Combustion Analysis of Nanoenergetic Materials

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Research Areas

- Flame spread across thin fuel films of nano metallic particles.
  - Combustion of nAl with O_2/Ar mixtures – unified theory developed.
  - Combustion of nAl with CO_2, CO, N_2O, and N_2.
- Combustion of nano metallic particles and flame propagation through quasi-homogeneous mixtures of nano metallic particles and liquid and gaseous oxidizers.
  - Combustion of nAl/liquid H_2O
  - Combustion of nAl/H_2O/H_2O_2
  - Combustion of nAl/CH_3NO_2
  - Combustion of nB/CH_3NO_2
- Combustion of nano metallic particles and flame propagation through quasi-homogeneous mixtures of nano metallic particles and solid oxidizers.
  - Combustion of nano Al/MoO_3 thermites – stoichiometry and channel size.
  - Combustion of nano Al/CuO thermites –fuel particle size, density, and dilution effects.
  - Combustion of nB in Al/CuO thermites.
- Self-assembly of ordered microspheres of a nanoscale thermite.

Research Areas

- Liquid propellants with nanostructured additives and nano aluminum gelled propellants.
- Temperature, pressure, and oxidizer particle effects on nanothermites.
- Nano intermetallic powder systems.

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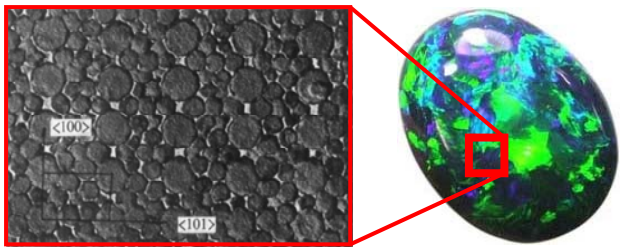
Self-Assembled Nanoscale Thermite Microspheres

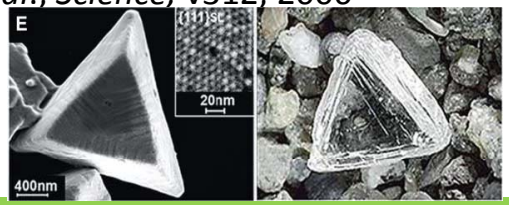
Opal gem: organized nanoparticle self assembly

Sanders, J. V., Murray, M. J., *Nature* v275, 1978.



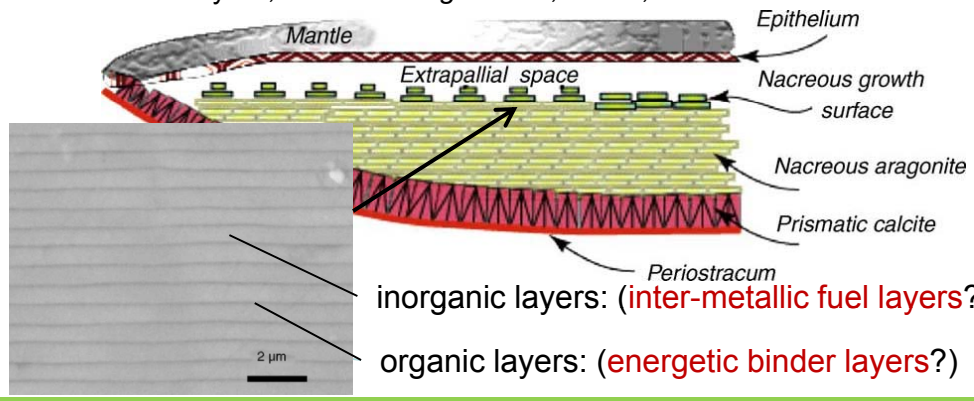
Laboratory assembled nAu & nAg composites

Kalsin *et al.*, *Science*, v312, 2006

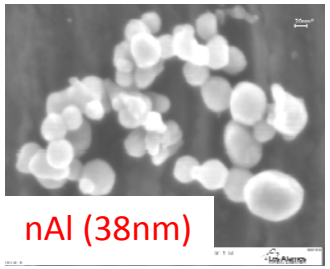


Structure of the Abalone Shell (A reactive material structure?)

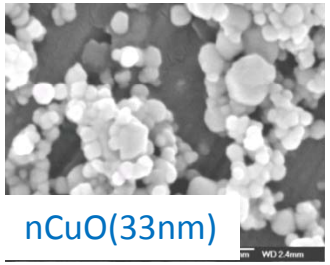
A. Lin and A. Meyers, *Mat. Sci. Eng. A* 390, 27-41, 2005.



- Create Self-Assembled Monolayer (SAM) on surface of particles
- Monolayers contain a functionalized group at tail end (either + or – charged)
- When mixed in a diluted and elevated temperature they form energetic macroscale structures with nanoscale constituents



nAl (38nm)

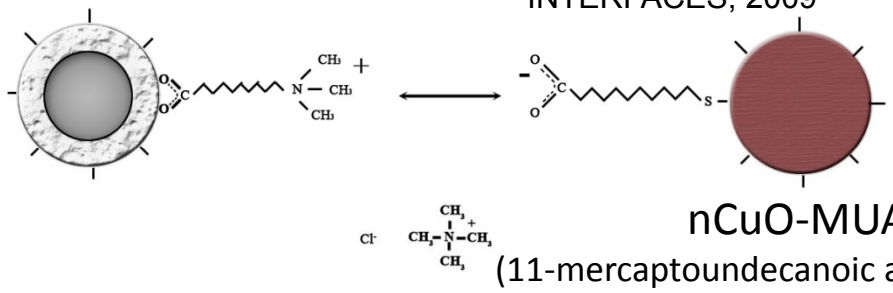


nCuO(33nm)

nAl-TMA

(trimethyl(11-mercaptoundecyl) ammonium chloride)

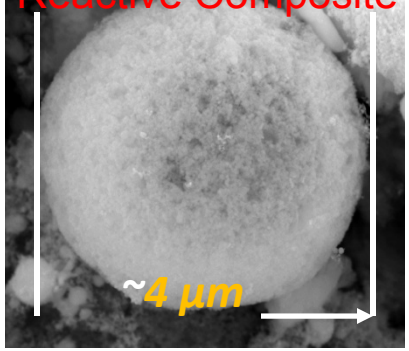
Malchi, J., Foley,T., Yetter, R.A., ACS APPLIED MATERIALS & INTERFACES, 2009



nCuO-MUA

(11-mercaptoundecanoic acid)

Reactive Composite



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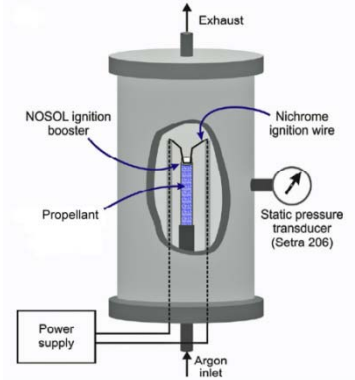
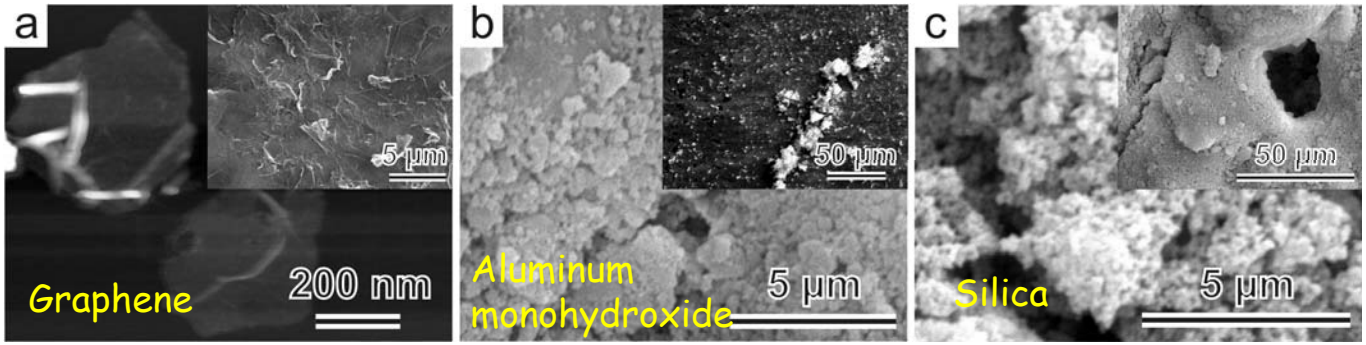
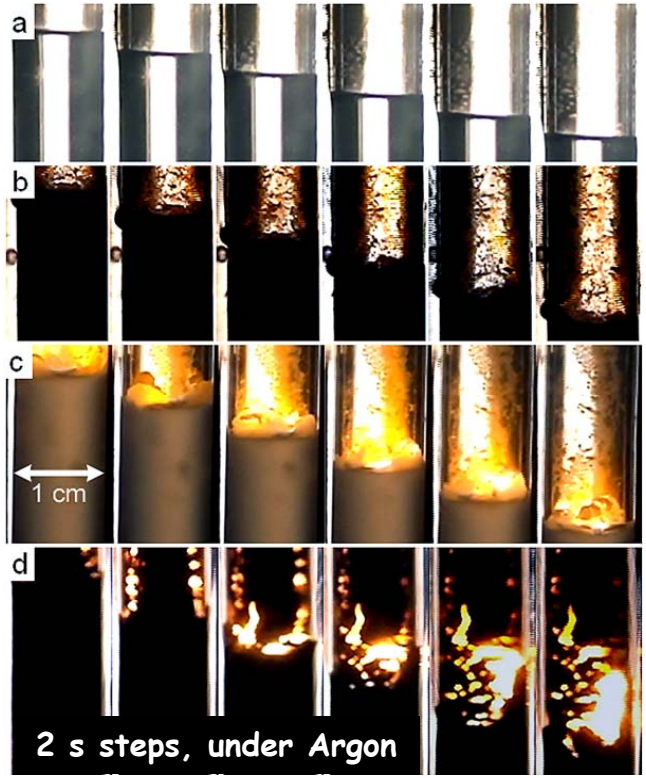
Nanostructured Additives for Enhanced Propellant Combustion





