3032.

Use I_2O_5 for biocidal delivery and reduction in reactive sintering ✓✓

Magnified Imaging of 3D Printed Films

How do we **resolve the combustion behavior** at µ-scale in time & space?

High speed camera
6,000-750,000 fps

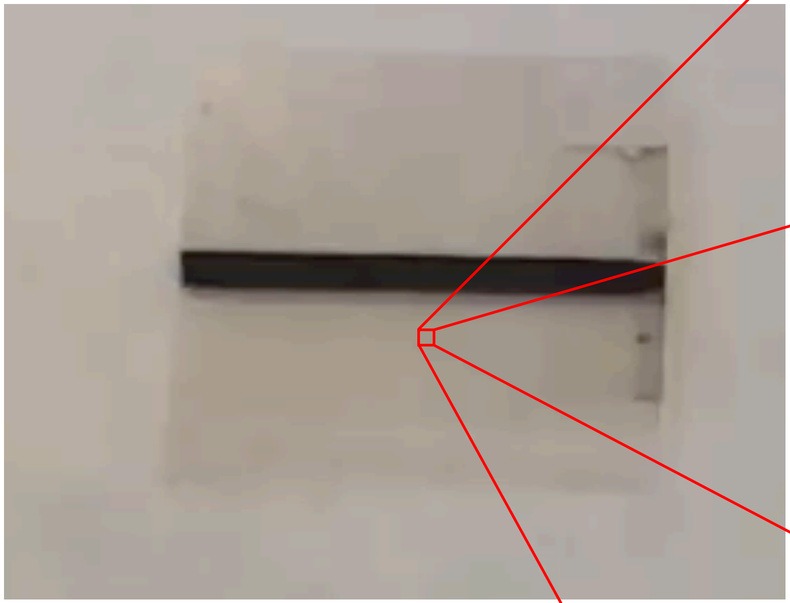
Long working-distance microscope

Glass
Coverslip

Original resolution ~20µm/pixel → **Resolution with Microscope: 1.7µm/pixel**

Magnified combustion of Al / I_2O_5 composite

Al / I_2O_5 / 6% HPMC / 4% PVDF



Hot particles ejected from the reaction **promote propagation via advection**.

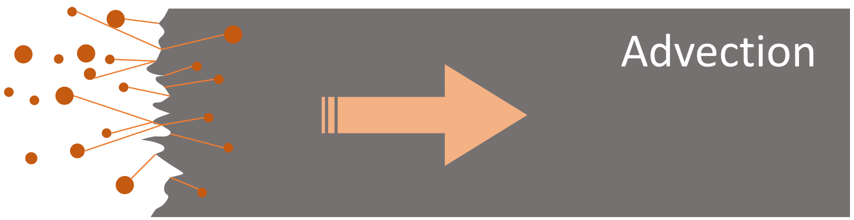
Final particle sizes are substantially smaller with I_2O_5 because **gas generation prevents reactive sintering.**

BUT SAMPLES FAILED TO CONSISTENTLY PROPAGATE !!

Underwhelming results for a superior oxidizer?

Although Al/I_2O_5 thermite powders burn in constant volume combustion cells, when incorporated into a high-loading propellant mixture, **samples failed to propagate**.

Previous calculations on energy transport in a theoretical Al/CuO burn tube showed that **convection, metal vapor condensation, and advection are critical to propagation**. [11]



