Energetic Materials Research Combustion at Texas Tech

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Texas Tech University Energetic Materials Combustion Group February 2015

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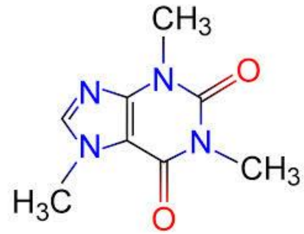

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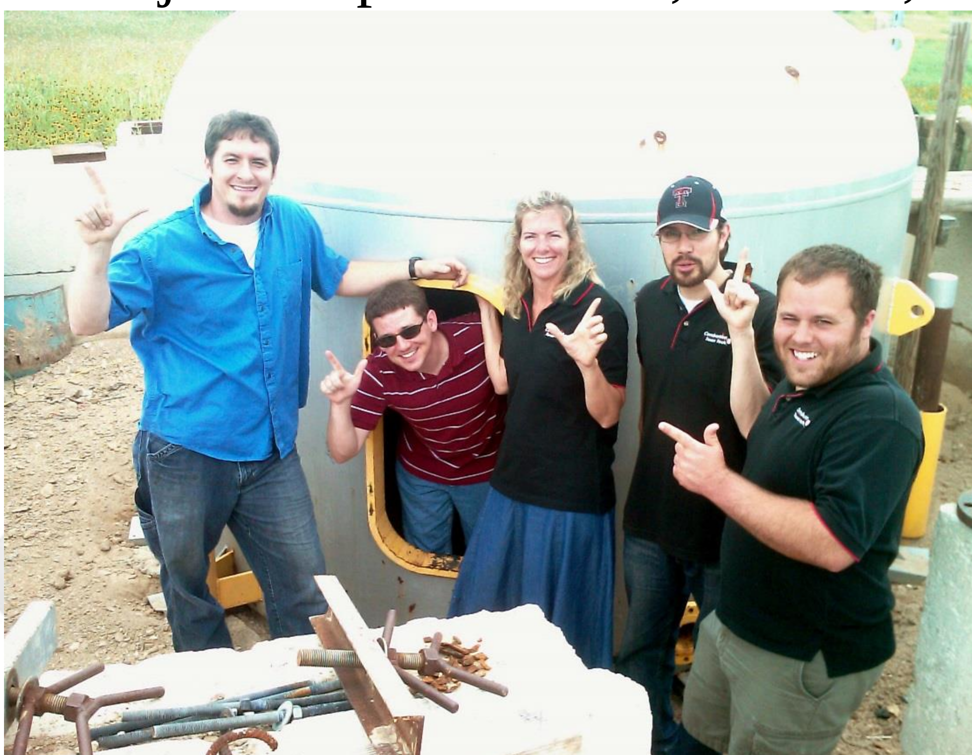
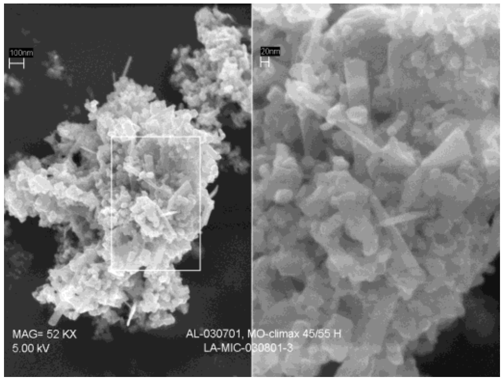
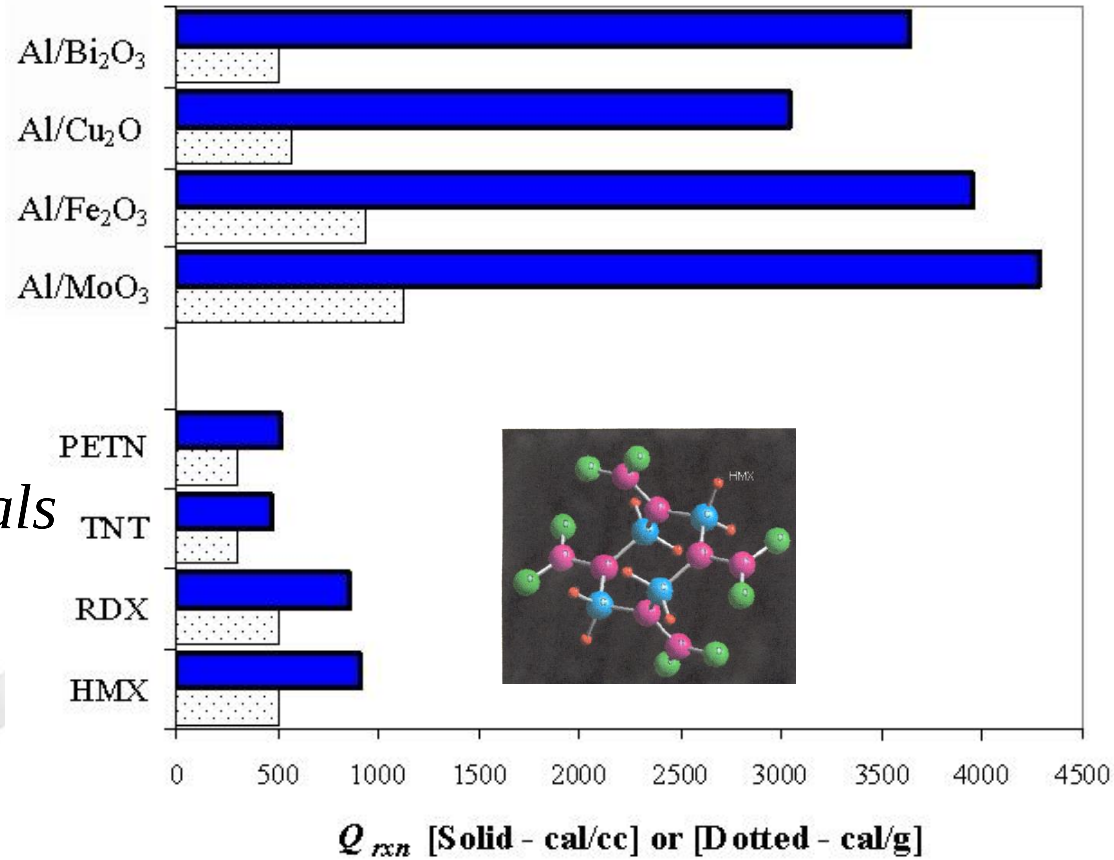
Combustion Lab at Texas Tech

- Vision - *Promote cleaner, safer, and more effective energetic composites through an understanding of basic combustion behaviors.*
- Since 2000 -15 PhD students and 30 MS students! Over 100 journal publications, 4 books, 3 book chapters, 2 patents



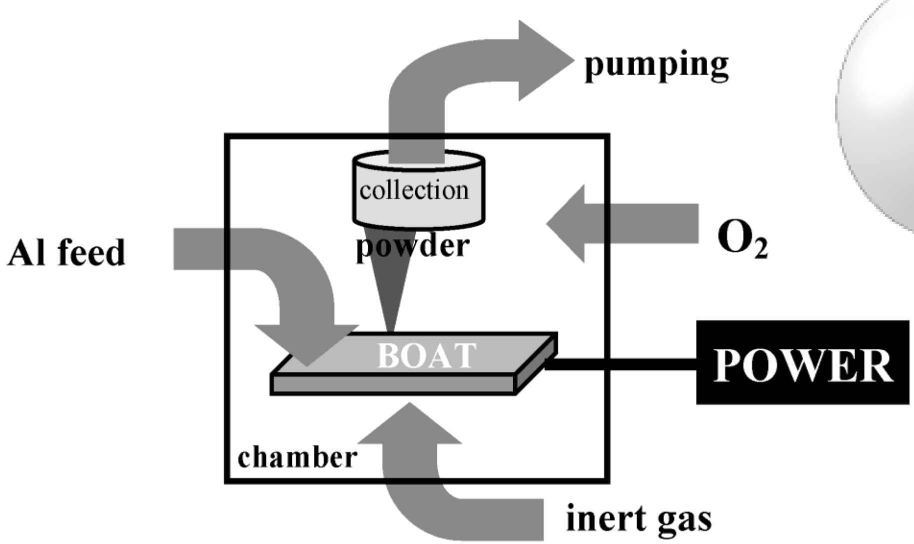
Overview

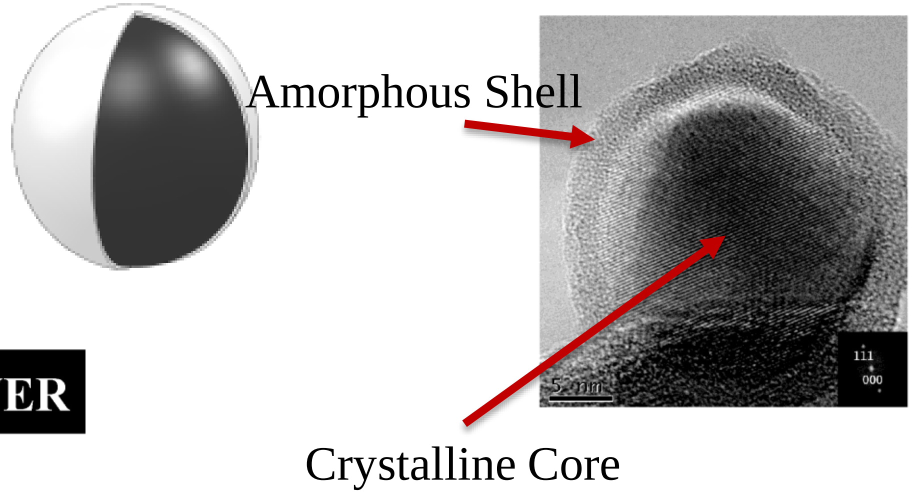


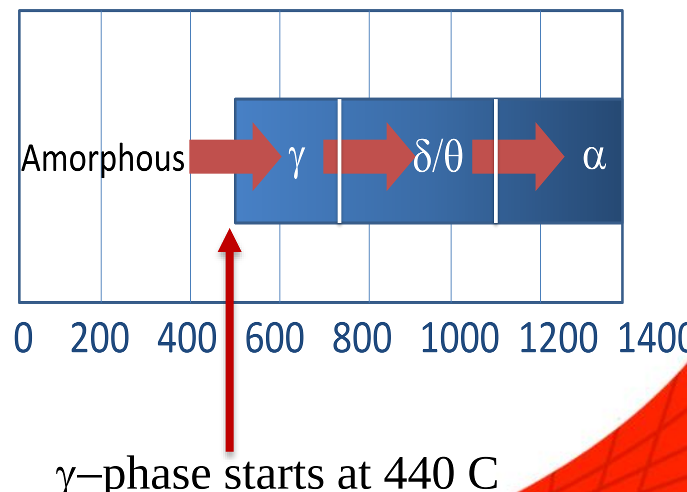


- *Synthesis of new materials*
- *Ignition sensitivity and safety*
- *Energy generation and transport*
- *Modeling reaction mechanisms*