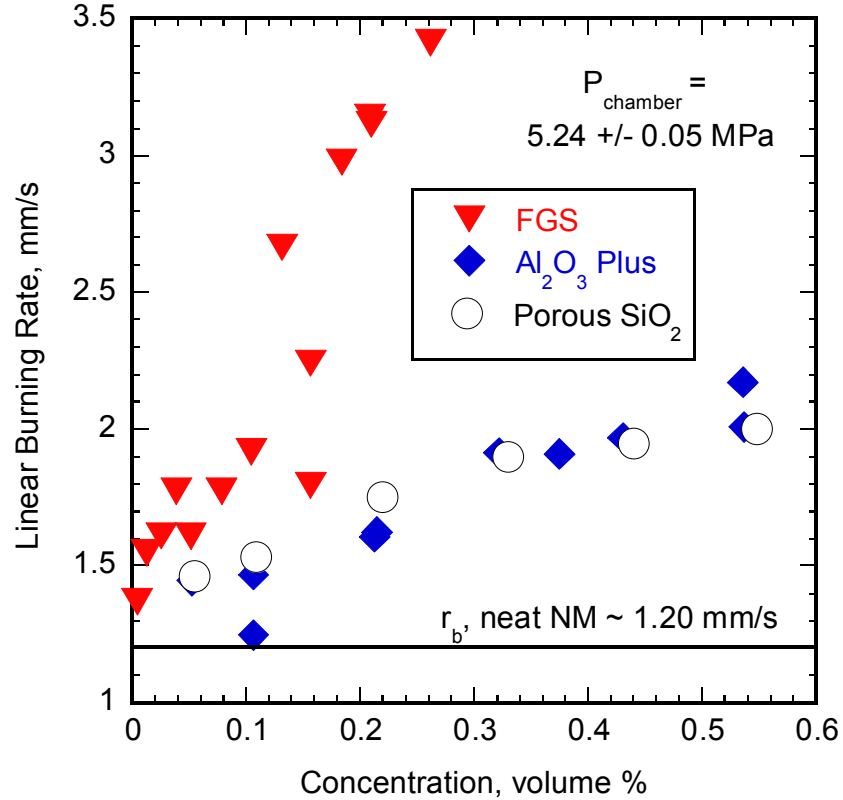


Neat NM; 5.23 MPa, r_b = 1.2 mm/s

NM + 0.5% (mass) AlOOH; 5.16 MPa, r_b = 1.6 mm/s

NM + 0.39% (mass) SiO_2 gel; 5.25 MPa, r_b = 1.9 mm/s

NM + 0.3% (mass) FGS_{22}; 5.16 MPa, r_b = 2.2 mm/s



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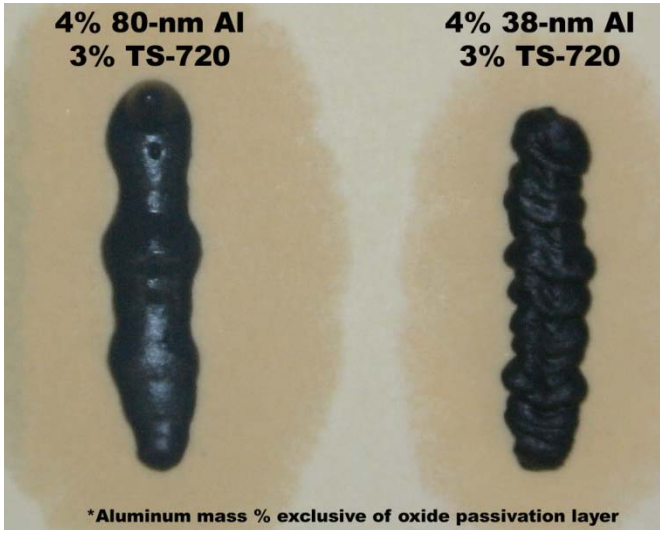
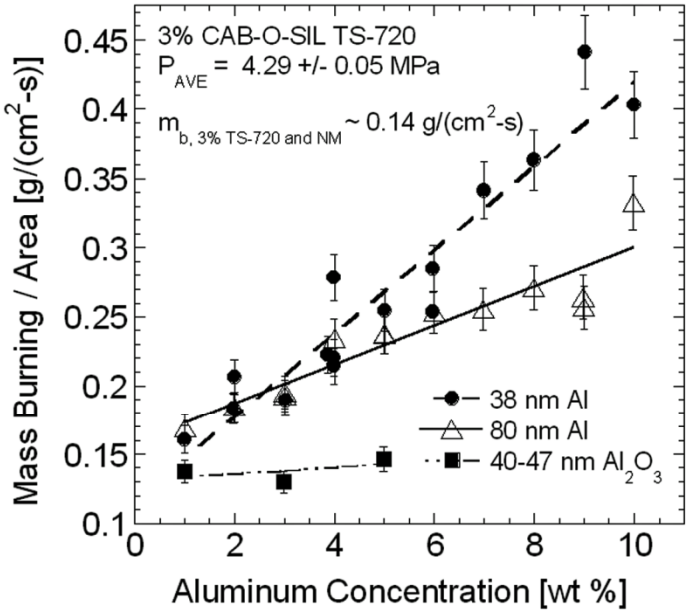
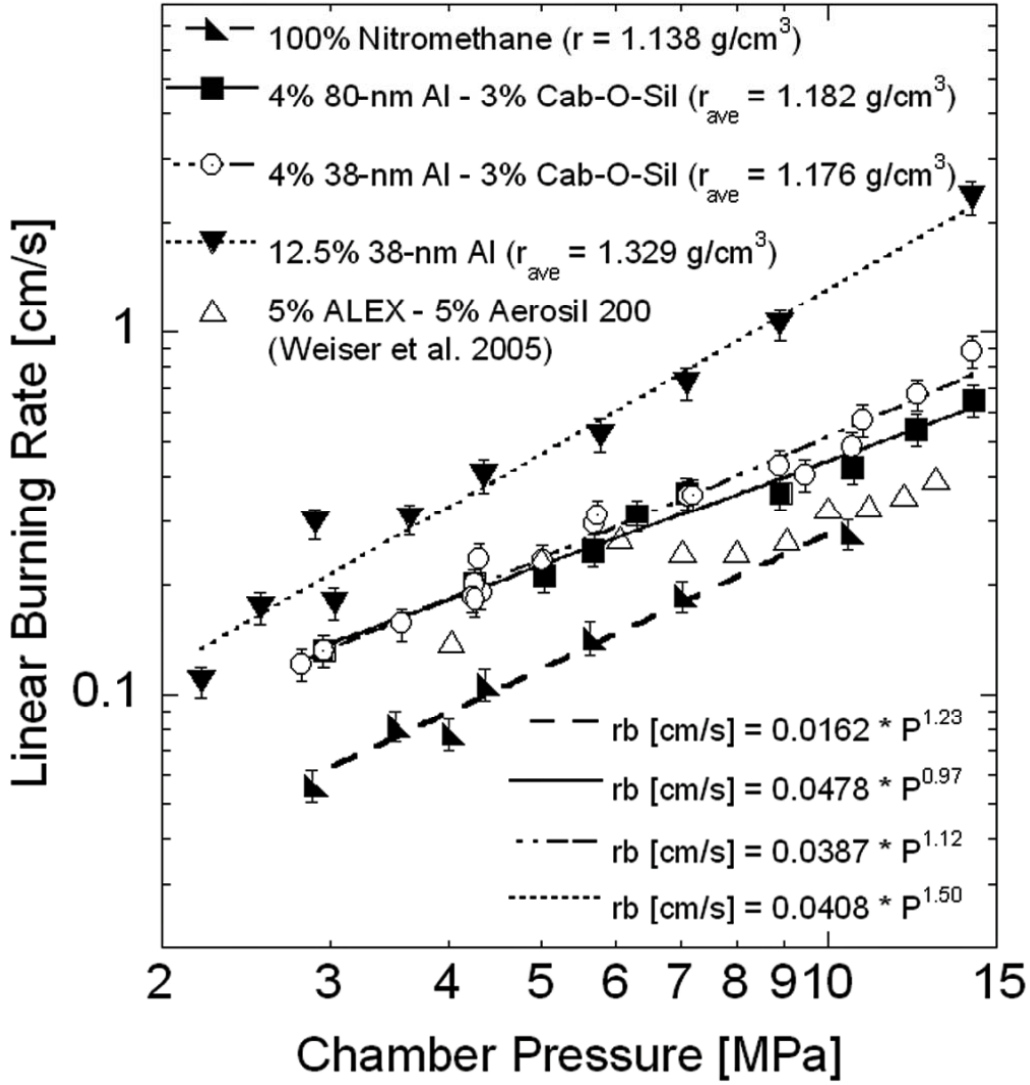
Combustion of Nano Aluminum Gelled Propellants