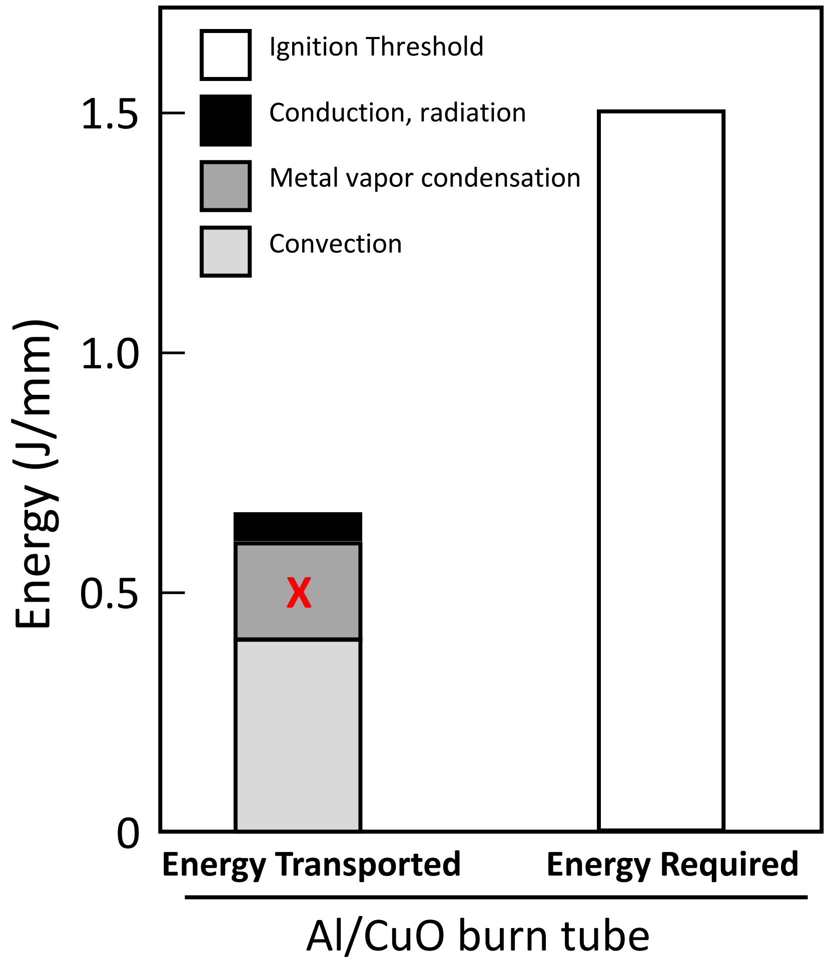
Hot particles ejected from the reaction **promote propagation via advection**. ✓✓

Gas generation **increases advection** and **prevents reactive sintering**. ✓✓

Example thermite reaction:

$Al_{(s)} + CuO_{(s)} \rightarrow Al_2O_{3(s)} + Cu_{(s)}$

$Al_{(s)} + I_2O_{5(s)} \rightarrow Al_2O_{3(s)} + I_{2(g)}$



NO METAL VAPOR CONDENSATION… ENERGY DEFICIT

[11] G. Egan & M.R. Zachariah, Combust. Flam. **162** (2015) 2959

Tipping the scale too far?

Problem

Reaction conversion increases by preventing reactive sintering.

Heat transfer increases by increasing advective heat flux.

Solution

Use a gas generating oxidizer

I_2O_5 as an oxidizer

Problem

Using a non-condensing metal oxidizer reduces potential heat transfer.

Solved one problem but created another.

Possible methods to promote propagation?

- Include a condensing metal oxidizer (Fe2O3, CuO) as a complementary mixture?
- Increase amount of particles being ejected (e.g. increase Al content)?

Evaluating addition of CuO to Al/I2O5

0% 25% 50% 75% 100%

% I_2O_5

100% CuO
Consistent propagation
~3 cm/s

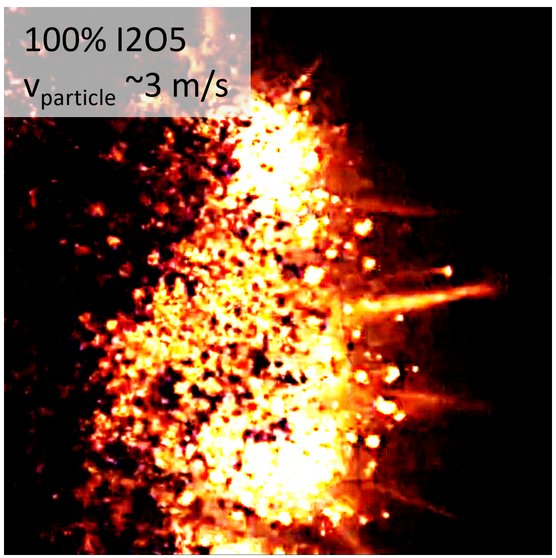
50% I2O5 / 50% CuO
Consistent propagation
~3 cm/s

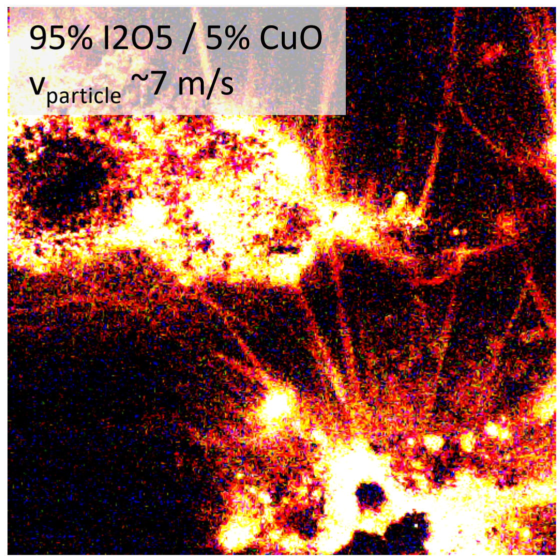
75% I2O5 / 25% CuO
Consistent propagation
~3 cm/s

