Nanoengineered Reactive Materials and their Combustion and Synthesis

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Course Length: 3 hrs

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Abstract

In the nanotechnology community, there has been tremendous progress in the molecular sciences toward the total command of chemistry at all length scales. This progress has been inspired by advances in the structural determination of biological systems. Similar advancements in assembly of molecular and nanoscale elements have been made in the pharmaceutical and microelectronics fields as well. These developments make it clear that in the foreseeable future it will be possible to synthesize any desired macroscopic structure with precise location of every atom. This course examines how nanotechnology methodologies are currently being applied to develop multifunctional smart reactive materials for combustion applications and the combustion methods for materials synthesis.

Outline

- Introduction
- Basics
- Synthesis and Assembly
- Combustion
- Applications

How small is “small”?

- Micrometer and nanometer
  - Both are invisibly small
- Micrometer
  - Size of red blood cell
- Nanometer
  - Size of small molecule
  - Five times the size of the hydrogen atom

S.F. Son and R.A. Yetter, Nanoenergetics, 2012

Reasons for Nanotechnology
"No Small Matter," by Frankel and Whitesides

- Information Technology
  - Smallest parts of transistors are nanoscale
  - Connecting wires are < 40 nm (less than 100 gold atoms laid end to end!)
- Life, and the Cell
  - Single-celled life is 1 to 10 μm
  - Within cells are complex, functional structures
- Physical Measurement at Atomic and Molecular Scale
  - Nanotechnology has driven and been driven by these capabilities
- Unique Properties of Really Small Materials
  - THIS IS WHAT WE CARE MOST ABOUT IN DEVELOPING REACTIVE AND ENERGETIC NANOMATERIALS
  - In a cup there are a million million million million molecules of water (10^{24}) with very few near the surface
  - In a 2 nm droplet there are ~1000 molecules
  - Nano-materials are in between single molecules and a continuum (lots and lots) of molecules
  - They are "all surface"; that is, all the molecules are close to the surface
  - Surface area and diffusion length scales can dramatically affect reactivity and mechanical properties

Frankel and Whitesides, No Small Matter, Belknap/Harvard, 2009

Reasons for Nanotechnology - continued

- Materials
  - Nanoscale phenomena control grain boundaries, behavior of crack tips, voids, and other interfaces
  - We can also make new materials with new properties
    - Self-assembled monolayers, rods or other shapes, tubes, etc.
    - THIS IS BECOMING MORE IMPORTANT IN NANOENERGETICS AND NANO REACTIVE MATERIALS
- Quantum Phenomena
  - Nano is at the scale where quantum effects begin to emerge
- Medicine
  - Nanostructures and nanoscience should be useful in selecting specific cells to destroy or protect, in precise delivery of drugs to tissues, etc.
- Energy and the Environment
  - Nanoscale catalysts are used to convert crude oil to usable fuels
  - Nanoscale particles naturally formed are important in cloud formation
  - NANOENERGETICS CAN APPLY TO ENERGY APPLICATIONS
    - e.g., ultra high surface area metal foams made via combustion synthesis for catalysts or hydrogen storage
  - Risks? Certainly. Safety is a current area of research.

Frankel and Whitesides, No Small Matter, Belknap/Harvard, 2009 S.F. Son and R.A. Yetter, Nanoenergetics, 2012

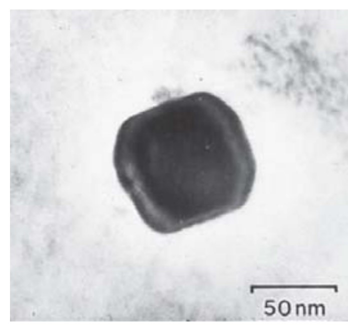
What Nanotechnology Is NOT

- It is not a panacea
  - It does NOT solve all materials problems
  - For energetic and reactive materials, it can potentially be a game changer with respect to kinetics (ignition and reaction times)
    - It generally will not change the energy content, but could allow some reactives that could not be considered otherwise (nSi is an example)
  - ***"Nano is sexy, but micro still pays many of the bills."*** - Frankel and Whitesides
- Nanotechnology is new, right?
  - Roman cup, Mayan paint, car tires, stop lights, etc., all use(d) nanomaterials
  - SEMs, TEMs, AFM, etc. make difference today! We've only been able to image nanomaterials for a few decades

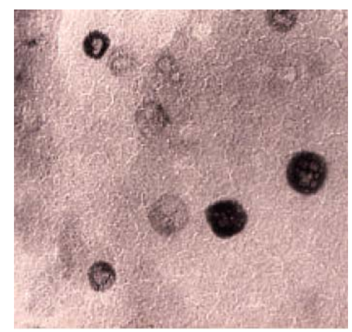
S.F. Son and R.A. Yetter, Nanoenergetics, 2012

The Lycurgus Cup – A Roman Nanotechnology

- When illuminated from outside, it appears green
- However, when illuminated from within the cup, it glows red
- Colloids of gold and silver alloy nanoparticles (~ 50-100 nm) with a Ag/Au ratio of 7:3 scatter/absorb light yielding the dichroic effects.
- The transmitted red color is due to tiny gold particles embedded in the glass, which have an absorption peak at around 520 nm. The reflected greenish color results from the silver particles.