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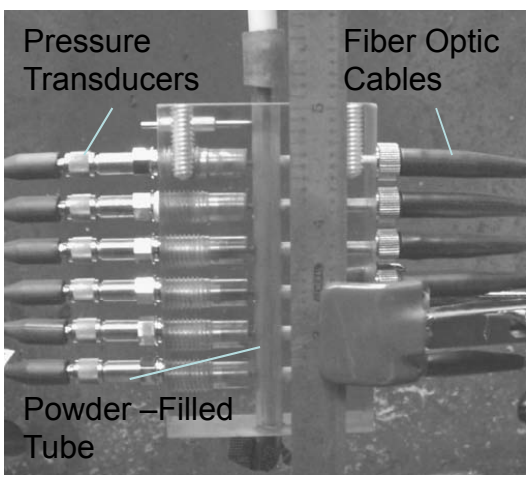
Propagation Mechanisms of Nanothermite Reactions

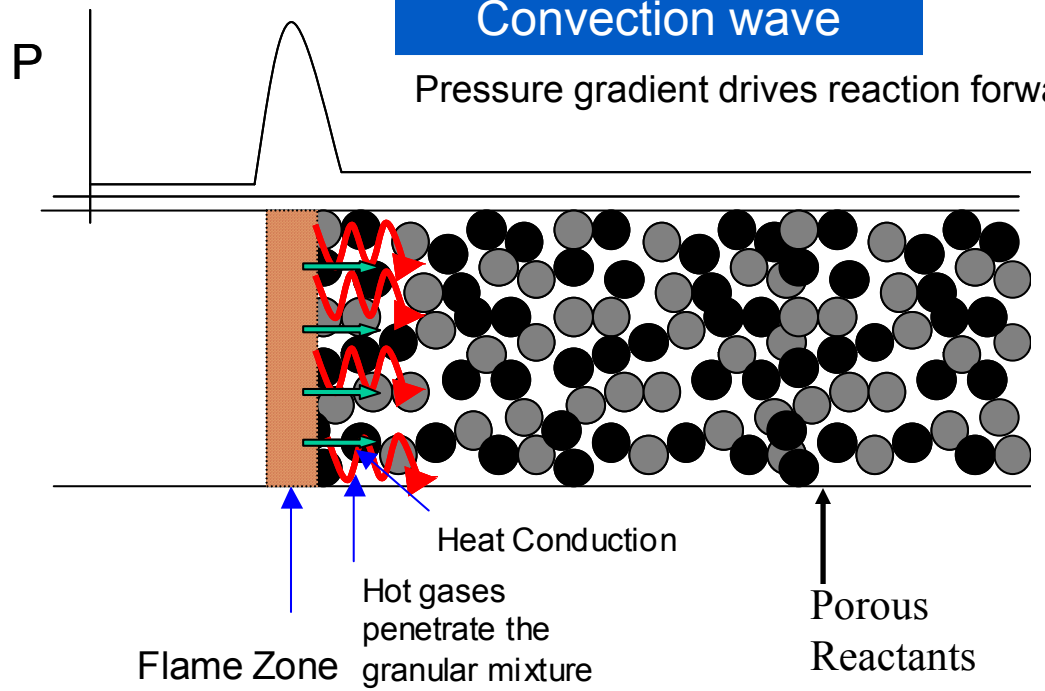
When ignited in a burn-tube, 'fast' nanothermites (Al/CuO, Al/MoO_3, Al/Bi_2O_3) react through a convective mechanism

Convective burning is driven by the creation of a large pressure gradient in the porous mixture, and not by a temperature gradient



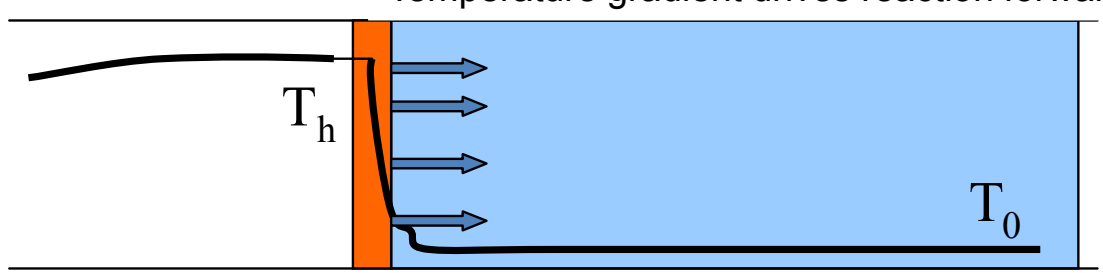
Convection wave

Pressure gradient drives reaction forward



Conduction wave

Temperature gradient drives reaction forward



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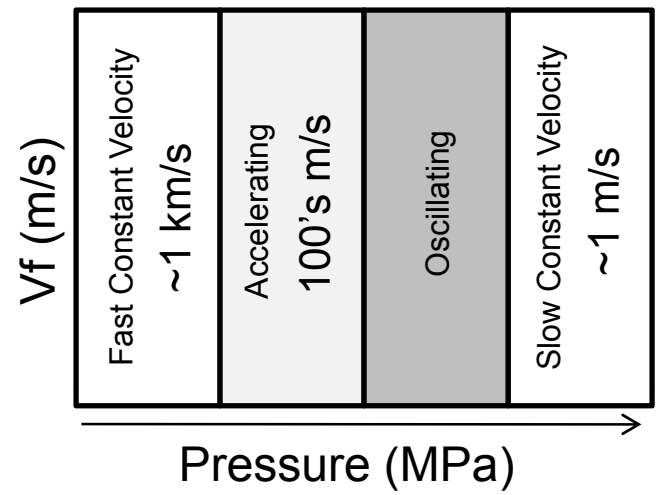
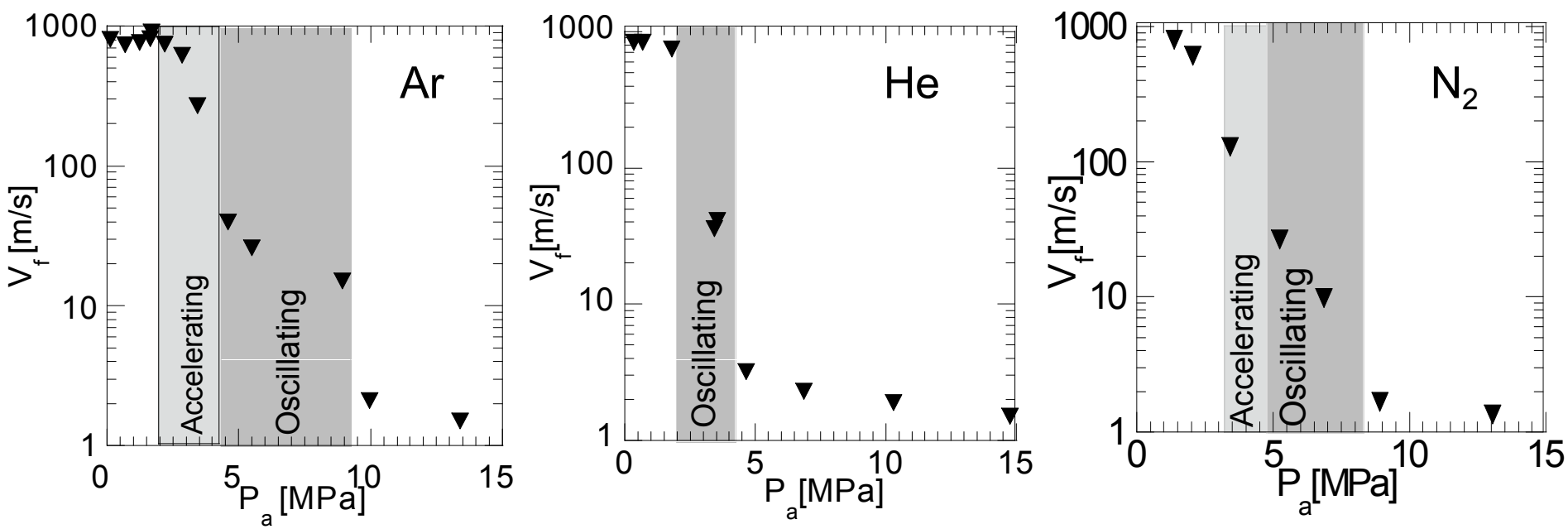
Effect of Pressure on the Propagation Rate in a Al/CuO Nanothermite