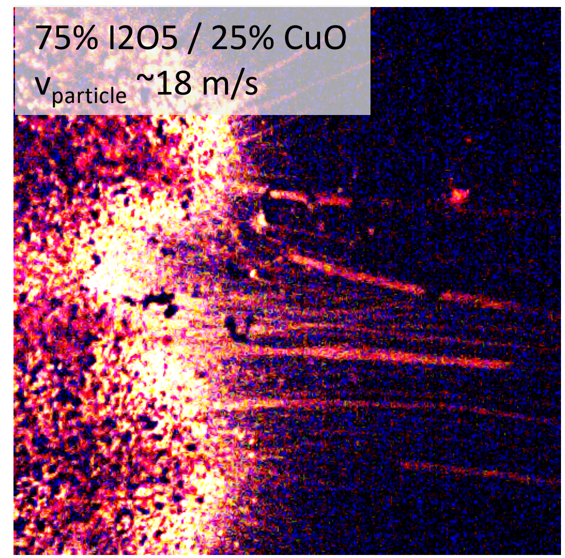
100% I2O5
Unable to sustain burn

95% I2O5 / 5% CuO
Inconsistent propagation
>6 cm/s

Small addition of homogeneously-dispersed CuO to sample enhances reliability in propagation







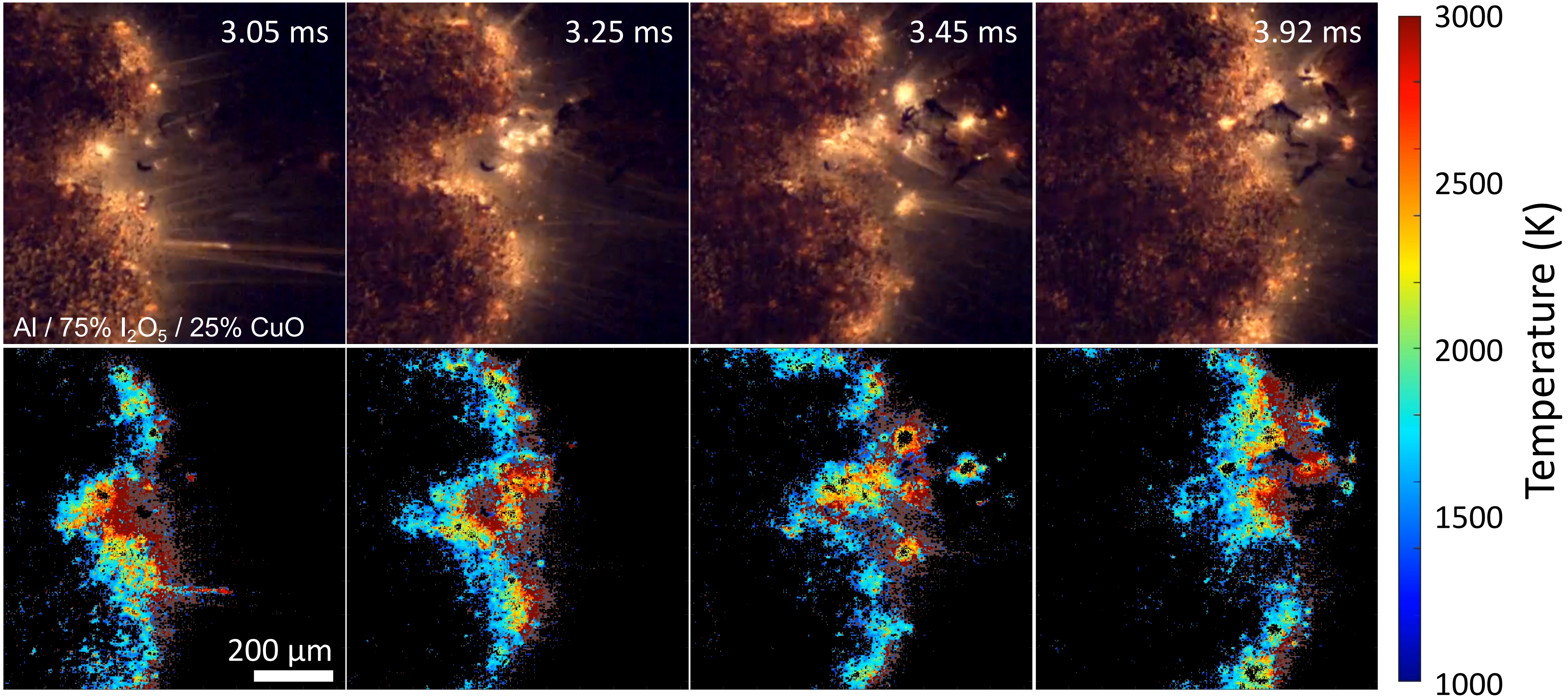
Pyrometry of propagating front to estimate heat transfer

Coupled high speed microscopy and pyrometry can help probe the role of Cu addition on heat transfer via advection and average flame speed in the film.