TEM of silver-gold alloy particle within glass



TEM of sodium chloride particles within glass

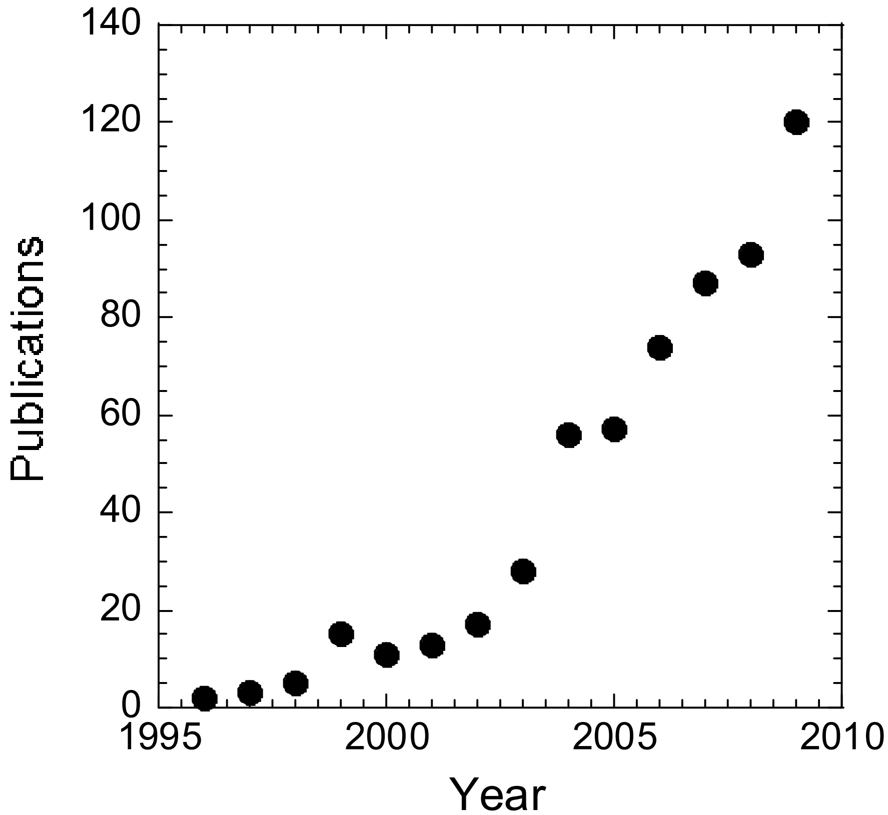
Freestone, I., Meeks, N., Sax, M., Higgitt, C., Gold Bulletin, 40, 4, 270,2007

S.F. Son and R.A. Yetter, Nanoenergetics, 2012

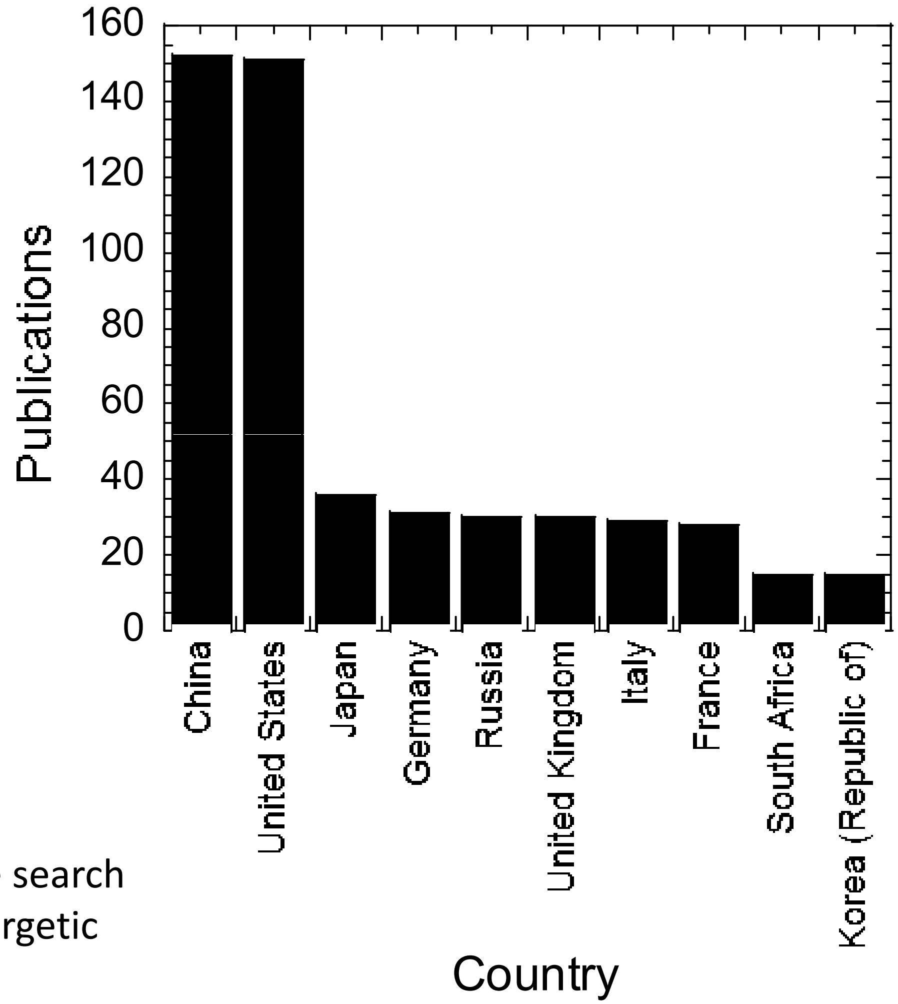
Why Combustion and Nanotechnology?