Al Powder Production < 25 microns



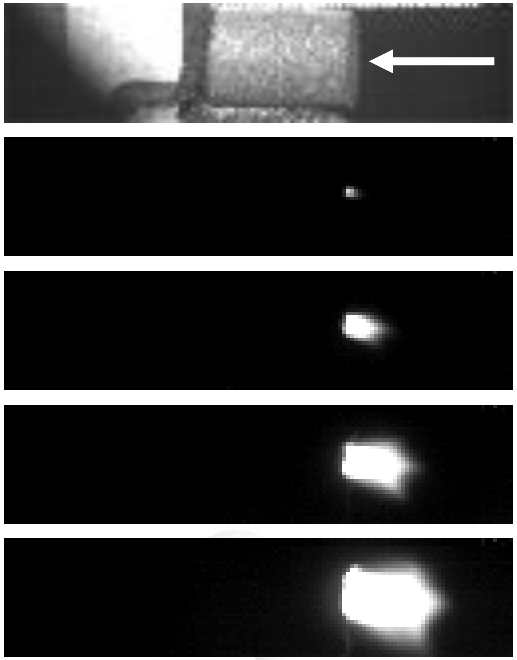




- High purity Al introduced to a heated ceramic (2000 C) with an inert (Ar) gas flow.
- Vapor phase Al travels, nucleates, and coagulates –
  - Cools and crystalizes as a solid
- Oxygen introduced after solidification (<660 C).
  - Typically in amorphous phase (~440 C - ambient)

Pellets: ignition time and burn rate measurements

High-Speed Imaging up to 150,000 fps



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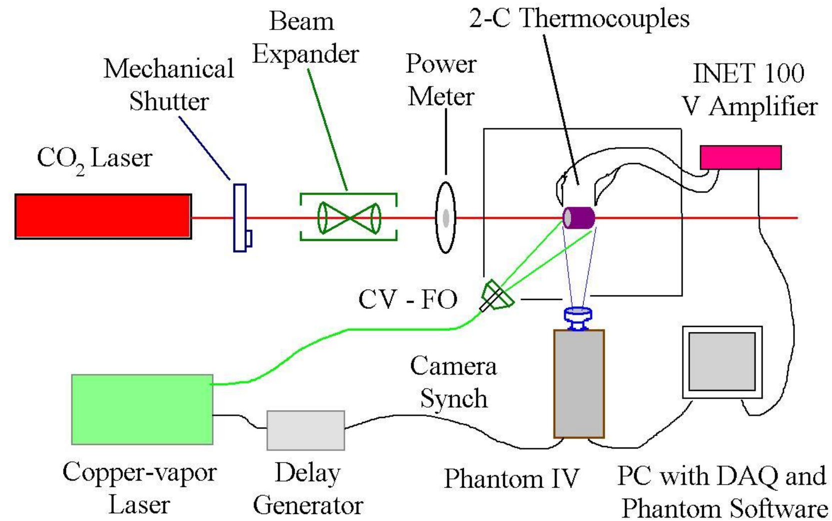
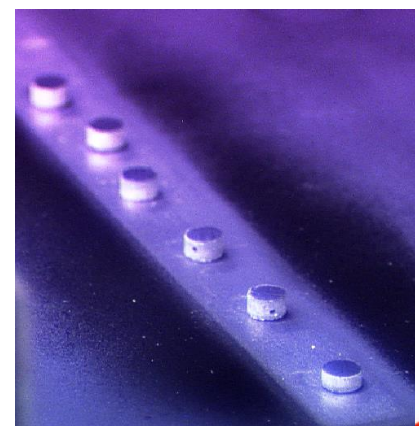
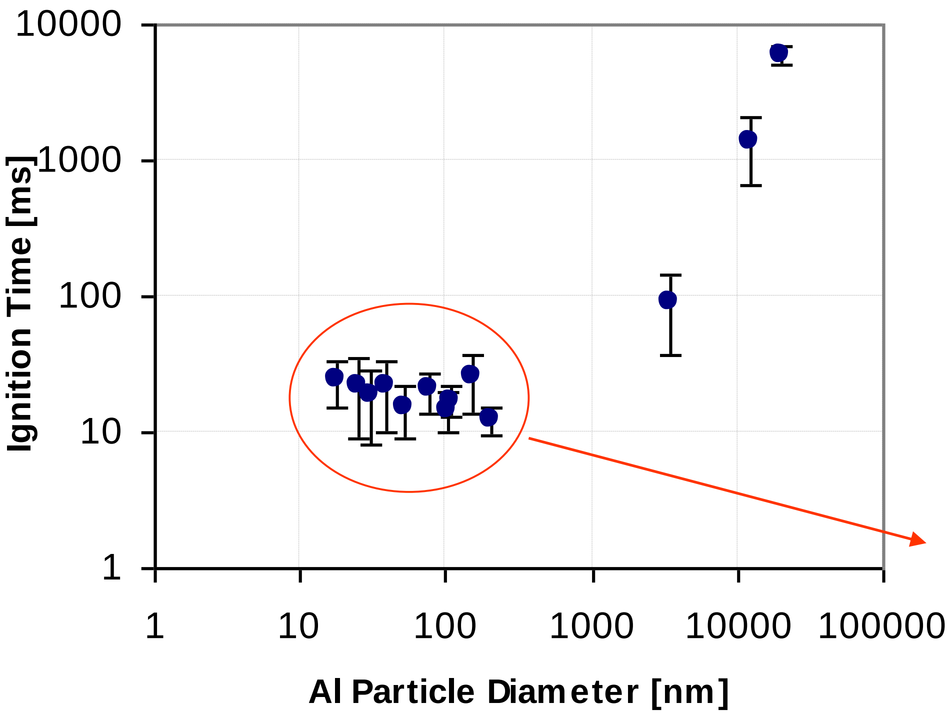




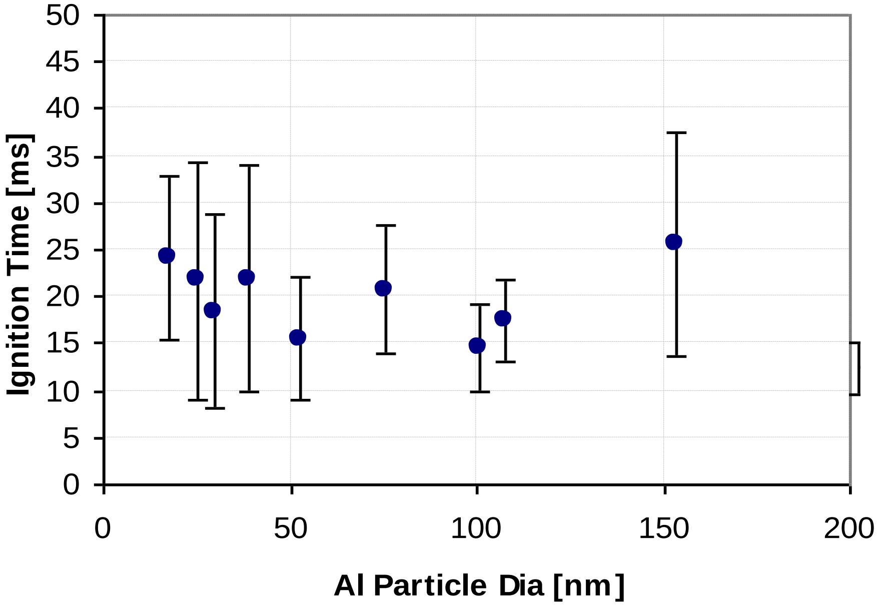
- Entire front face of pellet is exposed to Gaussian laser beam
- Ignition starts in the center (**hot spot formed**)
- Propagation both radially and axially

Granier et al, *Combustion Science and Technology* (2003)
Granier et al, *Combustion and Flame* (2004).

Al+MoO_3 ignition as a function of Al particle diameter



- Nano-Al reduces time to ignition by two orders of magnitude!

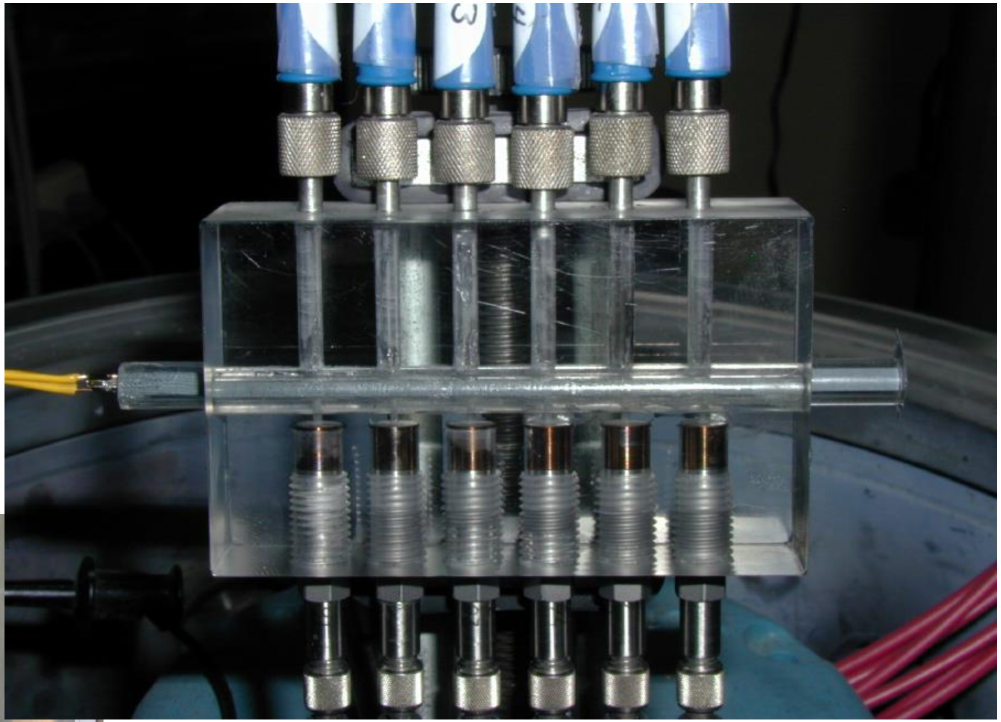


- Density held constant ~ 40% TMD
- Composition held constant ~ ϕ=1.2

Granier et al, *Combustion and Flame* (2004).