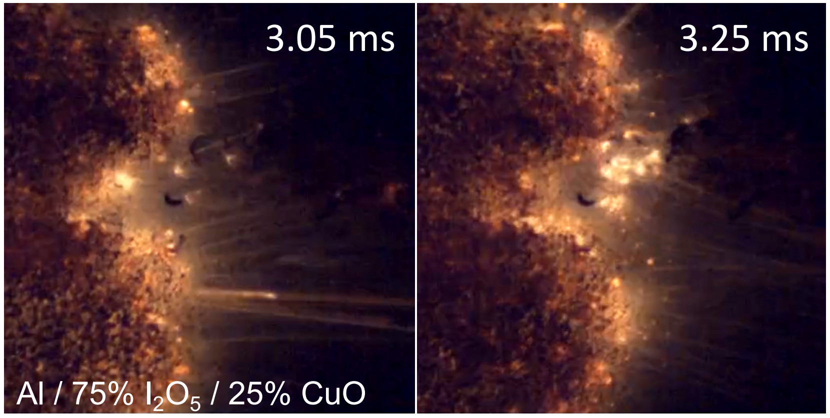
Combustion temperature of the composites remained relatively unchanged with the addition of CuO and equilibrium calculations suggest only a small change in predicted T.

Adiabatic Flame Temperature (Isobaric)

Al/I2O5	3856 K
Al/95% I2O5/5% CuO	3834 K
Al/75% I2O5/25% CuO	3716 K
Al/CuO	2845 K



Observed propagation phenomena



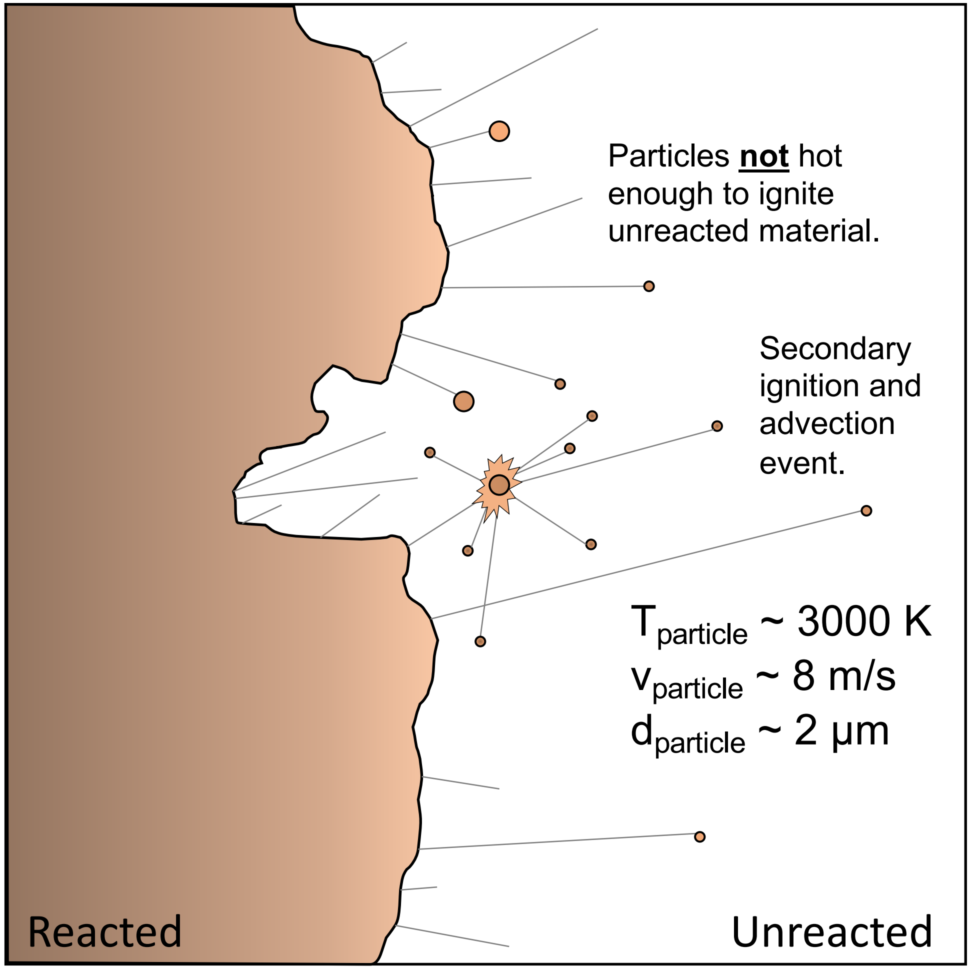
High-speed microscopy images clearly show advected particles that can **theoretically lead to secondary ignition events, however most advected particles do not** show such behavior.