Combustion and Nanotechnology

Number of publications devoted to fuels and energetic materials

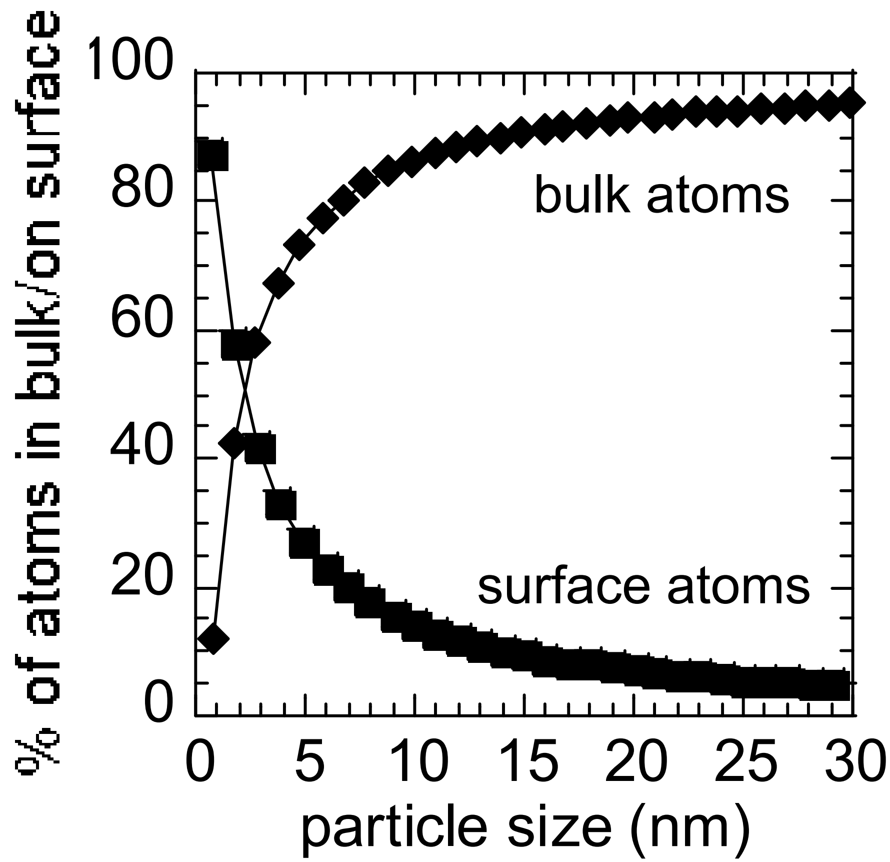


Where are they being studied?



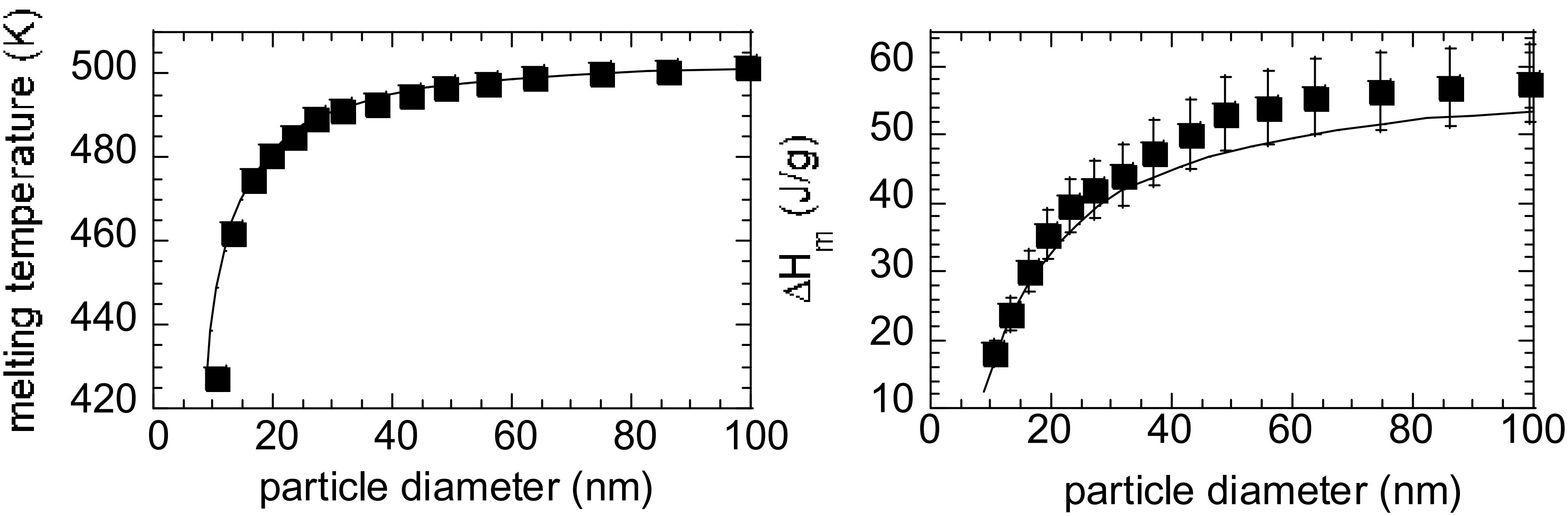
Number of publications by year and country for the search terms “nano” AND (“fuel” OR “propellant” OR “energetic material” OR “explosive”) from 1996-2010.

Surface to Bulk Atom Ratio for Spherical Iron Crystals



K.J. Klabunde, J. Stark, O. Koper, C. Mohs, D.G. Park, S. Decker, Y. Jiang, I. Lagadic and D.J. Zhang, *J. Phys. Chem*. 100, (1996) 12142-12153.

Melting Point and Normalized Heat of Fusion for Tin Nanoparticles



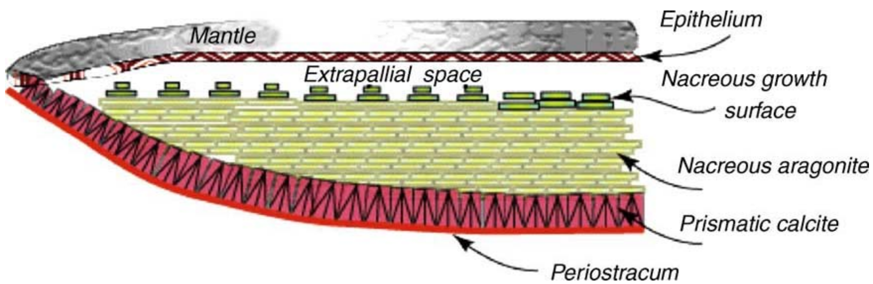
S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath, and L.H. Allen, *Phys. Rev. Lett*. 77 (1996) 99-102.