pressure and light intensity measurements

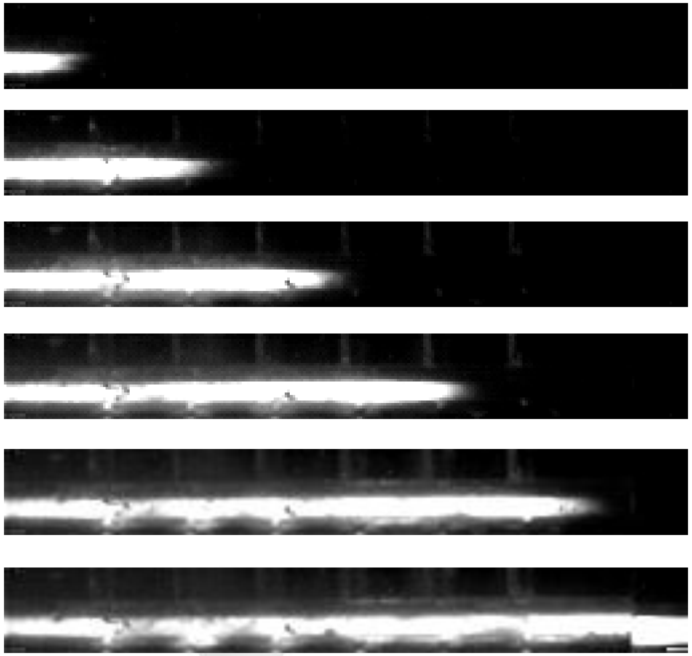
- Acrylic tubing
  - 10.0 cm length
- Instrumented with detectors spaced 1 cm apart
  - 6 photo-detectors
  - 6 pressure sensors

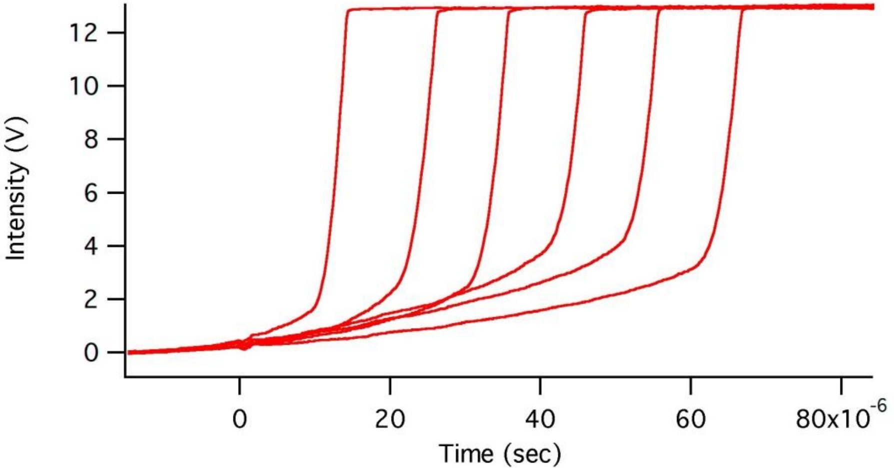


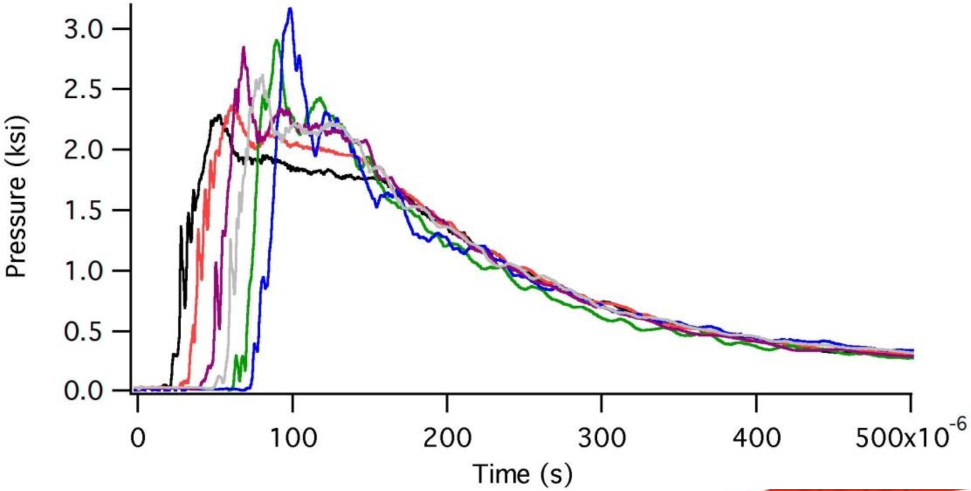
"The Bockmon Tube"

Bockmon et al, *J of Applied Physics* 2005

Flame Speeds of confined $Al + MoO_3$







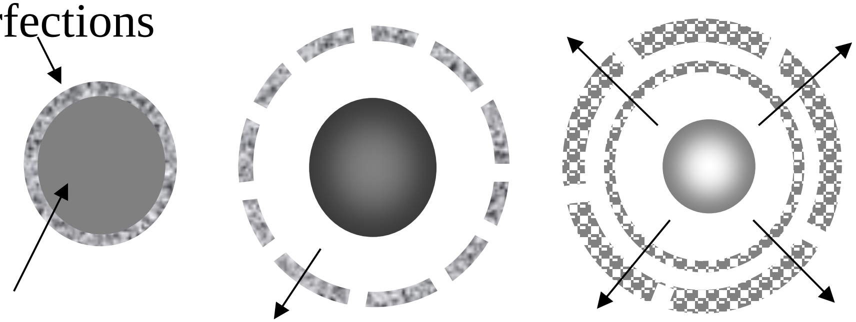
- Flame speed - optic signals & high speed camera
- Pressure history – mode of propagation & τ_{rxn}

Bockmon et al, *Journal of Applied Physics* 2005

New Mechanism for Fast Reactions of Al Nanoparticles During Fast Heating

Melt-Dispersion Mechanism

Alumina shell virtually free of imperfections



Aluminum core

Spallating alumina shell

Atomic size molten aluminum clusters disperse from an unloading wave at high velocity

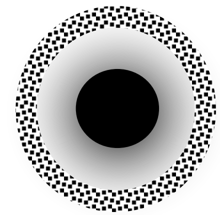
Characteristic Time

- For nanoparticles with the ratio of particle radius to shell thickness $M=R/\delta<20$, the oxide shell fractures after Al melting
- Melting is accompanied by a volume increase of 6% and generates large pressure in the melt (0.5-1.5 GPa)
- Dynamic spallation of shell results in complete exposure of the liquid Al droplet and creates an unloading wave with a tensile pressure up to 3-8 GPa.
- The tensile pressure in an unloading wave disperses the Al droplet into small clusters which fly at high velocity

Oxidation is not limited by classical diffusion.

1. V. I. Levitas, B. W. Asay, S. F. Son and M. L. Pantoya, *Appl. Physics Letters*, **89**, 071909 **(**2006).
2. V. I. Levitas, B. W. Asay, S. F. Son and M. L. Pantoya, *J. Applied Physics*, **101**, 0*83524* (2007).
3. V. I. Levitas, M. L. Pantoya, and B. Dikici, *Applied Physics Letters*, **91**, 011921 (2008).
4. V. I. Levitas, M. L. Pantoya, and K. Watson, *Applied Physics Letters*, **92**, 201917 (2008).
5. Levitas V. I. Combustion and Flame, 2009, **156**, 543.

Pressure in Al core and hoop stress in oxide shell



$$p = \frac{12(m^3 - 1)(\varepsilon_2^i - \varepsilon_1^i)G_2K_1K_2}{H} + \frac{2K_1(4G_2 + 3m^3K_2)\Gamma_1}{RH} + \frac{(2\Gamma_2 + p_gR)m^2K_1(4G_2 + 3K_2)}{RH}, \qquad (1)$$

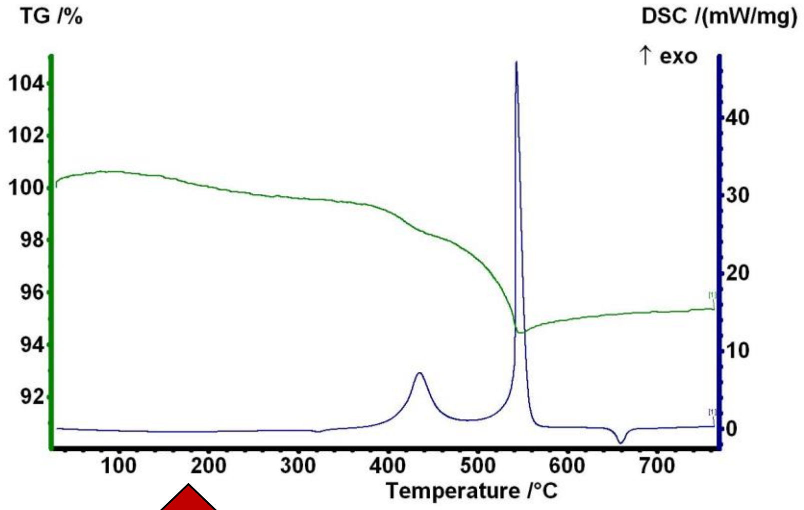
$$\sigma_h = -\frac{6(m^3 + 2)(\varepsilon_2^i - \varepsilon_1^i)G_2K_1K_2}{H} + \frac{4(m^3 + 2)G_2K_2\Gamma_1}{RH} + \frac{(2\Gamma_2 + p_gR)m^2(-2G_2K_1 + 3(2G_2 + K_1)K_2)}{RH}, \qquad (2)$$