- Nano-aluminum from Novacentrix (avg. d_p=38nm)
- Nano CuO from Sigma-Aldrich (avg. d_p=33nm)
- Studies conducted in an optical strand burner (V=23 liters)
- Pressurized with 3 different gases (Ar, He, or N_2)

- As pressure is increased, several different modes of propagation are observed
- Pressure at which propagation mode changes depends on pressurizing gas; He has a high thermal conductivity



$$2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$$



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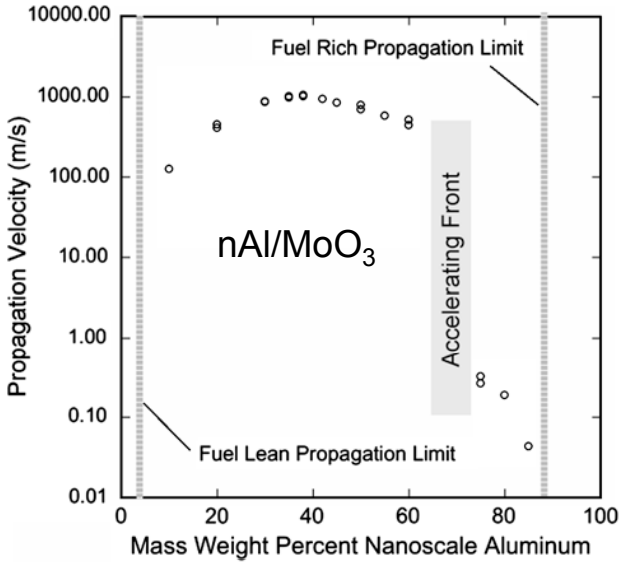
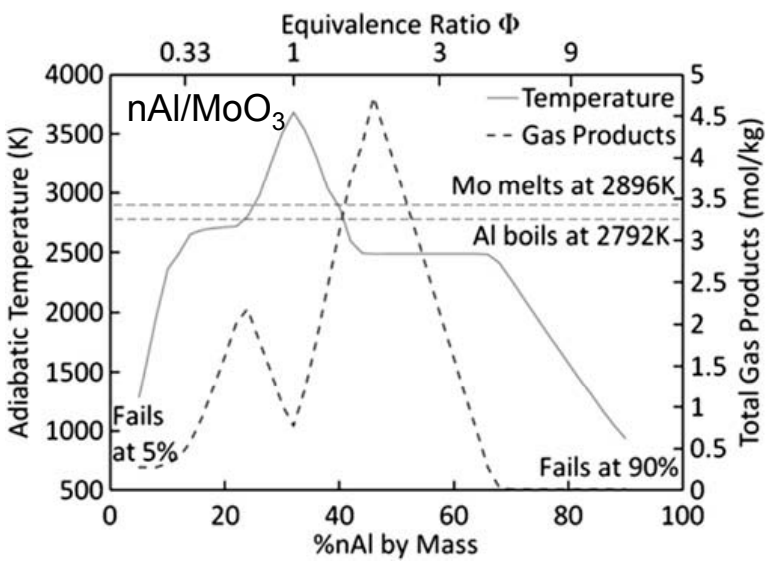
Temperature Measurements for understanding Gas Generation

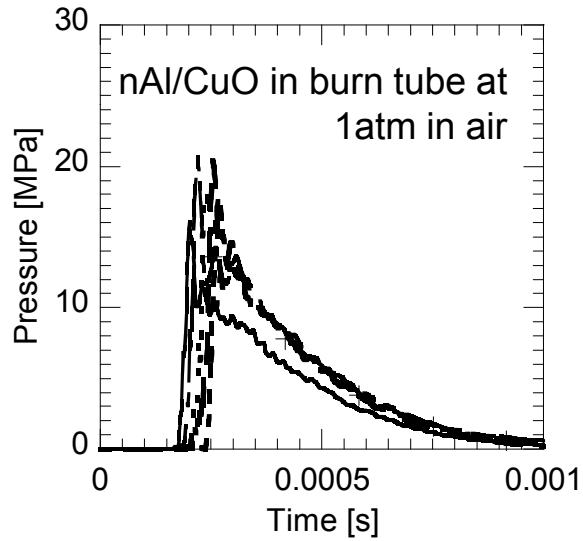




Previous work: gas fraction at equilibrium

Drawbacks:

- No intermediate gases (not present at equilibrium)
- Many of the equilibrium gases will not be realized until very high temperatures (ex. Cu: BP of 2835K)



The measured over-pressures (in excess of 10 [MPa]) can only be explained by gas generation

$$\Delta P = \left(\frac{N_{gen}}{V_{\text{int}}} + \frac{P_1}{\overline{R}T_1} \right) \overline{R}T_2 - P_1$$

Generation of gaseous species

Heating of interstitial gas

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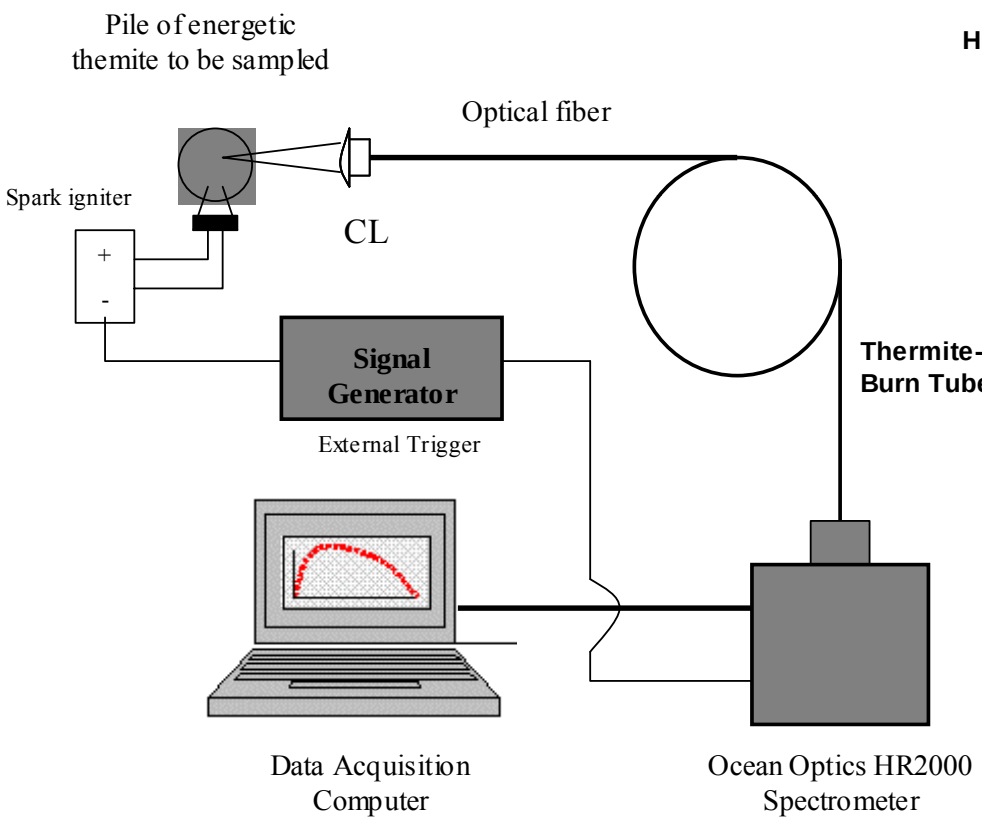
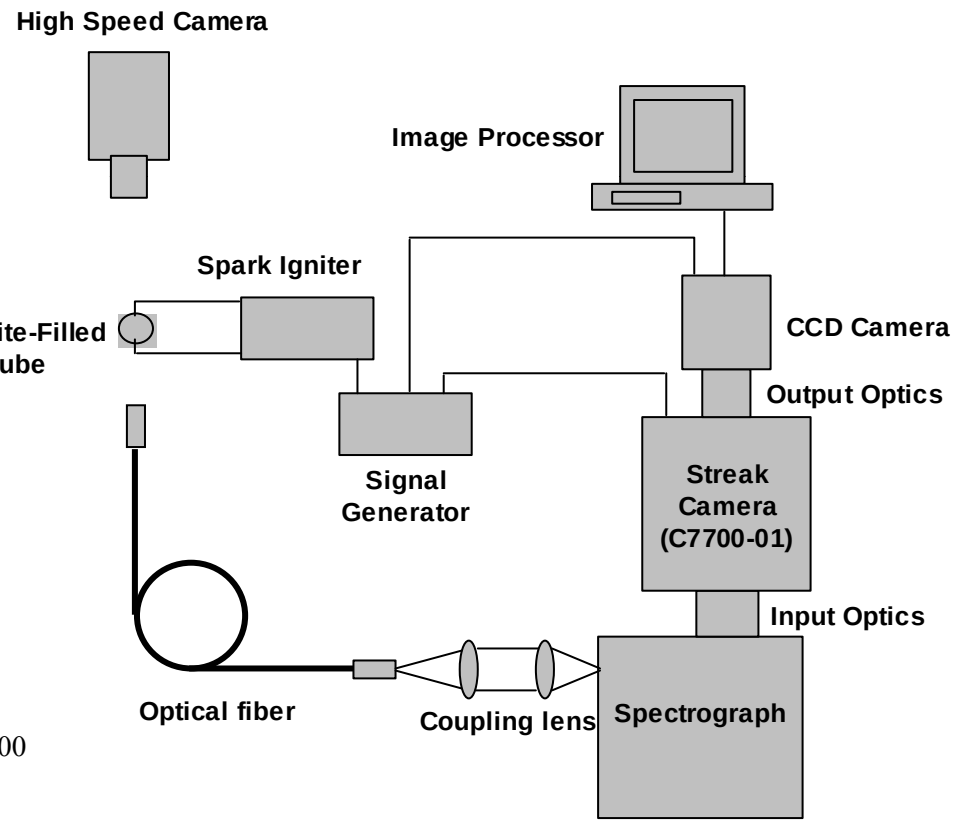
Optical Temperature Measurements