<u>For aluminum particles</u>:
Alavi, S. and Thompson, D.L., *JPC A* 110, 1518, 2006.
Puri, P. and Yang, V., *JPC C* 110, 11776, 2007. Also AIAA 2008-938 and AIAA 2007-1429.

Other Features of Nanoparticles

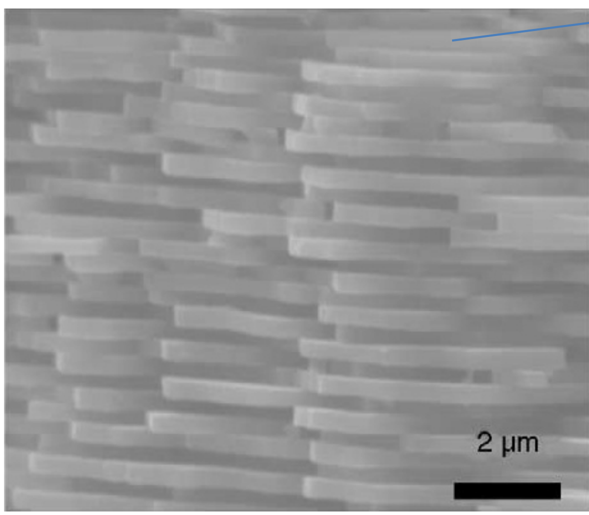
- Increased specific surface area
- Increased reactivity
- Increased catalytic activity
- Lower melting temperatures
- Lower sintering temperatures
- Superparamagnetic behavior
- Superplasticity

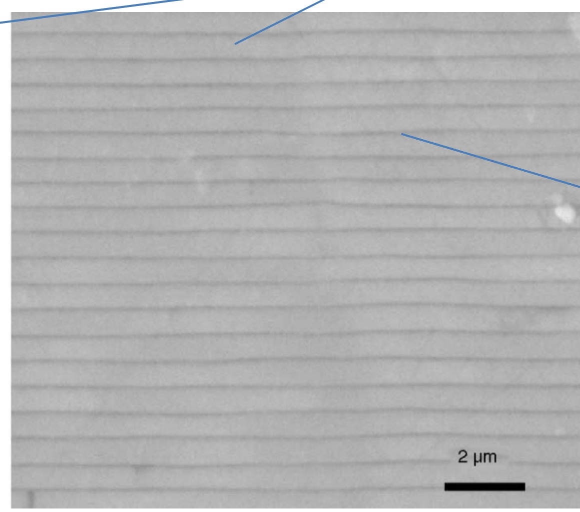
Structure of the Abalone Shell



Structure of the *nacre:*
95 wt.% inorganic material
5 wt.% organic material

inorganic layers: $CaCO_3$ - aragonite

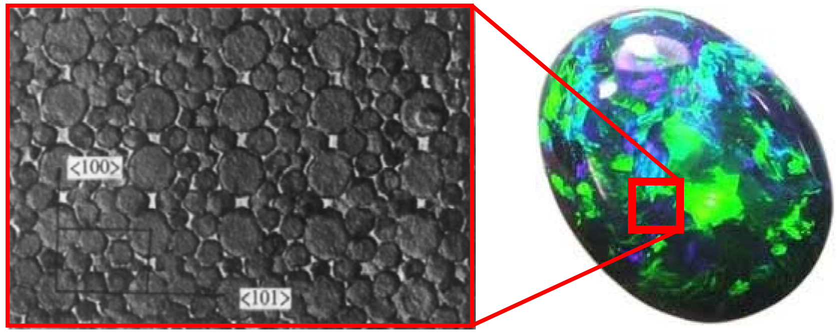




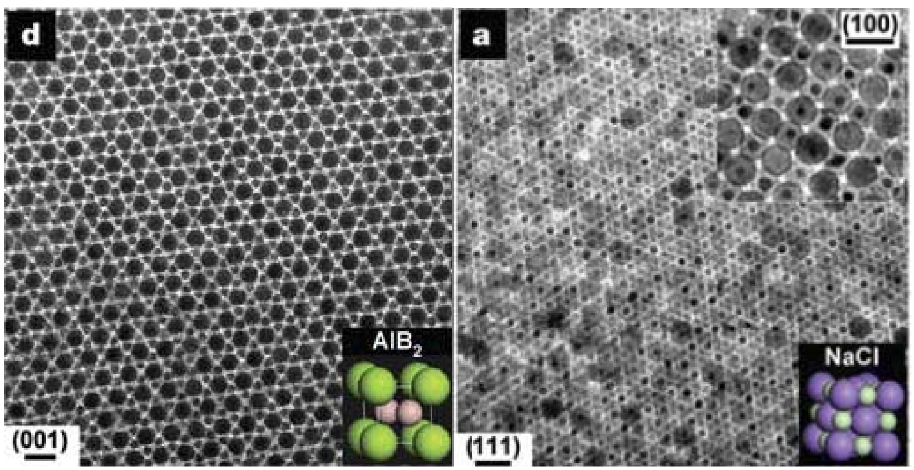
organic layers:

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

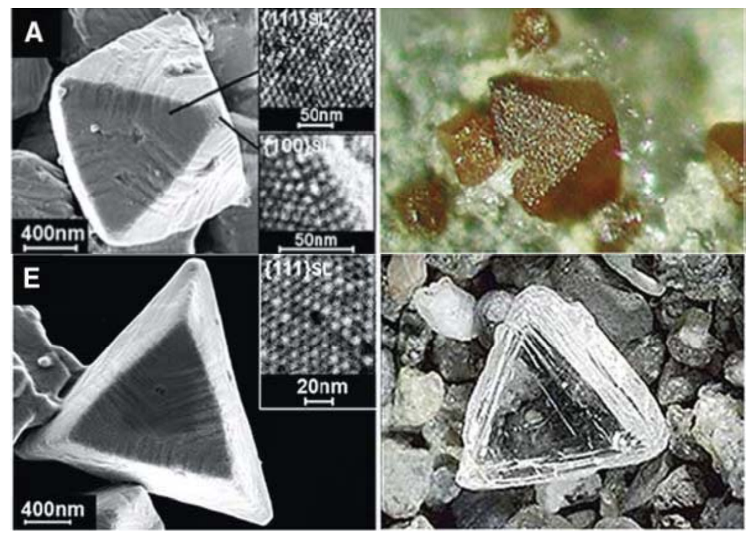
Nanoparticle Self-Assembly



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



Shevchenko, E. V., Talapin, D. V., Kotov, N. A., O'Brien, S., Murray, C. B., *Nature* v439, 2006