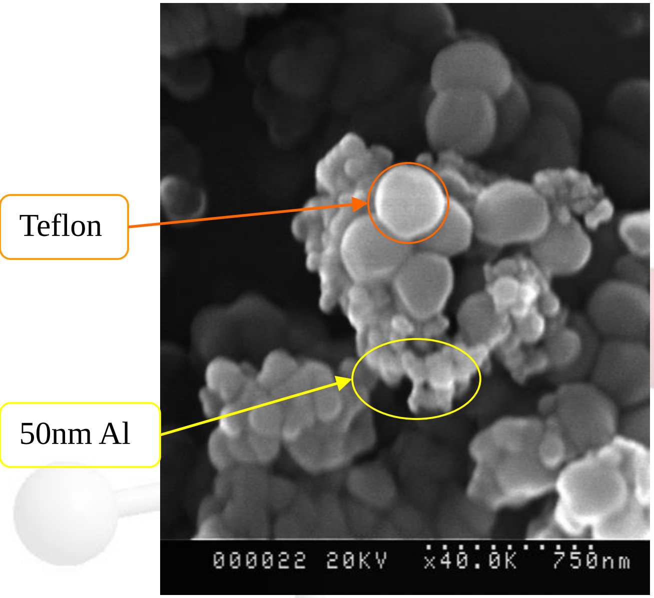
$$\varepsilon_1^i = -(\alpha_1^s(T_m - T_0) + (1 - f)\alpha_1^s(T - T_m) + f\alpha_1^m(T - T_m) + f\varepsilon^m);$$

$$\varepsilon_2^i = -\alpha_2(T - T_0),$$

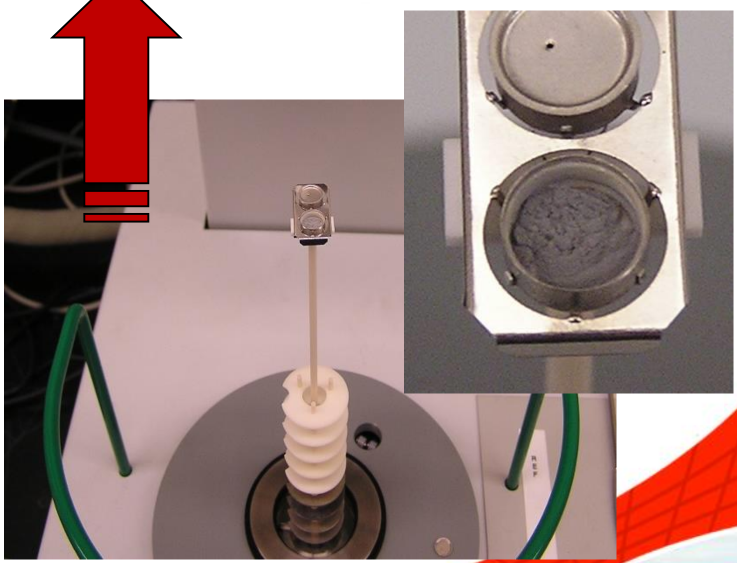
Exothermic Surface Chemistry Al-F

- Our early work explored unique kinetics of Al + fluorine reactions
- DSC – TGA analysis



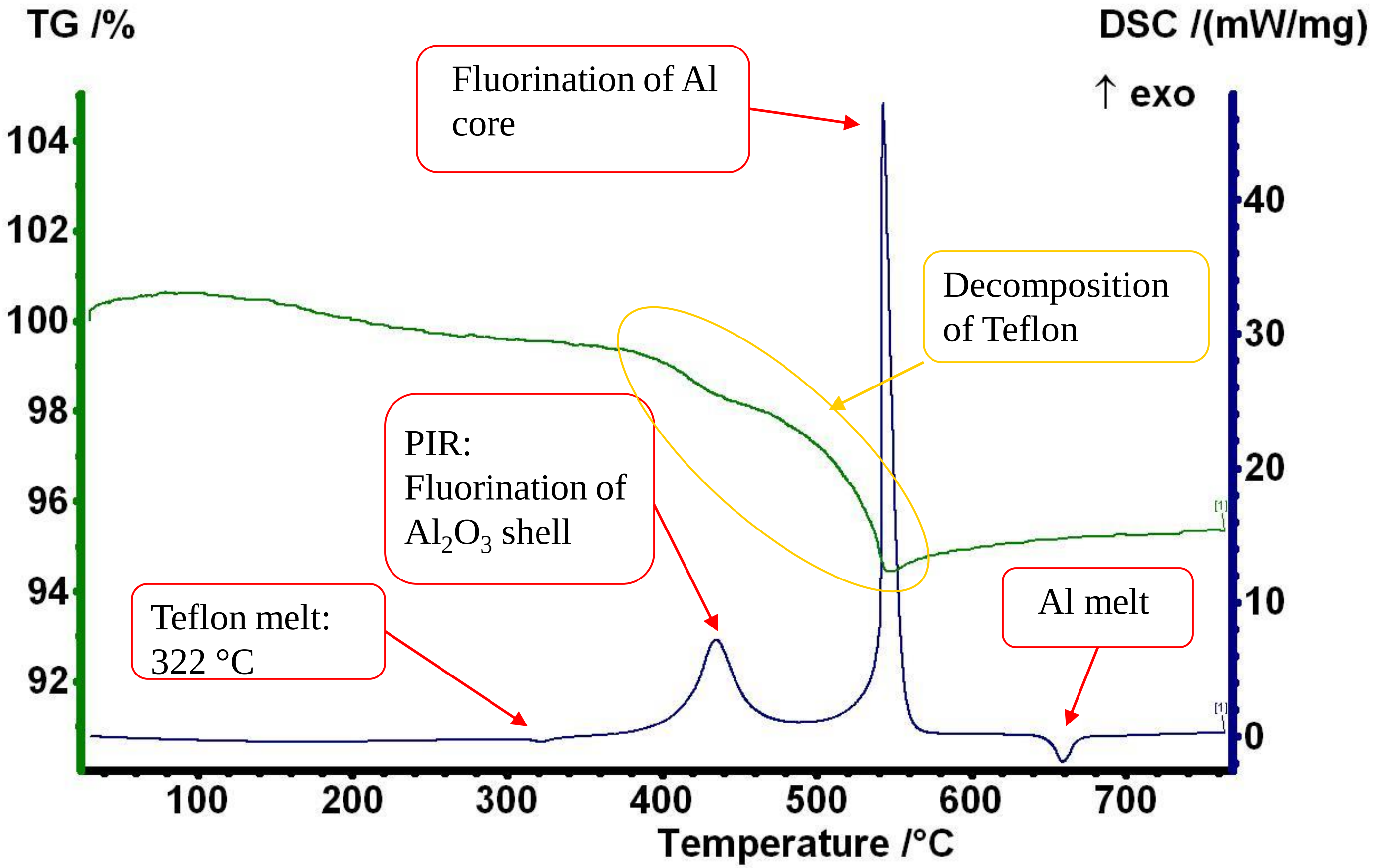


10 mg samples



Osborne et al. Comb Sci Tech 2007

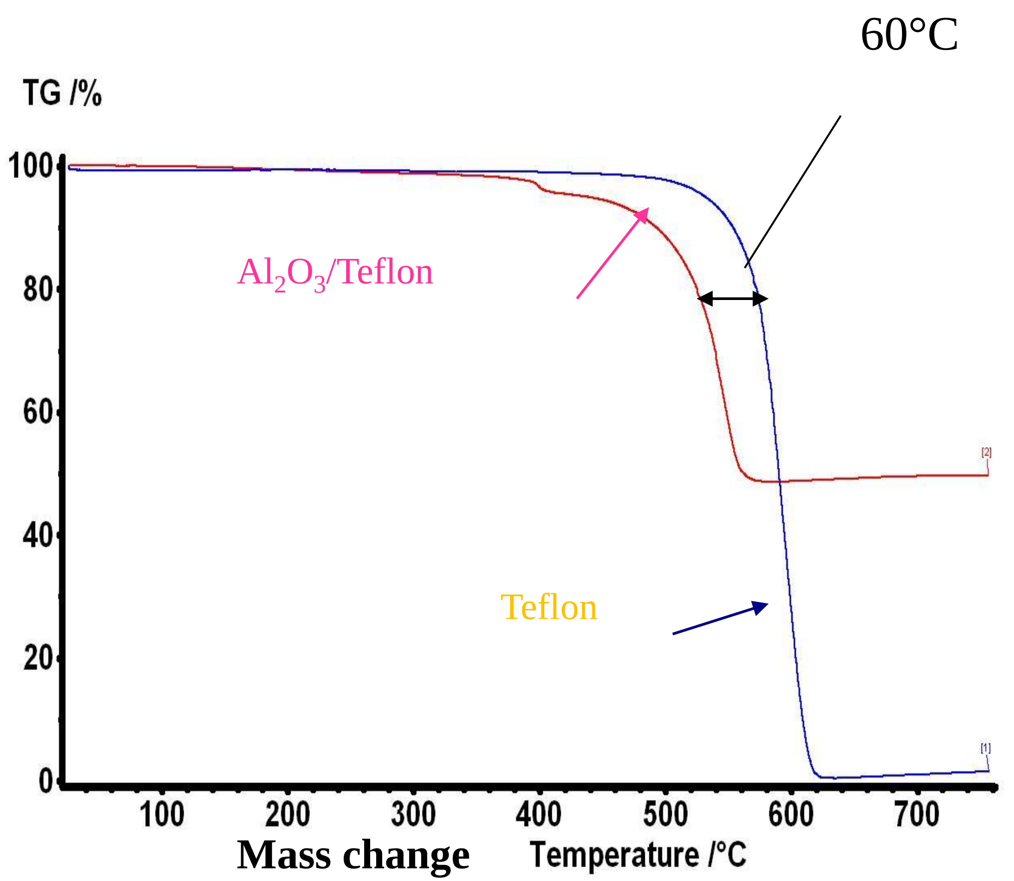
50nm Al / Teflon (70/30)



Osborne et al. Comb Sci Tech 2007

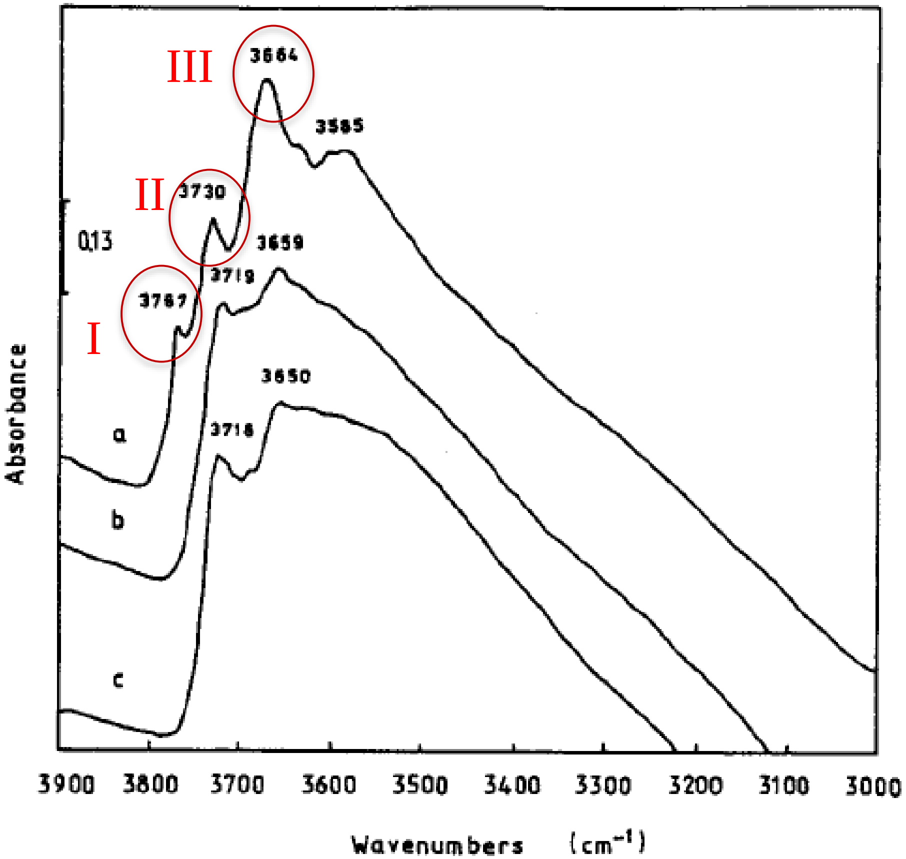
PIR effects on Teflon degradation

- PIR causes Teflon to degrade at lower temperatures
- In case of 15nm γ-Al_2O_3/Teflon, 60°C lower onset temperature.
- Stripping fluoride ions from polymer during PIR causes chain to become unstable, requiring less energy to degrade.