Time integrated temperature measurement set-up



Temporally resolved temperature measurements via streak camera



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Optical Pyrometry requires consideration of Material Spectral Emissivity

In general: $\varepsilon = \varepsilon(\lambda, T)$

Simplest Solution:

$\varepsilon = const.$ → Two-color pyrometry

More Accurate Solution:

Assume emissivity has a known relationship with λ ($\varepsilon \sim \lambda^n$) →

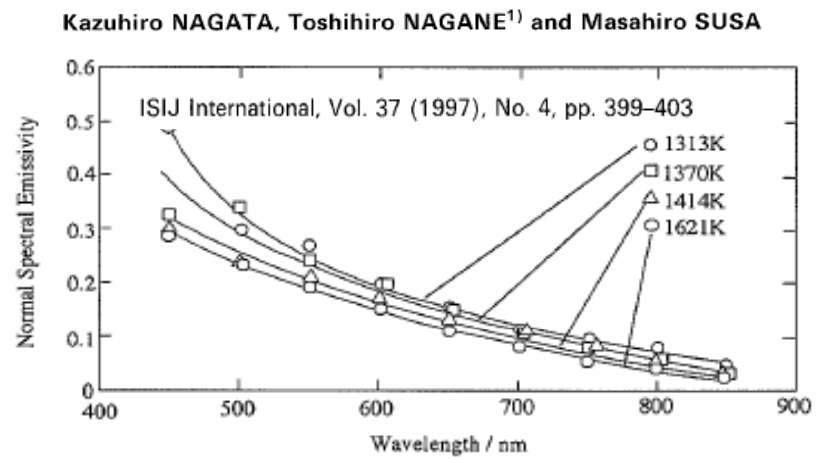


Fig. 8. Normal spectral emissivity of liquid copper at different temperatures as a function of wavelength.

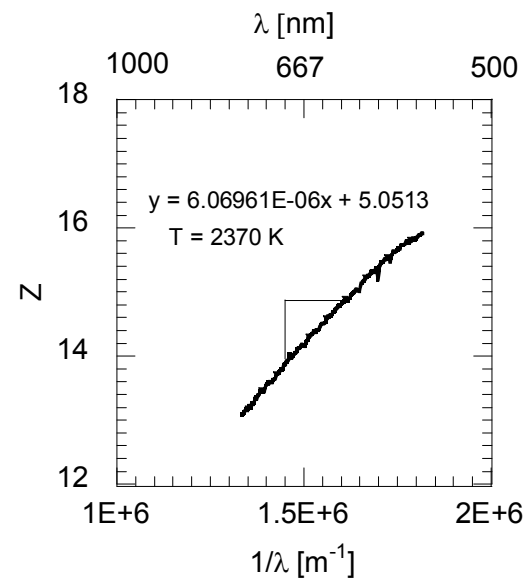
Planck's Law

$$E(T,\lambda) = \varepsilon(\lambda,T)\cdot\frac{C_1}{\lambda^5\left[e^{C_2/\lambda T}-1\right]}$$

$$\varepsilon(\lambda) = \frac{C_3}{\lambda}$$ → $\varepsilon \sim \lambda^{-2}$ and ε =const, also considered

Curve Fitting Equation [used by Ng *et al Review of Scientific Instruments (2001)]*

$$Z = Ln\left(\frac{C_1}{\lambda^6}\cdot E(\lambda,T)\right) = \frac{C_2}{\lambda\cdot T} - Ln(C_3)$$



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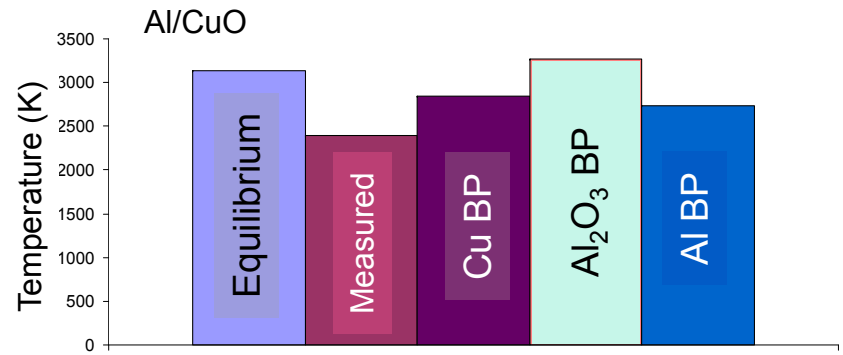
Temperature Measurements Suggest that the Final Products are not Gasified

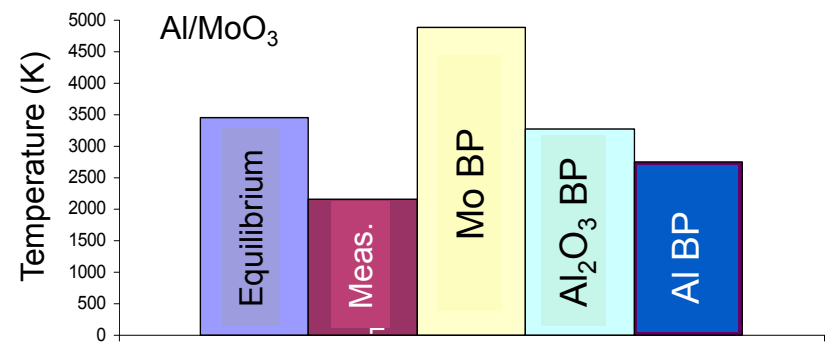
$$2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$$

Burn Tube Propagation Rate ~ 1 km/s
Combustion Temperature ~ 2350±150 K



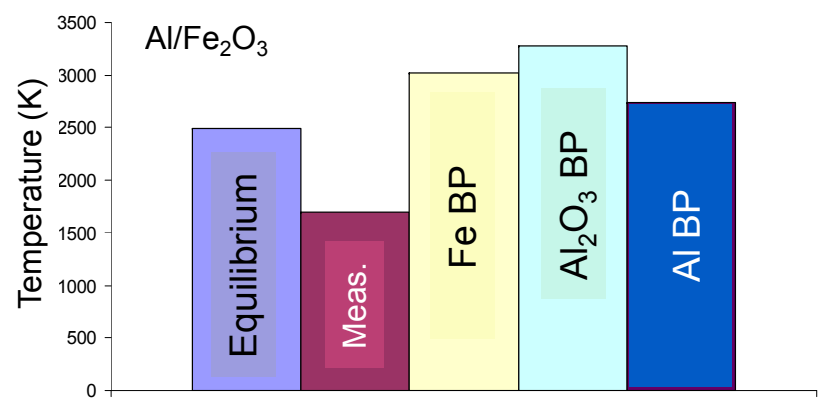
$$2Al + MoO_3 \rightarrow Al_2O_3 + Mo$$