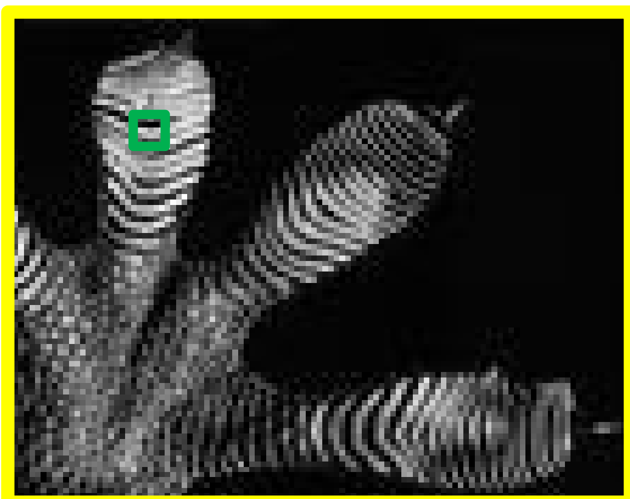


Kalsin, A. M., Fialkowski, M., Paszewski, M., Smoukov, S. K., Bishop, K. J., Grzybowski, B. A., *Science* v312, 2006

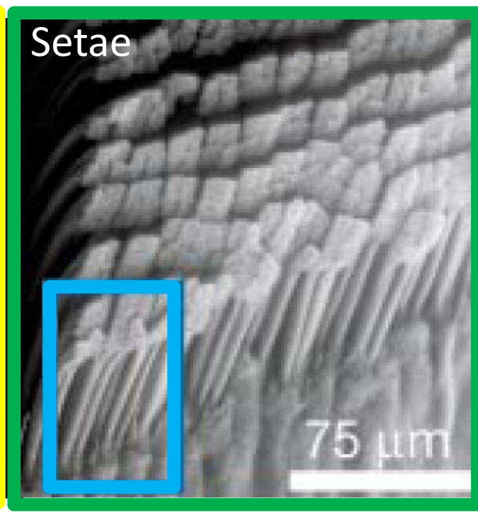
Multiscale Structures

Gecko foot-hair micro/nano-structures

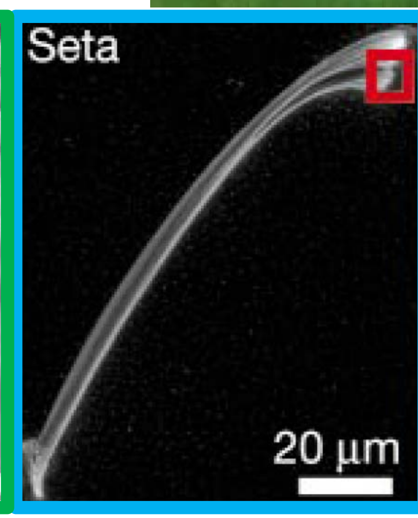
- Climb rapidly up smooth vertical surfaces
- Foot sticking and releasing mechanism critical
- Compliant micro- and nanoscale high aspect ratio beta-keratin structures at their feet to adhere to any surface with a pressure controlled contact area
- Adhesion is due mainly to molecular forces (van der Waals forces)