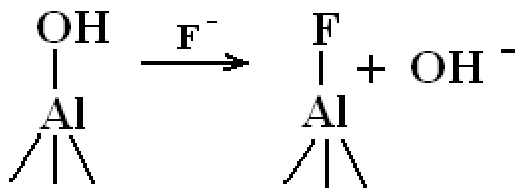


Mass change

Hydroxyl bonding



Sarbak 1997

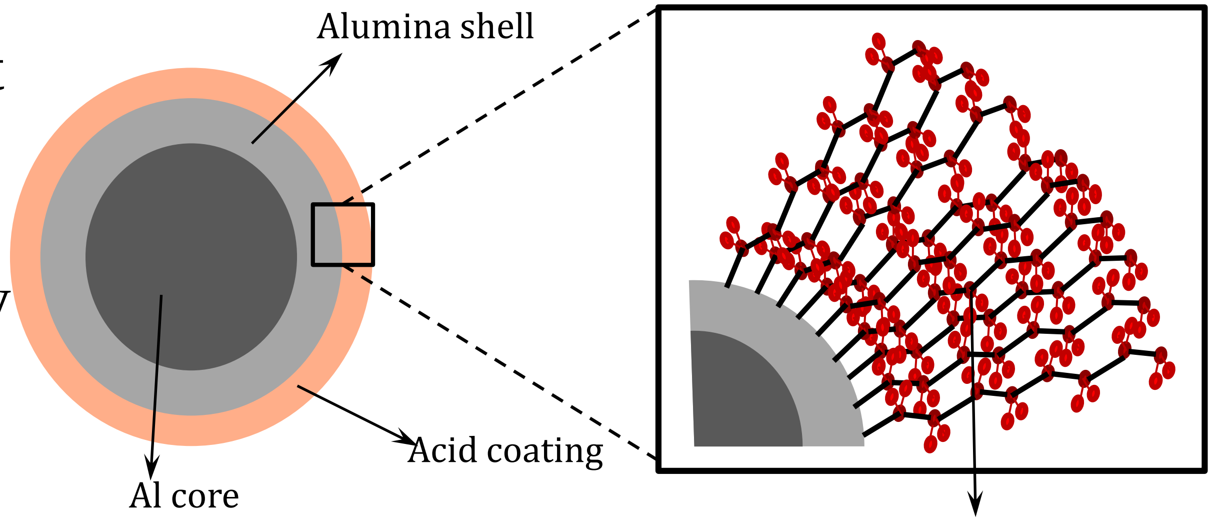


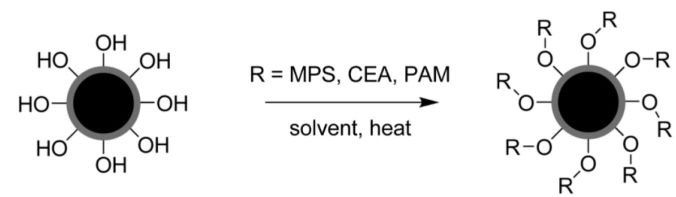
Fluorine OH substitution

- FT-IR of γ-Al_2O_3 - Hydroxyl groups bound to surface in many ways
- Tetrahedrially coordinated aluminum (I)
- Two alumina ions with one in the tetrahedral coordination and the other in octahedral coordination (II)
- Three octahedrally coordinated aluminum ions (III)

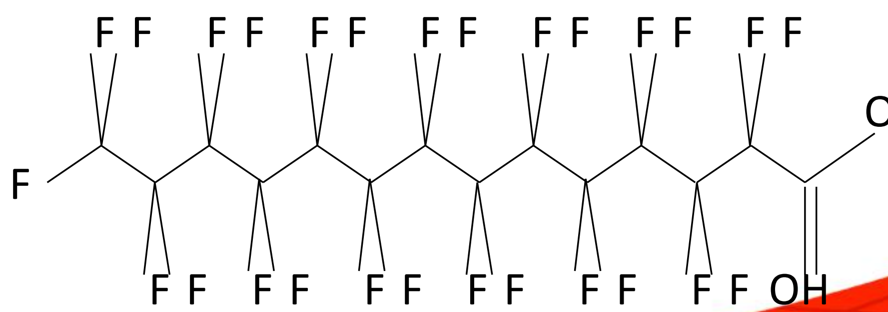
Polymer Coated Al particles

- How does surface functionalization affect combustion performance?
- How is PIR affected by functionalization?
- Can the combustion performance be controlled by changing the surface functionalization?



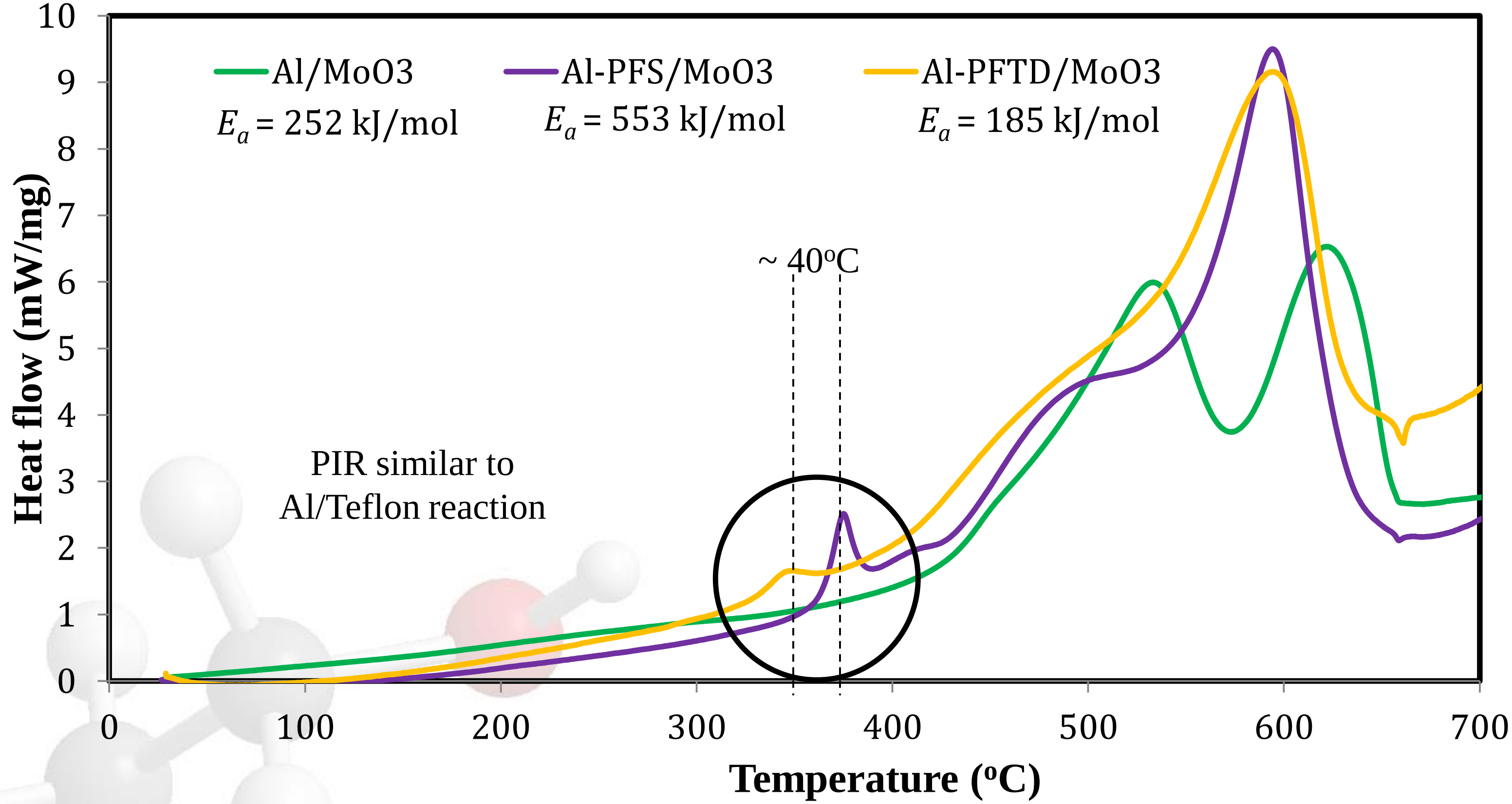


Perfluoro tetradecanoic acid (PFTD)



Kappagantula et al. JPC C 2012
Kappagantula et al. SCT 2013

DSC of Polymer Coated Al Mixtures

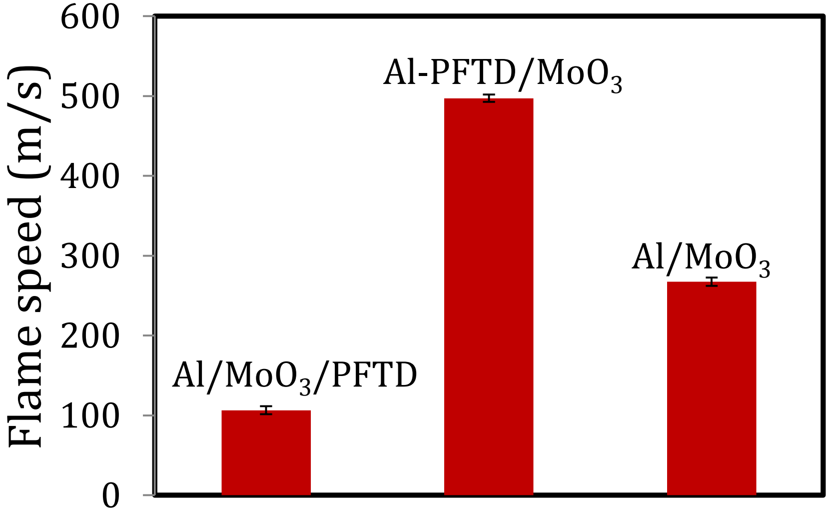


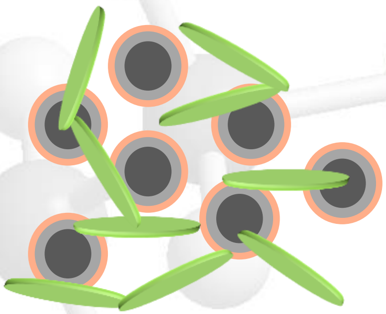
10 K/min

Kappagantula et al. JPC C 2012

Flame Propagation Results

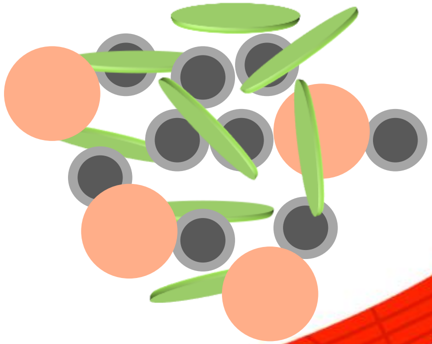
Sequential images of the flame propagating along the tube





Al-PFTD/MoO_3

Same chemistry, but different locations of PFTD acid creates difference in burning and thus, different flame velocities.