How to estimate energy carried by a single advected paticle?

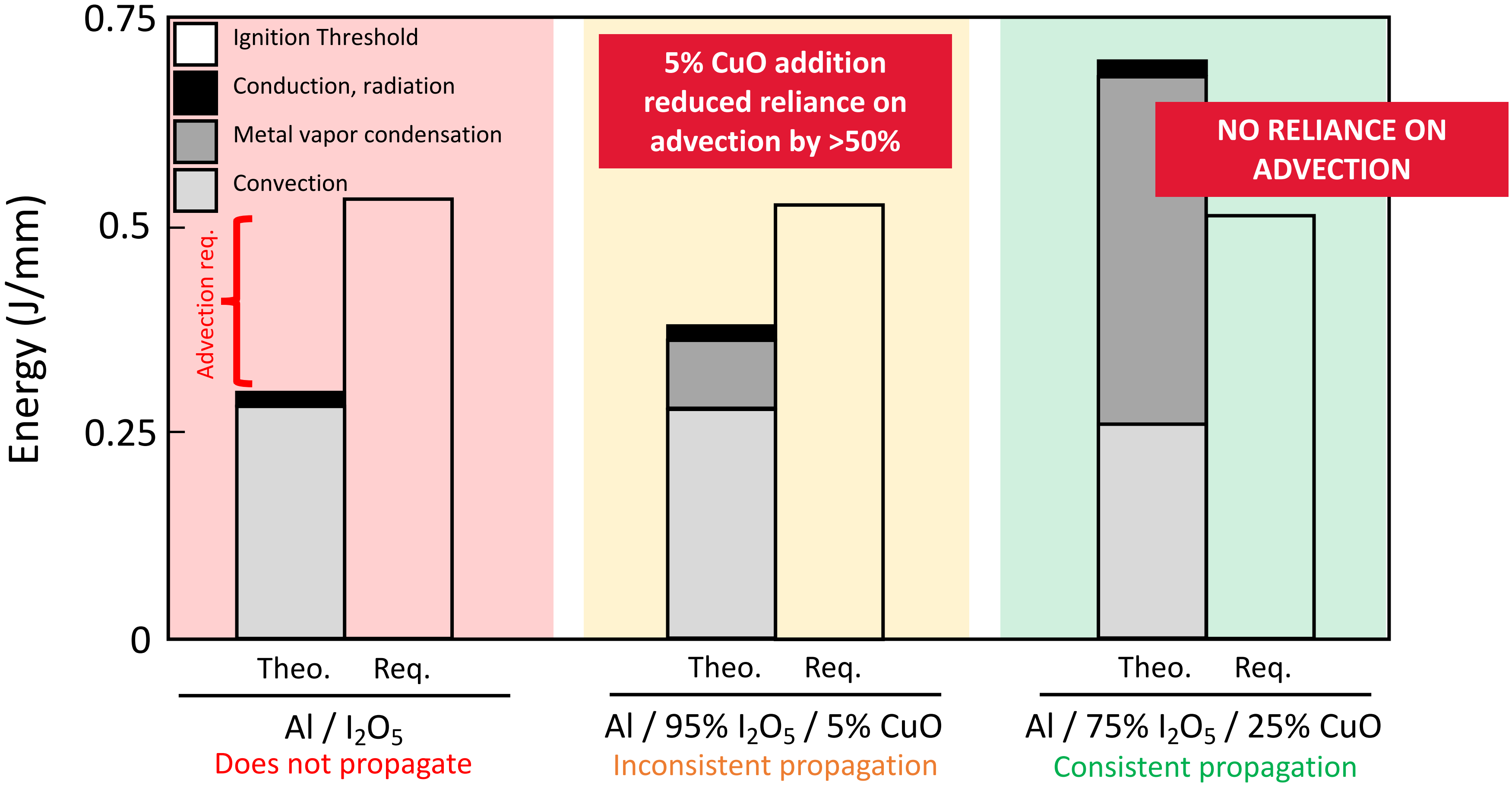
$$E_p = \rho_p V_p C_p (\mathrm{T_{ad}} - \mathrm{T_{ign}})$$

Single particle carries ~0.1 µJ

Not enough energy to consistently ignite area around final particle destination, but could theoretically enhance propagation.