Burn Tube Propagation Rate ~ 1 km/s
Combustion Temperature ~ 2150±150 K



$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$

Burn Tube Propagation Rate ~ 0.1 m/s
Combustion Temperature ~ 1700±150 K



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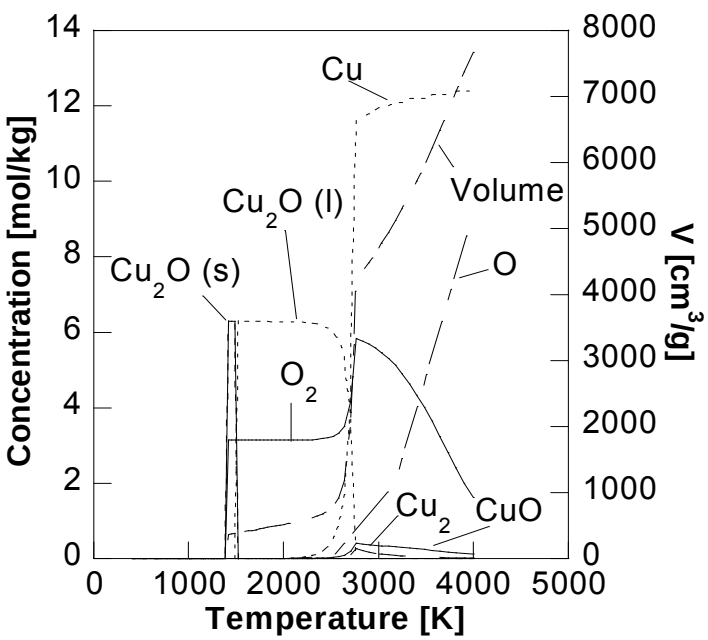
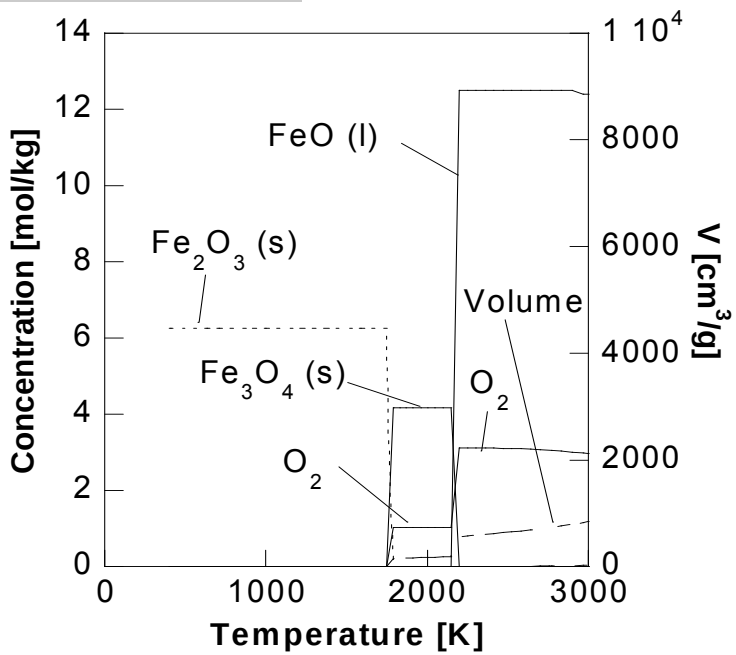
Metal Oxides Vaporize or Decompose at Low Temperatures

Compound	T_{mp} (K)	T_{bp} (K)	T_{vol} (K)
Al	1687	3013	n/a
Al_2O_3	2345	3253	n/a
CuO	1500	decomposes	1400
Fe_2O_3	1855	decomposes	1750
MoO_3	1075	1428	n/a

$$2CuO \rightarrow Cu_2O + \frac{1}{2}O_2$$

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$$





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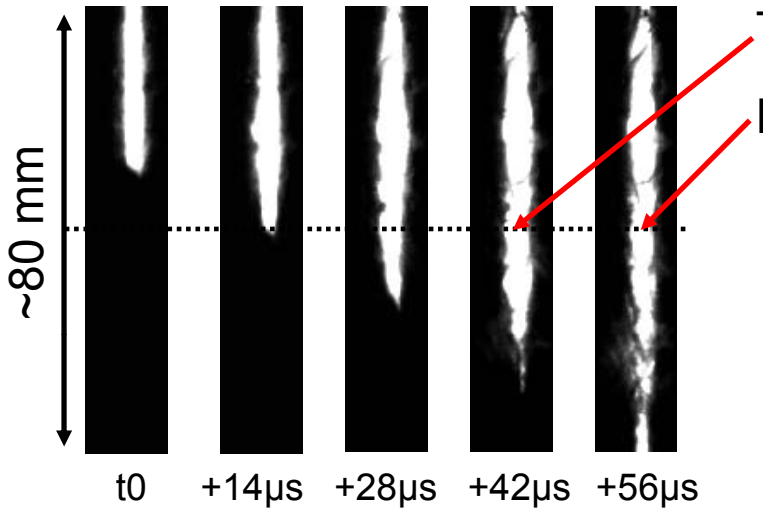
Temperature continues to Rise after Luminous Front Passes

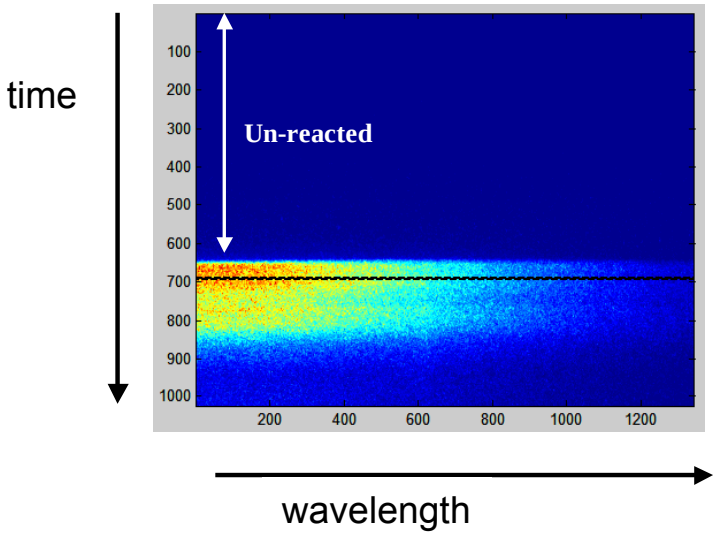


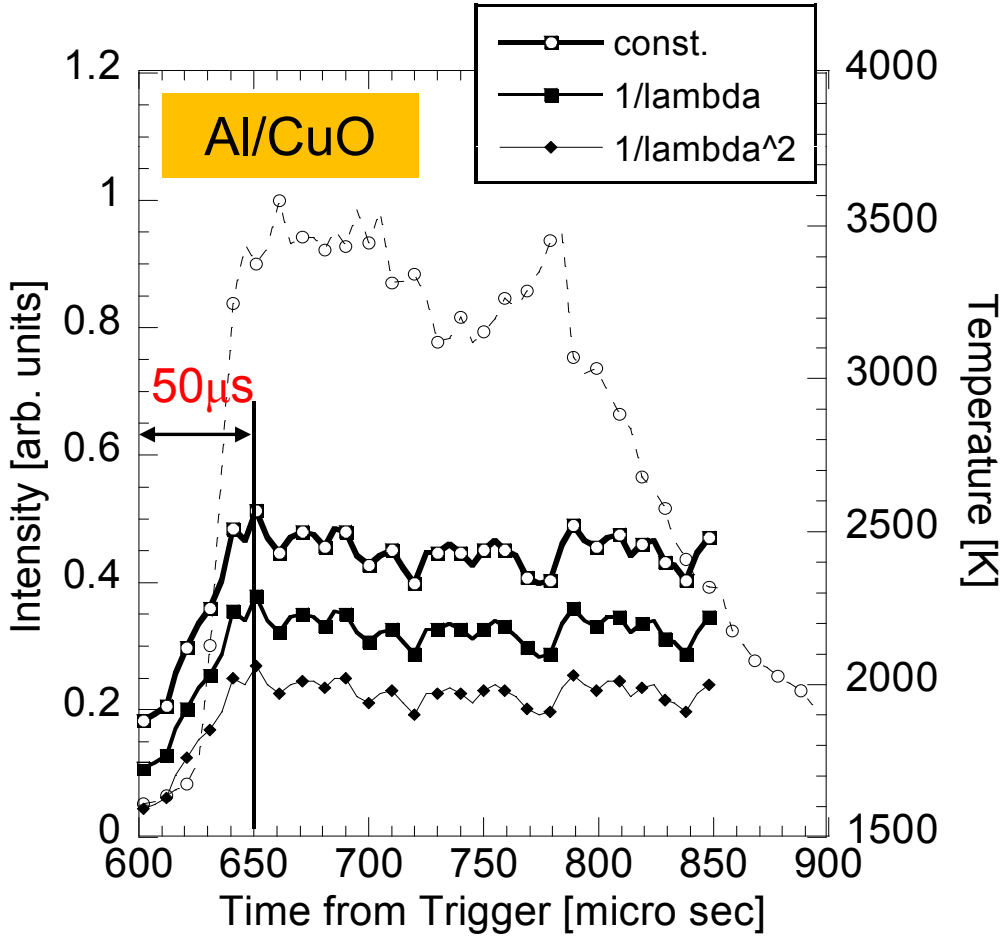
T still increasing,

Energy being released

Wave speed ~ 800 m/s

800m/s x 50μs = 40 mm





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Effects of Oxidizer vs Fuel Particle Size