Al/MoO_3/PFTD

Kappagantula et al. SCT 2013

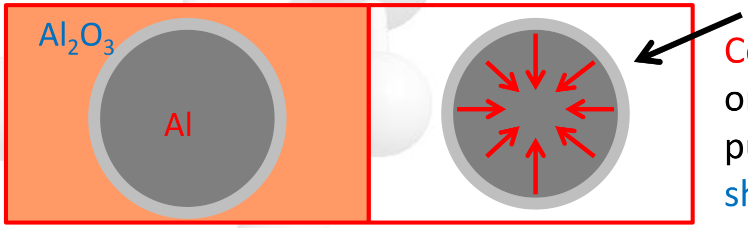
Residual Stress Development & Treatment

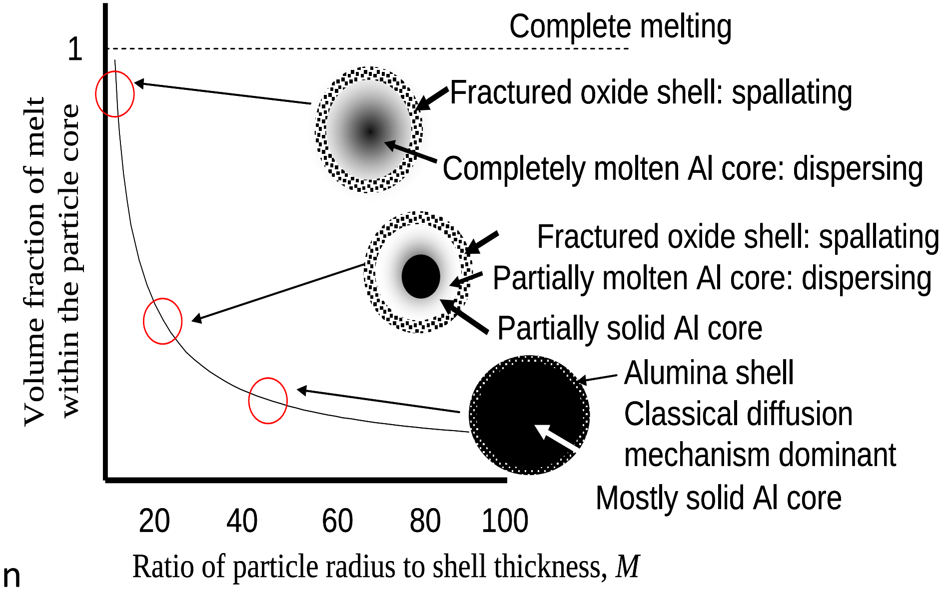
- Thermally induced stress affect mechanical properties
- Cooling from 440 C to ambient will induce shrinkage in the core while the shell remains rigid
  - $\alpha_{ox} = 5 \times 10^{-6}\ K^{-1}$ & $\alpha_m = 23 \times 10^{-6}\ K^{-1}$
- Shell – Core interface is in a state of tension

Creating compressive stress in shell and tensile stress in core will delay fracture of shell and promote shell spallation and smaller fragmentation

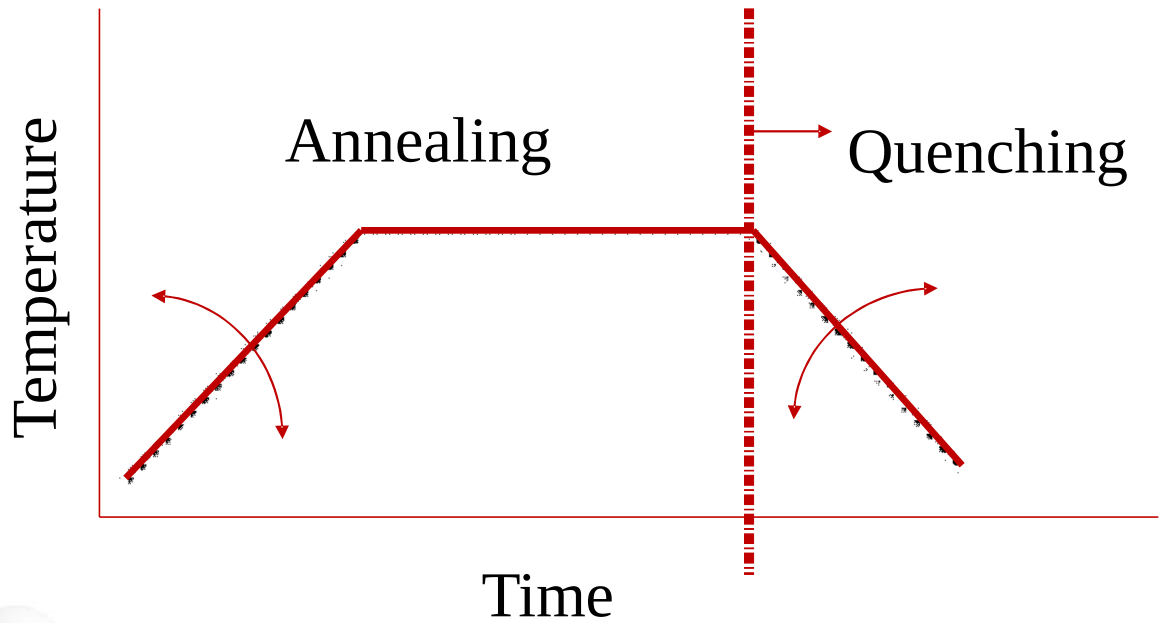
Biaxial strain

$$\epsilon = -\Delta\alpha\,(T_2 - T_1)$$





Relieving Thermal Stresses



- Stress relief can be achieved with thermal treatment:

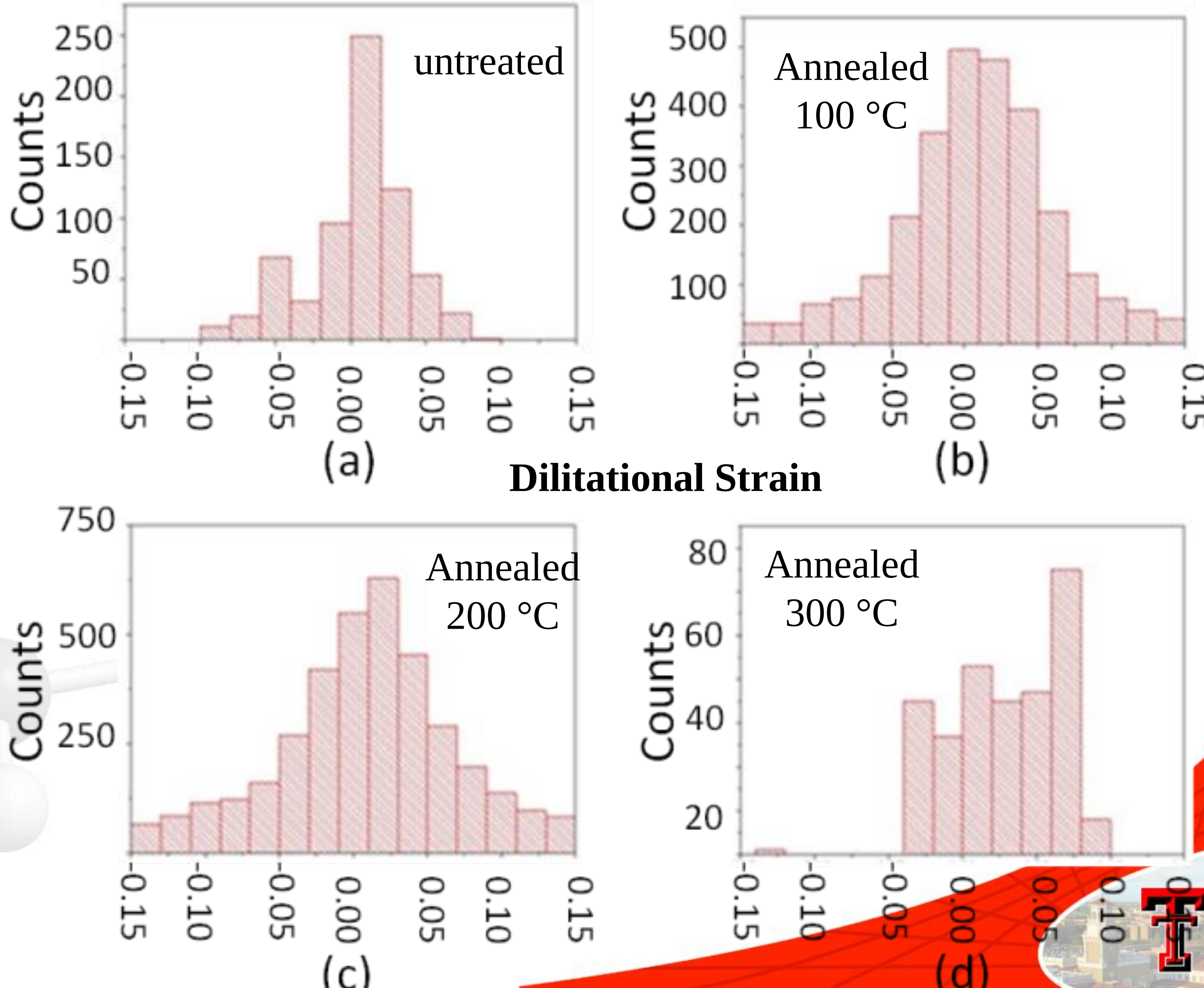
  annealing and quenching – ***apply to particles to effect reactivity***

  - Uniform heating to a prescribed temperature (< 660 ^{o}C) *Recovery*
    - Particles experience a zero-stress state at 300 ^{o}C (*Zachariah* JPC 2012)
  - Holding at prescribed temperature
  - Cool to control stress development and *improve* mechanical properties.