Revisiting heat transfer requirements for propagation



Reliability of Al/I2O5 propellant successfully enhanced by introducing a condensable metal vapor.

Assumptions:

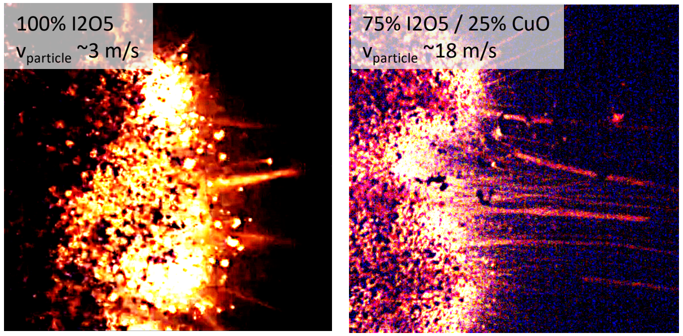
2mm-diameter tube packed at 6% of theoretical max density, ~0.83mg/mm.
Ignition temperature ~860K.
Achieves adiabatic flame temperature for pure thermite and has propagation rate of pure thermite (~m/s-km/s).
Convection/metal vapor condensation assumed to follow Darcy's law for flow in a porous media (~40% of total flow, 67% porous).
Final products have properties of Al2O3.

Conclusions

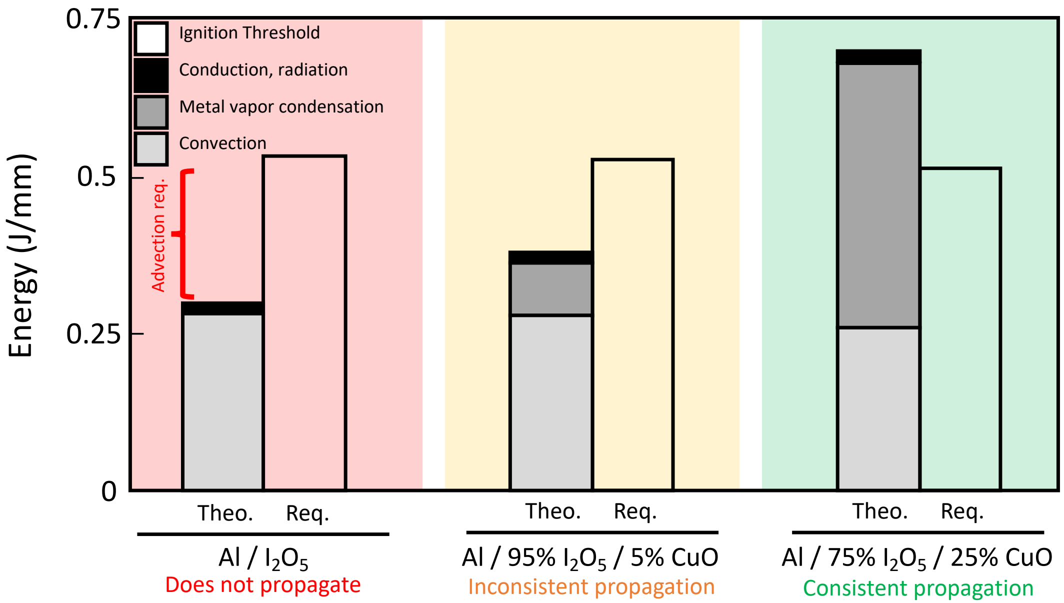
I_2O_5 can be used as a reactive oxidizer with **desirable biocidal byproducts** that can eliminate biological threats (contamination, bioweapons, etc.) that **prevents reactive sintering, enhances advective heat transfer, and increases gas production**.

However, incorporation of I_2O_5 into a high metal loading printed propellant resulted in an **increased reliance on advection for propagation** since there was no condensable metal vapors and **samples did not propagate**.

Incorporation of small amounts of **condensable metal vapors (CuO/Cu) into the reactive mixtures increased reliability of the sample to propagate** and reduced advective heat transfer requirements.



Observed advective heat transfer in reaction front.