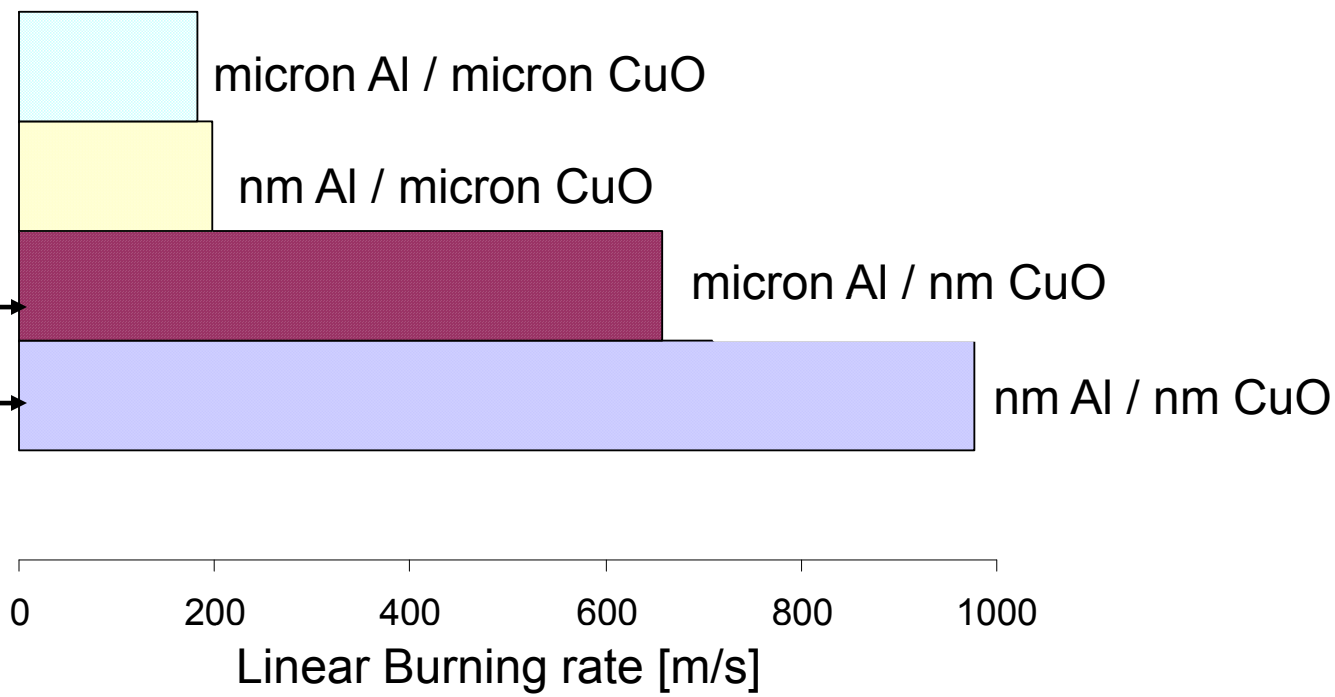
Aluminum: nanoparticles (38nm) from Technanogy, micron-particles (2μm) from Valimet
Copper-Oxide: nanoparticles (33nm) and micron particles (3μm) from Sigma Aldrich

	Linear Burning Rate [m/s]	Mass Burning Rate [kg/s]	Energetic Mass Burning Rate [kg/s]	Avg. mass per run [g]	% mass Al_2O_3
Nano Al/ Nano CuO	977	3.79	3.14	0.31	17.1
Micron Al/Nano CuO	658	4.77	4.72	0.58	1.0
Nano Al/Micron CuO	197	1.31	1.08	0.53	17.1
Micron Al/Micron CuO	182	2.02	2.00	0.89	1.0

Linear propagation rate was more dependant on the CuO particles size

$$2CuO \rightarrow Cu_2O + \frac{1}{2}O_2$$

Evidence that the oxide decomposition drives convective burning



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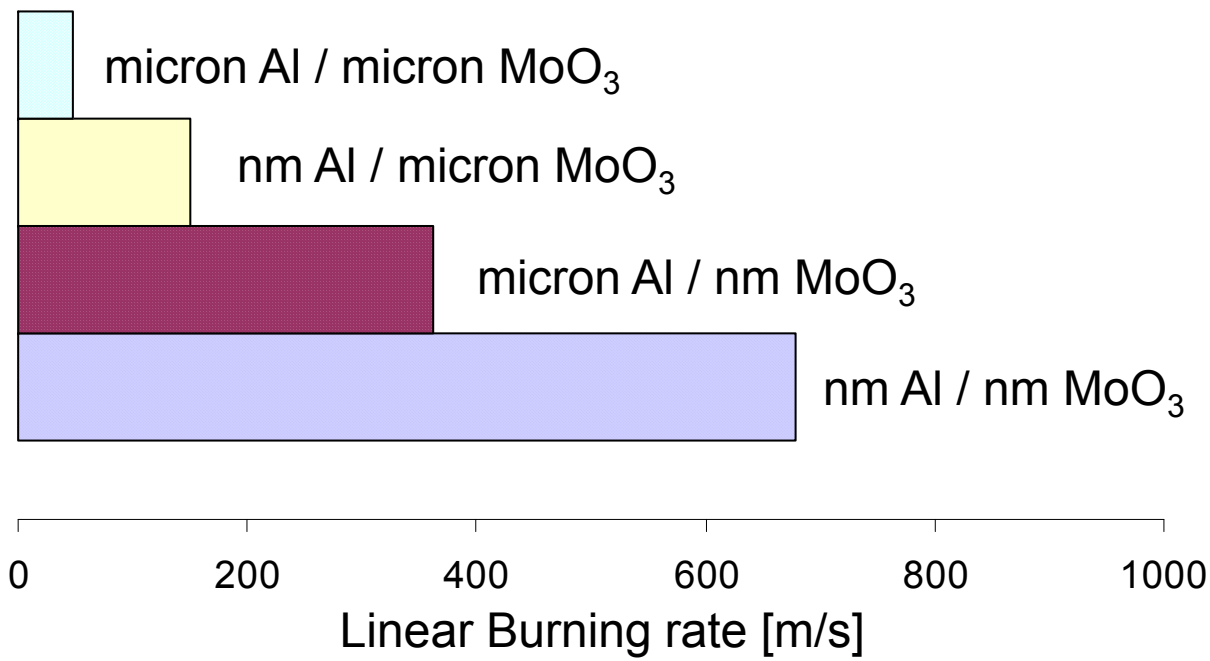
Al/MoO_3 System has Similar Trend

	Linear Burning Rate [m/s]	Mass Burning Rate [kg/s]	Energetic Mass Burning Rate [kg/s]	Avg. mass per run [g]	% mass Al_2O_3	Oxide Shell Thickness (nm)
Nano Al/ Nano MoO_3	678	1.95	1.43	0.23	26.4	6.21
Micron Al/Nano MoO_3	362	1.54	1.51	0.34	1.7	22.26
Nano Al/Micron MoO_3	151	0.45	0.33	0.24	26.4	6.21
Micron Al/Micron MoO_3	47	0.52	0.51	0.89	1.7	22.26

MoO_3 vaporizes at relatively low temperatures. Reducing the size of these particles promotes convective burning



reducing the oxidizer particle size has greater impact on increasing propagation rate