Results: Synchrotron X-ray Diffraction

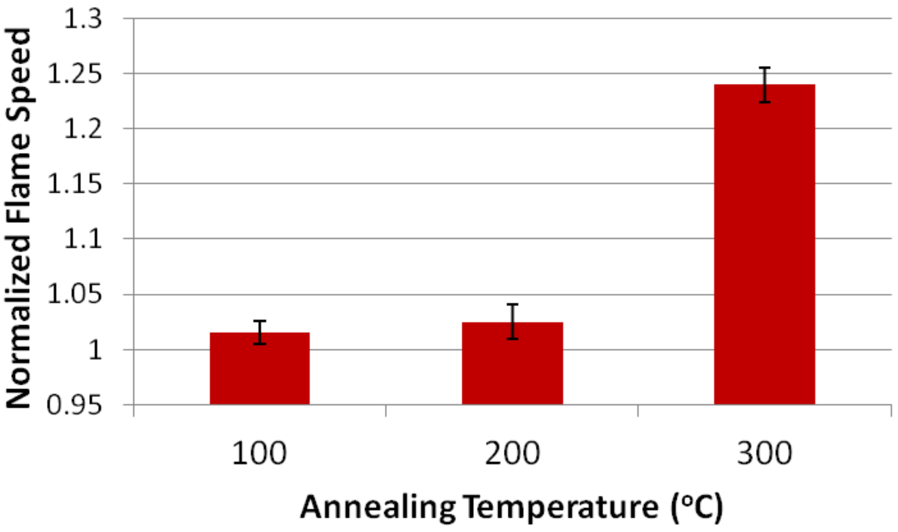
Dr. Nobumichi Tamura – Lawrence Berkeley Laboratory

- Samples annealed to 100 & 200 °C show negligible change in dilatational strain.
- Samples annealed to 300 °C increase by 660% in dilatational strain.



Al+CuO Flame Speeds

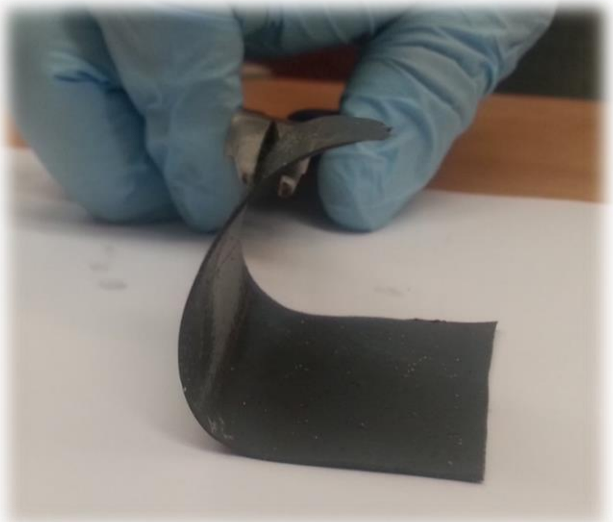
- Flame speeds negligibly effected by annealing to 100 and 200 °C
  - 2-3% increase
- Al annealed to 300 °C shows a 24% increase from the untreated Al
- Synchrotron XRD shows considerable increase in dilatational strain for 300 °C annealing.

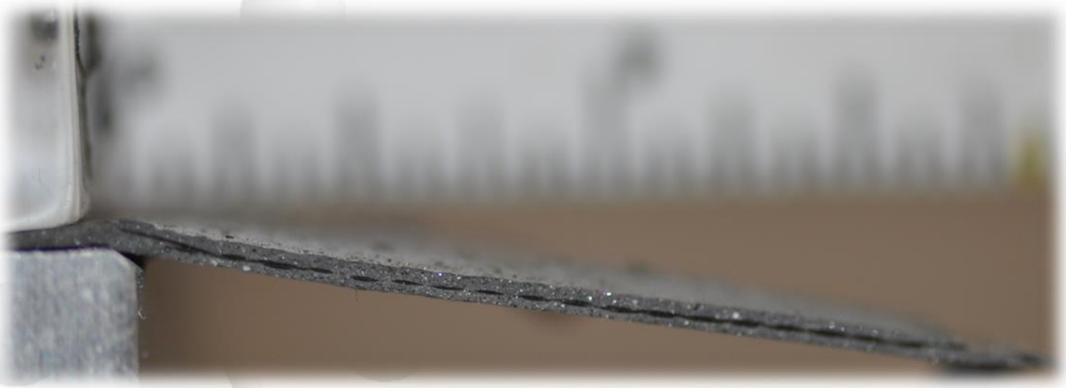


Levitas et al. *Scientific Reports* 2015
Levitas et al. *Journal of Applied Physics* 2015
McCollum et al. *Acta Materialia* In Press

Objectives

- ❑ Synthesize flexible free standing thermite films
  - New approach using blade casting
  - Thermite + binder + solvent + additive
  - Reinforcement fabric included in film
- ❑ Study multiple properties of synthesized films
  - Examine combustion of films using high speed imaging techniques
  - Determine maximum strength and stress of films



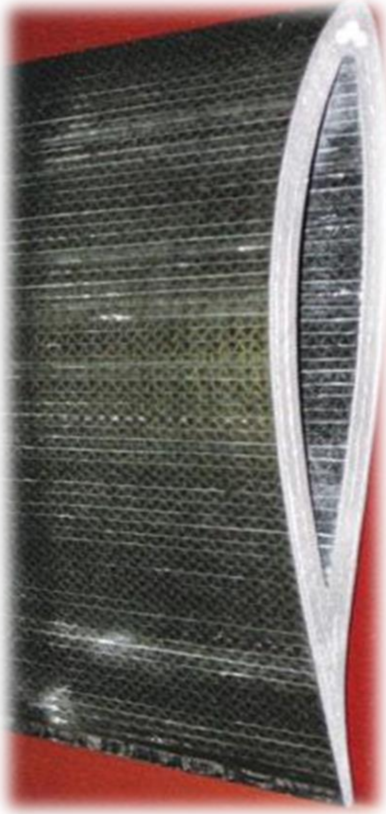


Meeks et al. *Comb Flame* 2013
Meeks et al. *Comb Flame* In Press
Clark et al. *AIP Advances* 2015
Clark et al. *Surf. Coatings & Tech* 2015

Sandia
INL

Materials

- Why Al + MoO_3
  - Al+MoO_3 is a well characterized energetic material
  - Previous study coated substrates[1]
    - Mg+MnO_2+PVDF+NMP
- Why $KClO_4$ as an additive
  - $KClO_4$ enables consistent self propagation
  - Adds heat and increases reaction temp
  - High oxygen content
- Why carbon fiber as a reinforcement fabric
  - Well characterized reinforcement fabric
  - Used in applications needing high strength and low weight



[1]Meeks et al. *Combustion and Flame* 2014

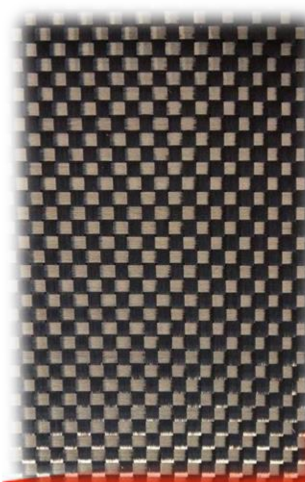
Materials

Material name	Supplier	Average characteristic size (μm)
Al	Nova Centrix (Austin, Tx)	0.080
MoO_3	Alfa Aesar (Ward Hill, Ma)	14.0
$KClO_4$	Sigma Aldrich (St. Louis, Mo)	151.0
Mold Max 30	Smooth-On (Easton, Pa)	liquid
Xylene	Macron Fine Chemicals (Center Valley, Pa)	liquid
Carbon Fiber	ACP Composites (Livermore, Ca)	N/A

Aluminum

Carbon fiber

Potassium Perchlorate

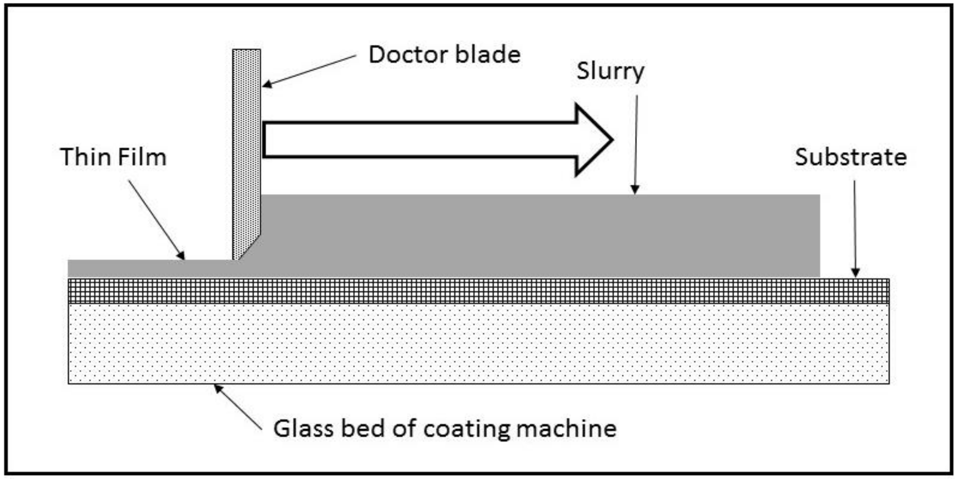


MoO_3

Mold Max 30

Synthesis procedure

- Slurry is mixed using a planetary mixer
- De-aerated in vacuum chamber
- Loaded into the blade casting machine and draw across Mylar™ substrate
- Film is allowed to dry for 24 hours at room temperature
- Film is separated from substrate