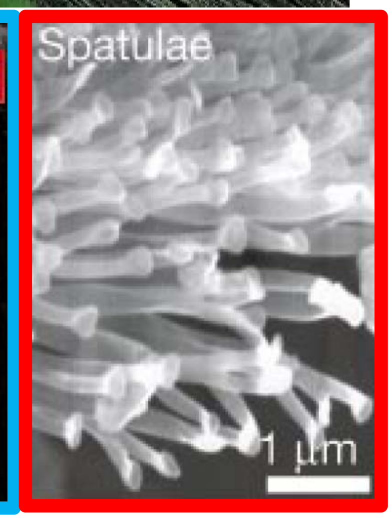
Gecko foot



Rows of setae from a toe



Single seta

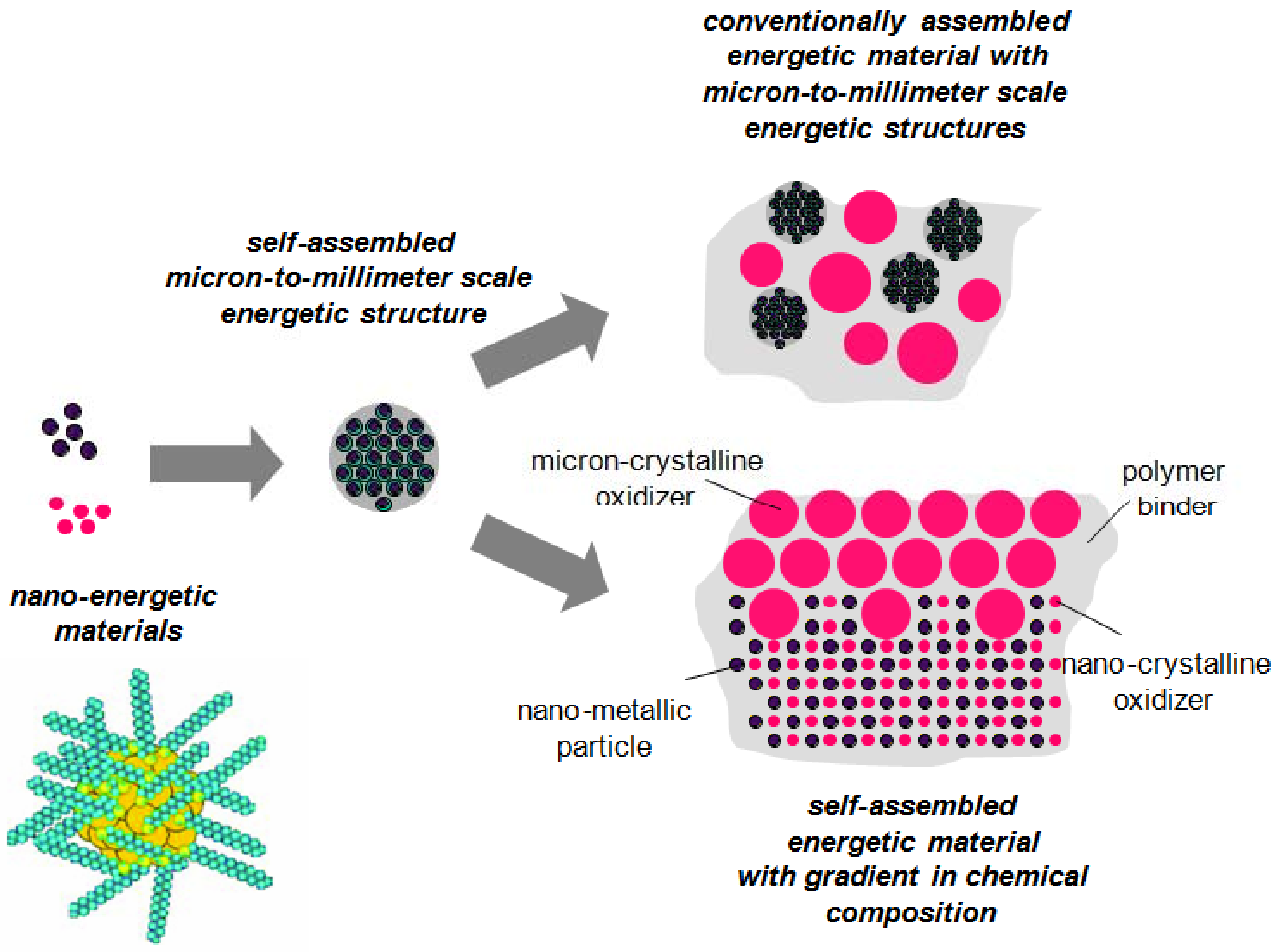


Finest terminal branch of seta called spatulae

- Foot hairs start from the micrometer scale (stalks or seta) and go down to 100-200 nm diameter (spatular stalks) by branching.
- Each foot has ~ 500k setae, each 30-130µm long with 100's of spatular stalks.
- At the ends of the spatular stalks are oriented caps (spatulae) with diameters of 300-500 nm.