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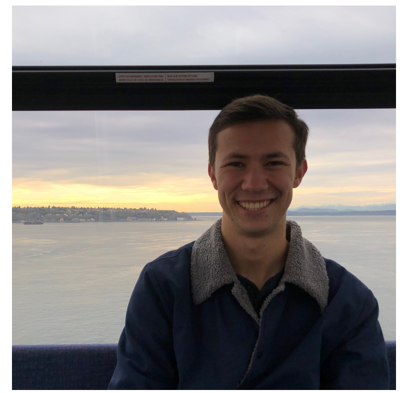
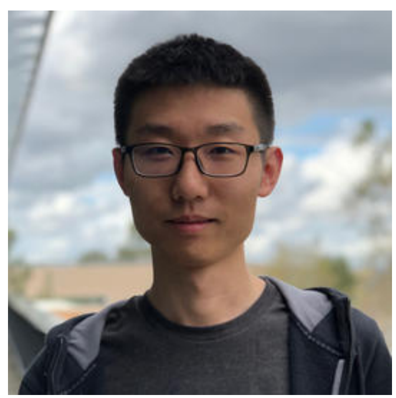
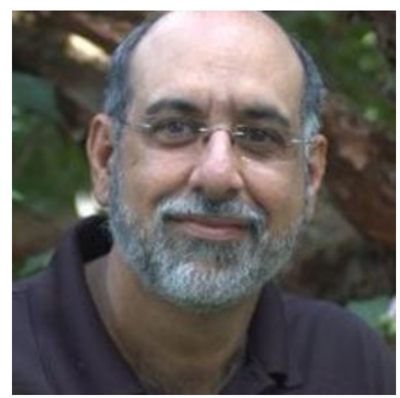


Spencer G. Hamilton

Prithwish Biswas



Feiyu Xu



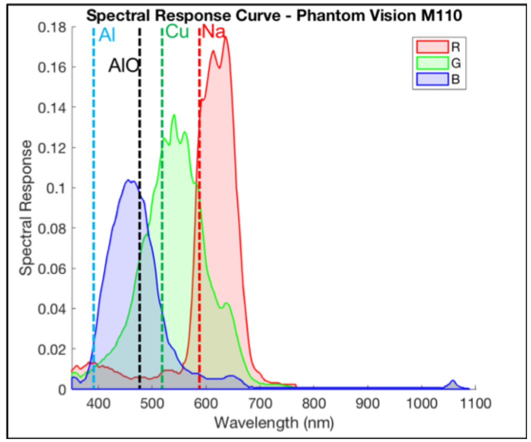
Michael R. Zachariah

Color Camera Pyrometry

$$L(\lambda,T)=\frac{\varepsilon * 2\pi hc^2}{\lambda^5\left\{\exp\left(\frac{hc}{\lambda KT}\right)-1\right\}}$$

$$\frac{I_i}{I_j}=\frac{\psi_i\int L(\lambda,T)\chi_i(\lambda)d\lambda}{\psi_j\int L(\lambda,T)\chi_j(\lambda)d\lambda}$$

$$\left(\frac{I_i}{I_j}\right)_{exp}=C_{ij}\left(\frac{I_i}{I_j}\right)_{theor}$$

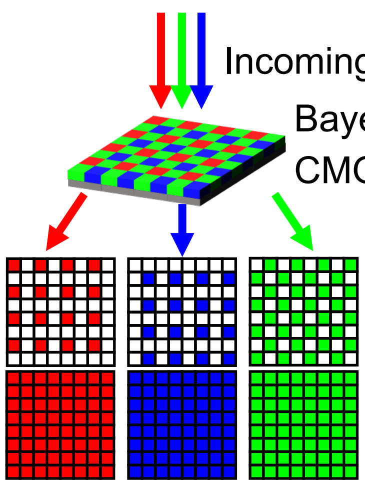


Planck's Law for radiating blackbodies

Theoretical channel intensity ratio as a function of T

Calibration factor for each channel ratio, used for T measurements.

Raw image demosaicing to recover RGB at every pixel.



Incoming light

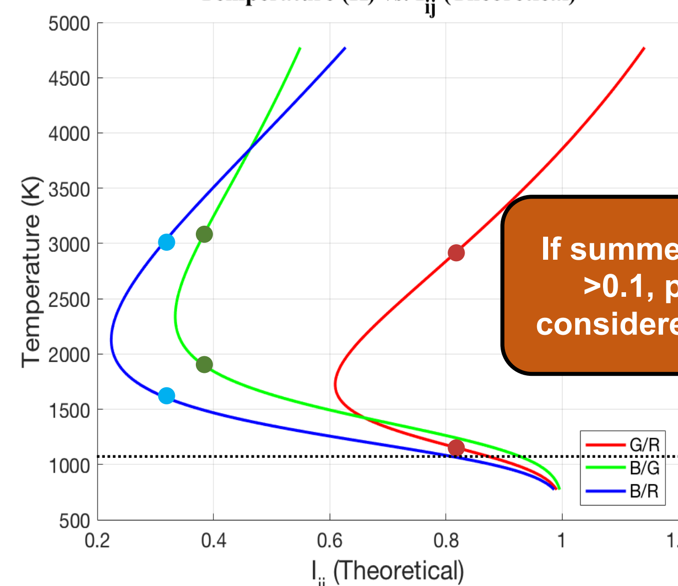
Bayer color filter array (top)