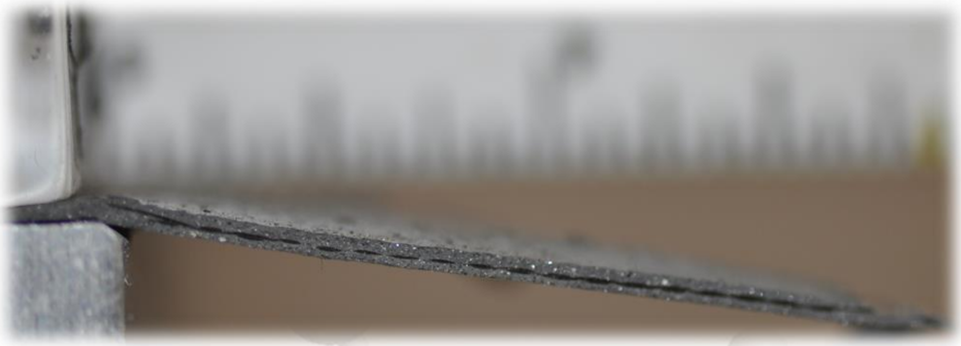
Meeks et al. *Combustion and Flame* 2014

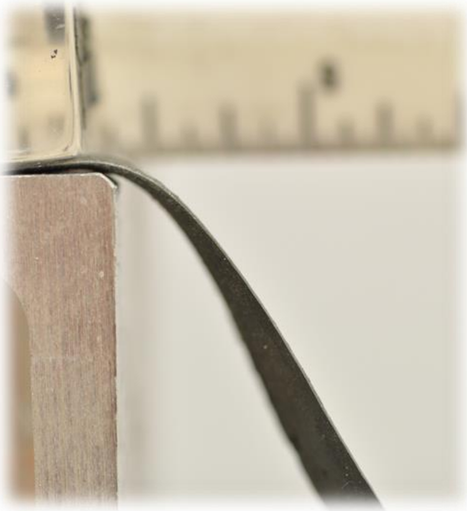
Mechanical property testing

- 20 mm x 63 mm samples cut for mechanical testing
- Films loaded into testing jig on a SATEC 60HVL Universal Testing Machine
- Samples were loaded until taught
- Tensile load of 444.82 N/min applied to samples

Mechanical property testing

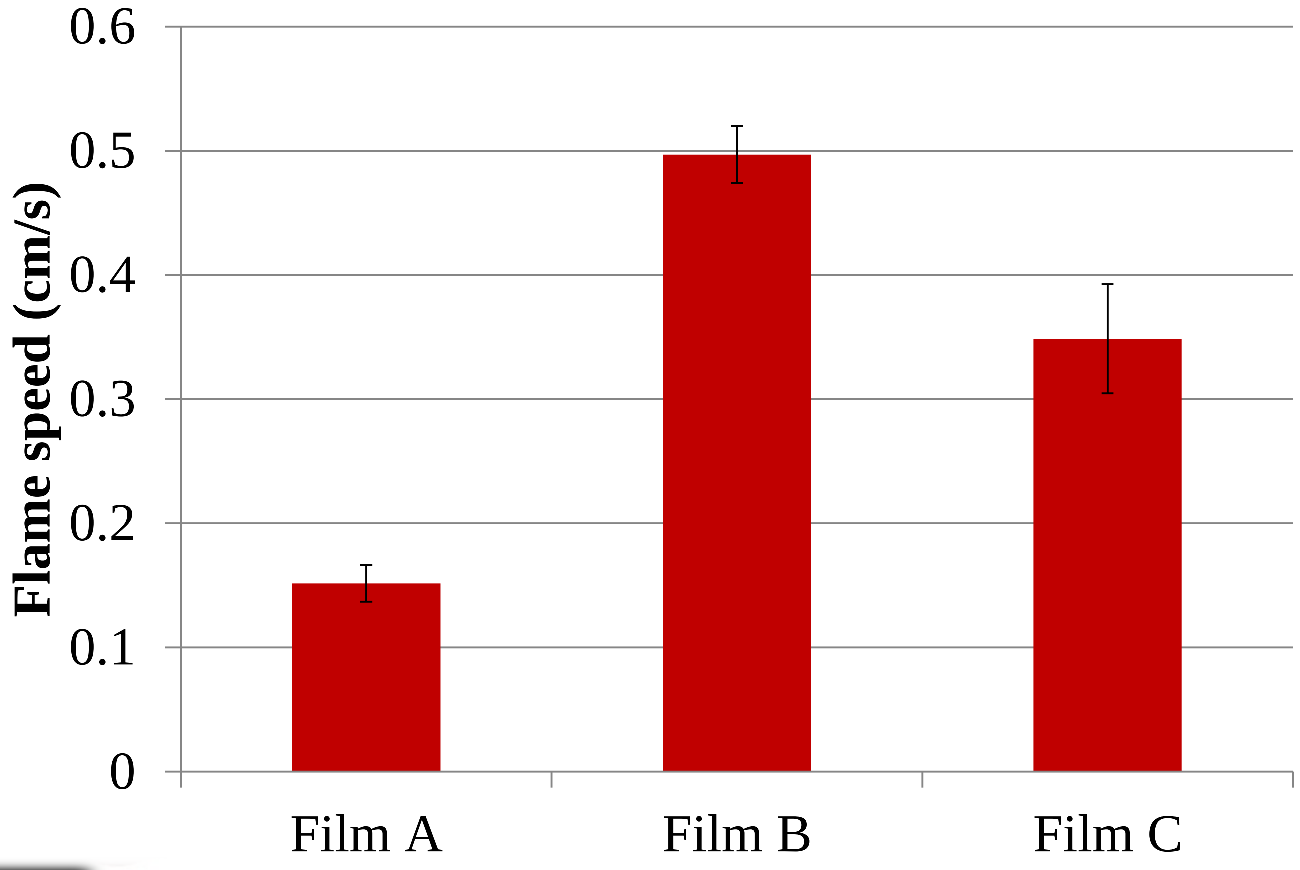
Sample name	Maximum Load (N)	Sigma Maximum (kPa)
Film B	22	861
Film C	709	168420



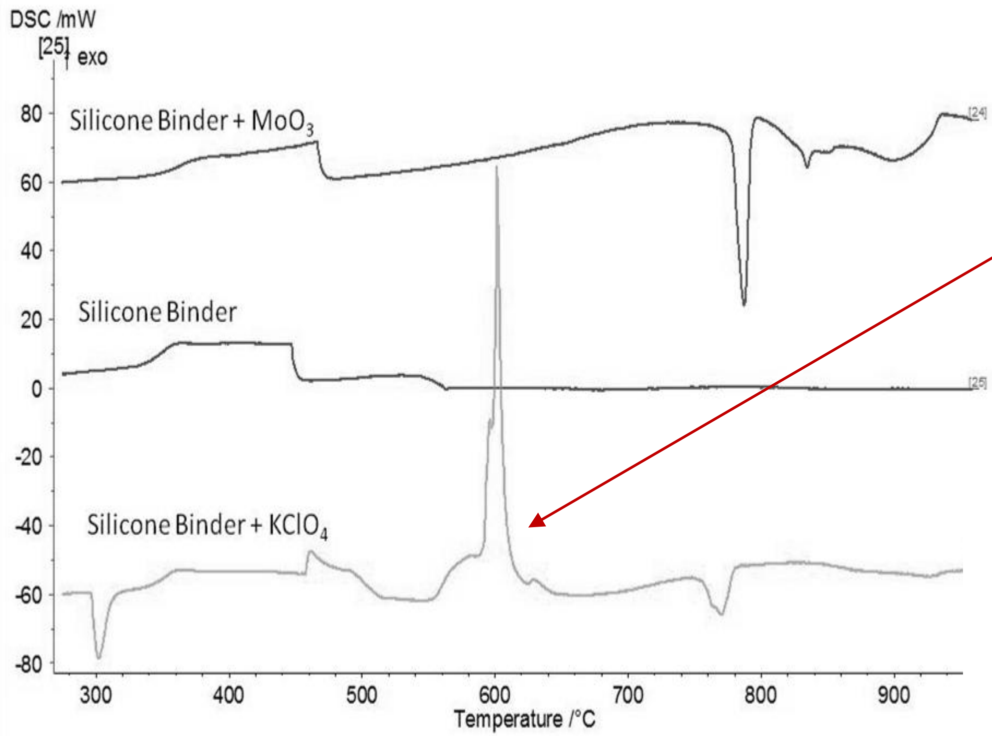


- ❑Film B failed upon initial loading
- ❑Inclusion of reinforcement fabric increases strength by ≈3200%
- ❑Sigma maximum values change drastically due to two factors
  - ❑Increased maximum load held by Film C
  - ❑Decreased cross sectional area

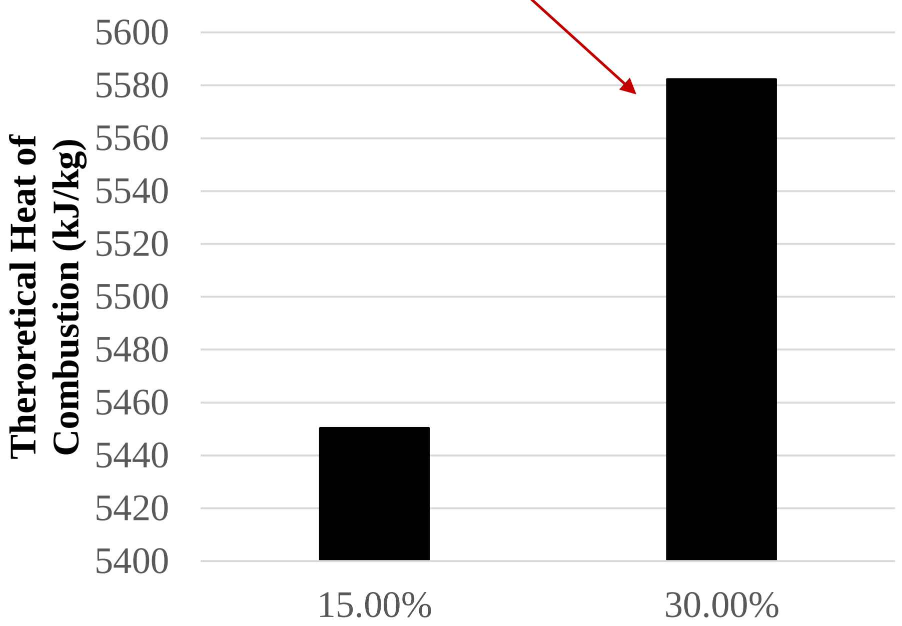
Combustion characterization



Combustion characterization



Silicon binder is reactive as a fuel with KClO4



Future Directions

- New formulations that exploit optimum reactivity
  - Chemistry issues
  - Engineered properties
  - Support scalability – mg → g → kg quantities
- Safety testing
  - Single lab/facility for standardized tests
  - Single lab/facility for environmental impact studies
- Characterization
  - Performance per application
    - Reaction kinetics
    - Gas generation
    - Heat of combustion
    - Flame temperature