Autumn, K., *et al.,* Nature, 405, 681-684, 2000

Organization and Assembly at the Nanoscale: Example of an Energetic Material



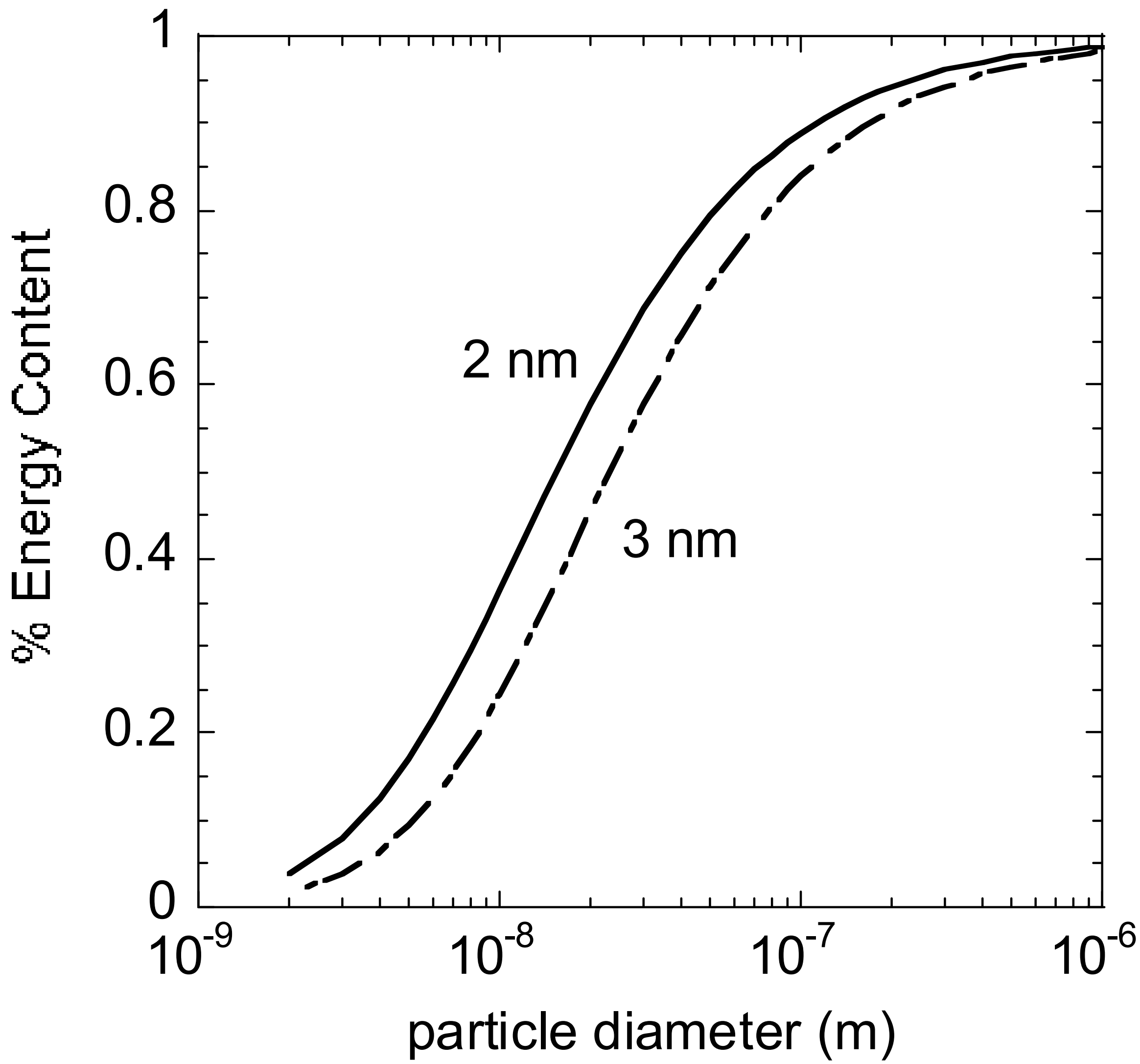
Probing Questions

- Limited fundamental understanding of which type of supramolecular structures provide desirable performance in combustion, mechanical, and hazard characteristics.
- How do we systematically prepare fuel nanostructures with controlled shapes and sizes?
- What are the desirable shapes and sizes of these nanostructures?
- What kind of synthetic passivation layers are needed to produce rugged systems resisting oxidation during storage, while decreasing sensitivity?
- What sorts of oxidizer nanostructures can be synthesized?
- Given fuel nanostructure, what are the best forms for the oxidizer: fuel coatings, oxidizer nanostructures, or polymer matrix oxidizer?

Probing Questions – cont'd

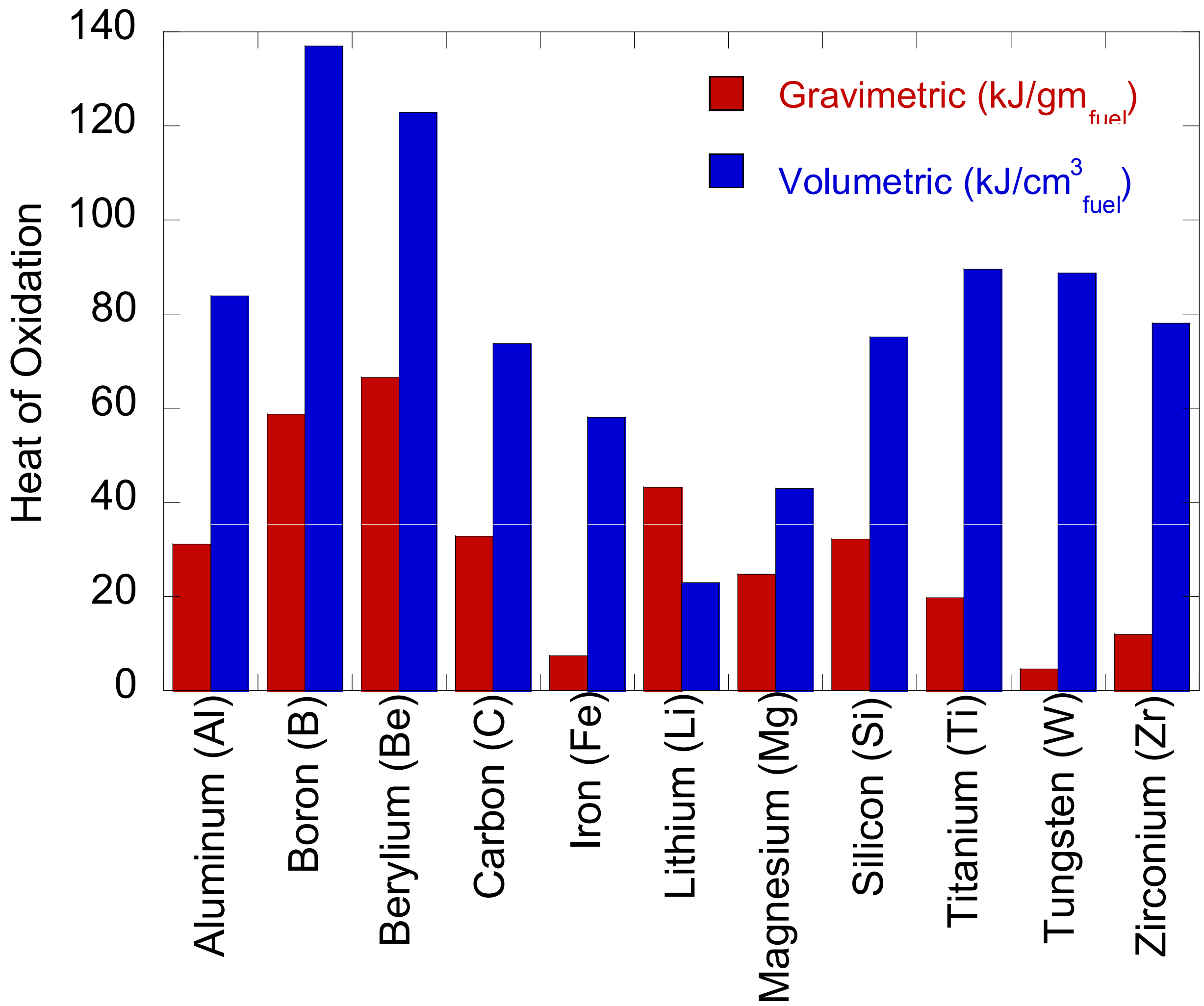
- At what length scales do chemical reaction dynamics become significant/dominant?
- What structures allow us to control the rate of energy release over a wide range of conditions: passivation layers, 3D architectures, or concentration gradients?
- What structures lead to focused or directional energy release?
- What structures lead to reduced sensitivity?
- What are the fundamental mechanisms of initiation? How do thermal and shock initiation differ?
- What structures lead to detonation?
- Can the structures be made smart?
- How best to couple the output of nanoenergetics to usable functions (e.g., power, mechanical force, desired chemicals)