CMOS camera sensor (bottom)

Raw image – single channel per pixel

Demosaiced image from interpolation

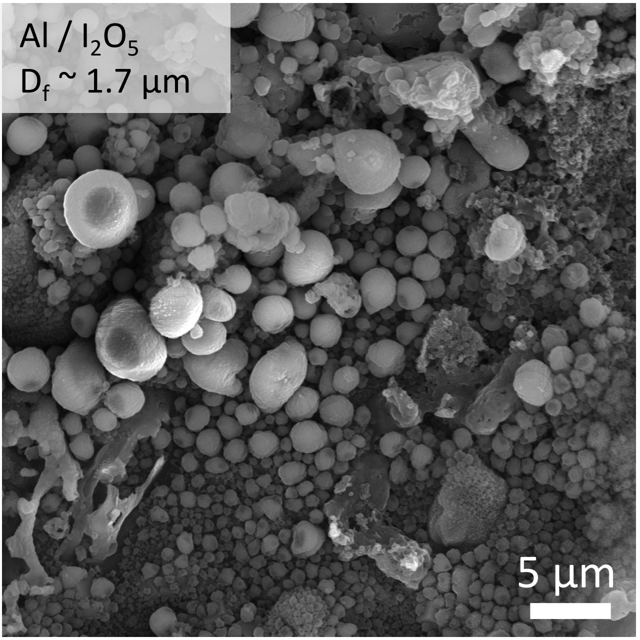
3 simultaneous channel ratio error minimization.

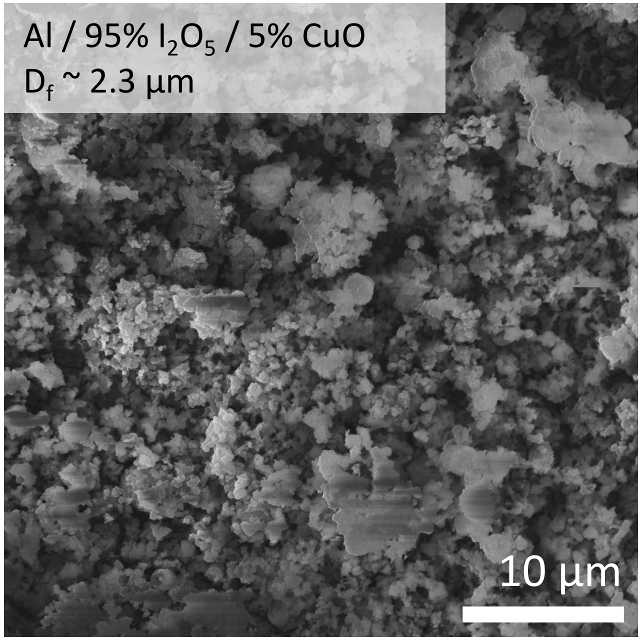


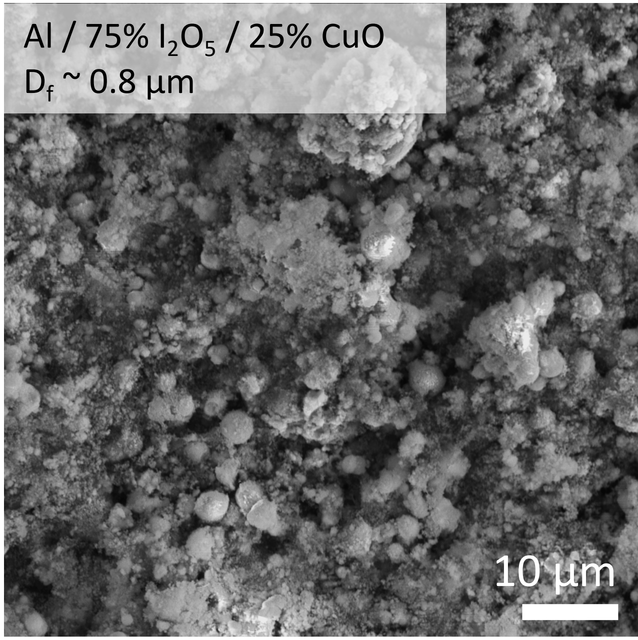
If summed error is >0.1, point is considered invalid.

[8] R.J. Jacob*, **D.J. Kline***, M.R. Zachariah, J. Appl. Phys. 123 (2018) 115902

The role of gas generation on reactive sintering







Increasing CuO content, final particle size

As %CuO increases, reactive sintering and final particle size increases.