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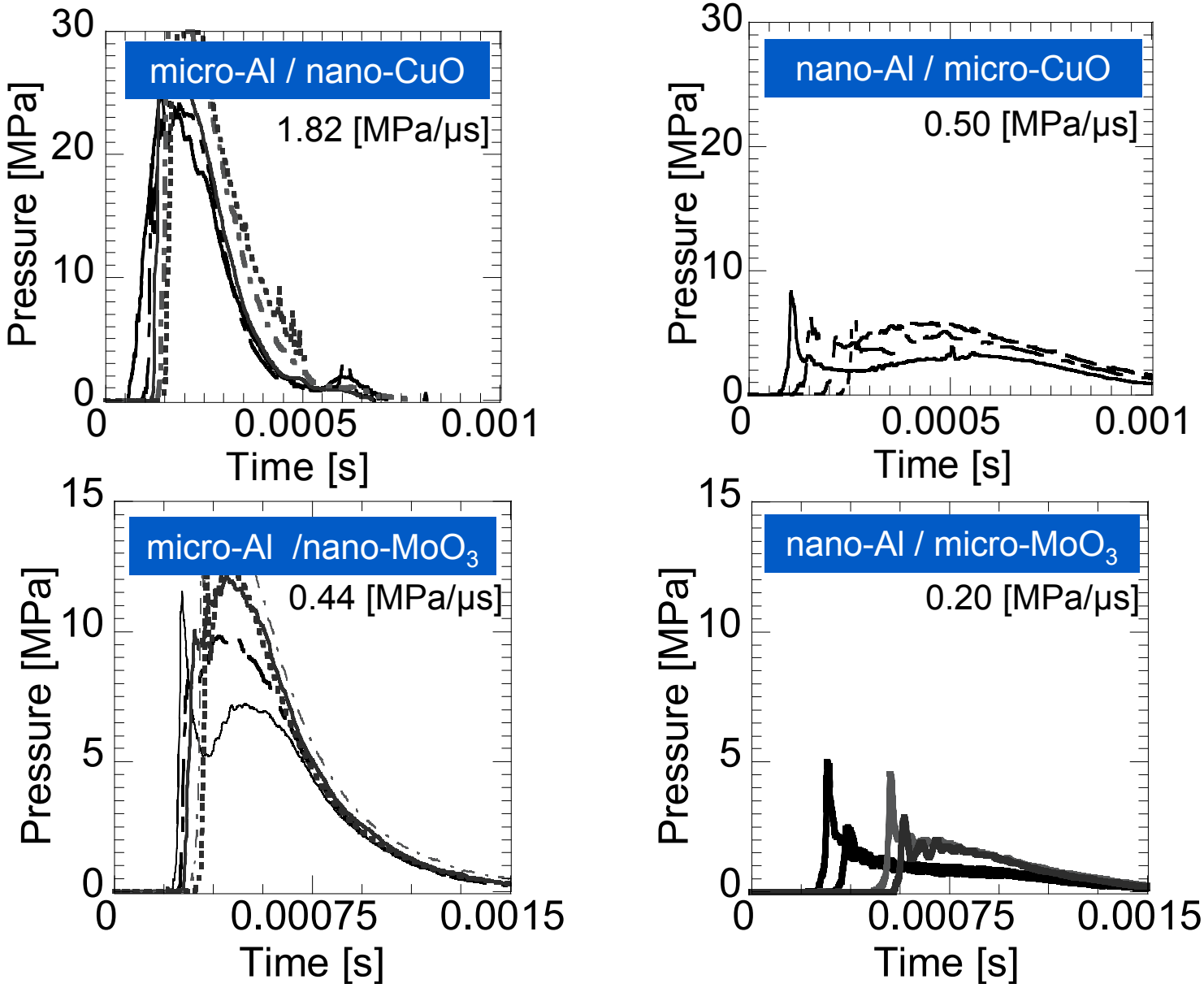
Pressure Profiles for Mixtures of Al/CuO and Al/MoO_3 with different Powder Sizes



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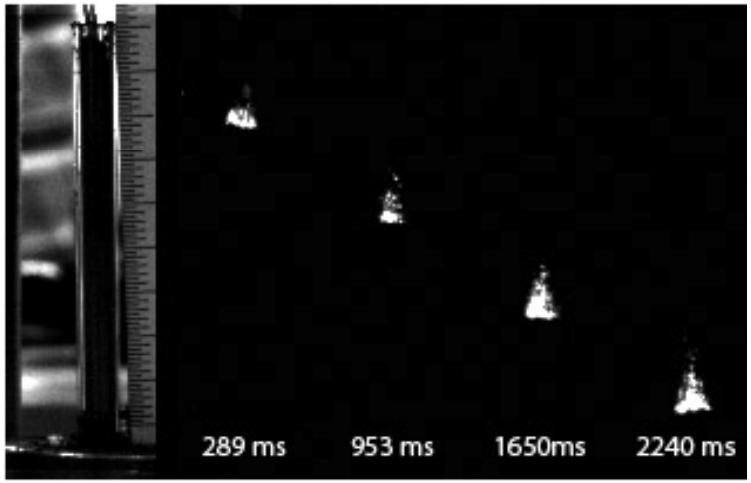
nNi-nAl Burning Rates

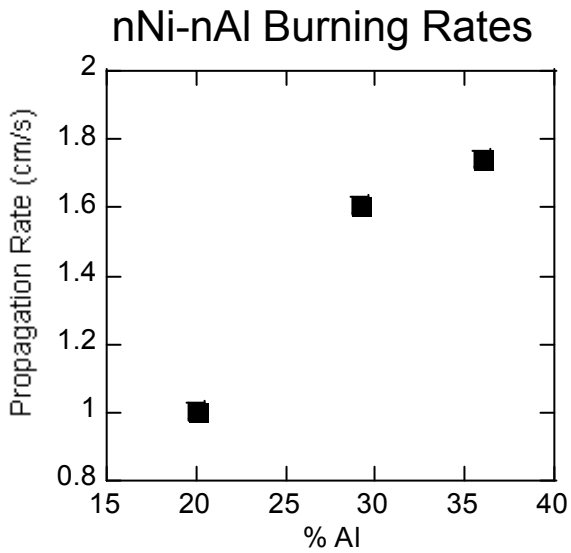
- Al + Ni → AlNi -1.38 kJ/g
- T_{af} = 1912 K
- Vertical glass tubes 2” in length
- Ignited with Nichrome wire
- Flame propagation measured with Phantom 7.3

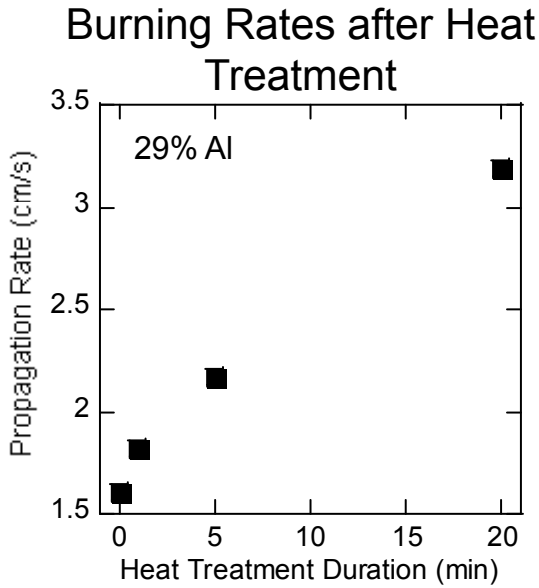
Material	Manufact.	Size (nm)	Morphology	Purity (%)
Al	Novacentrix	80	Spherical	80
Ni	Alfa Aesar	5-20	Spherical	99.9

Stoichiometry Combination	Molar Ratio Al : Ni	Mass Percentage (%) Al : Ni
1	1 : 1	29.2 : 90.8
2	1 : 0.56	36 : 64
3	1 : 1.38	20 : 80

Heat treatment performed on nm Ni powder in oven at 250 °C







Our work has led to the following conclusions…

- Further evidence showing that the fast propagation rates in nanothermites are induced by the convective burning mechanism
- Increasing ambient pressure leads to decreased gas generation and a change in the propagation mechanism
- Gas generation is due to decomposition of oxide particles
- Temperature rise takes place over a thick region
  - Reaction relies on pressure, not temperature, gradient to drive propagation
  - Need only heat mixture to point of gas generation to propagate
- Reducing the size of oxidizer particles seems to increase rate of gas generation and promote convective burning

Summary - continued

- Electrostatic self-assembly of nanoscale thermites into microspheres show improved mixing over sonication.
- Nano functionalized colloids of metal oxides and graphene demonstrated to affect pressure exponent and burning rate. Nano aluminum affects burning rate.

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2008-2009 Publications

"Combustion and conversion efficiency of nanoaluminum-water mixtures," Risha, GA; Sabourin, JL; Yang, V; Son, SF; Tappan, BC, COMBUSTION SCIENCE AND TECHNOLOGY, 12, 2127-2142, 2008.

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