Energy Content as a Function of Particle Diameter



Some Basics

Heats of Oxidation of Several Materials



Thermodynamic Considerations

- For oxygen containing environments, early studies (Glassman, Von Grosse and Conway) recognized
  - The importance of the volatility of the metal vs the metal oxide
  - The relationship between the energy required to gasify the metal or metal oxide and the overall energy available from the oxidation reaction – a limiting flame temperature

$$\Delta H_{vap\text{-}dissoc} > Q_R - (H^o_{T,vol} - H^o_{298}) = \Delta H_{avail}$$

Glassman, Combustion, Academic Press, 3rd Edition, 1996

Thermodynamic Considerations – Cont'd

Metal	T_{bp} (K)	Oxide	T_{vol} (K)	$\Delta H_{f,298}$ (kJ/mol)	ΔH_{vol} (kJ/mol)	H_{Tvol}-H_{298} + ΔH_{vol} (kJ/mol)
Al	2791	Al_2O_3	4000	-1676	1860	2550
B	4139	B_2O_3	2340	-1272	360	640
Be	2741	BeO	4200	-608	740	1060
Cr	2952	Cr_2O_3	3280	-1135	1160	1700
Fe	3133	FeO	3400	-272	610	830
Hf	4876	HfO_2	5050	-1088	1014	1420
Li	1620	Li_2O	2710	-599	400	680
Mg	1366	MgO	3430	-601	670	920
Si	3173	SiO_2	2860	-904	606	838
Ti	3631	Ti_3O_5	4000	-2459	1890	2970
Zr	4703	ZrO_2	4280	-1097	920	1320

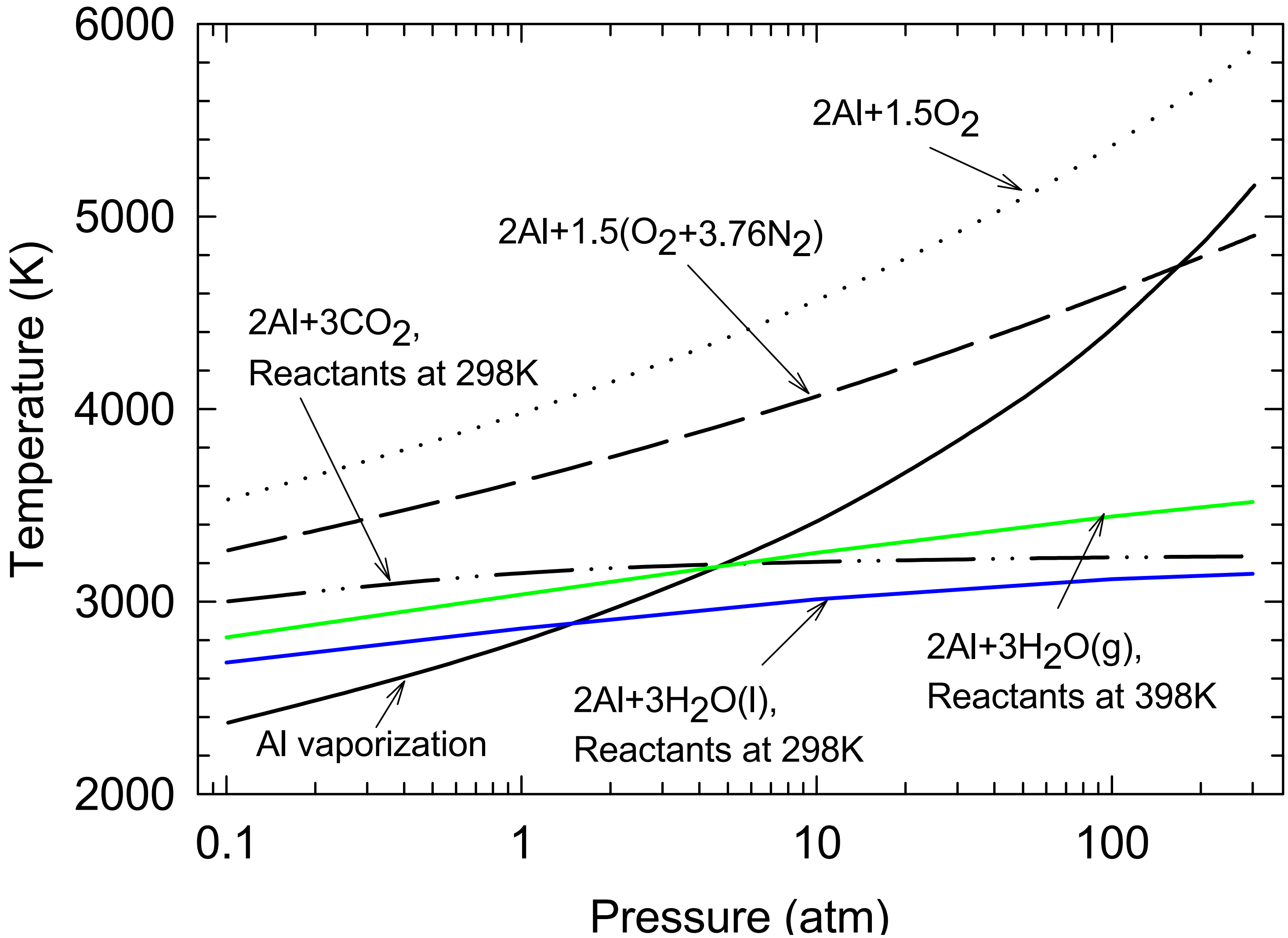
Glassman, Combustion, Academic Press, 3rd Edition, 1996

Classification of Metal Combustion

I	Volatile Product				Nonvolatile product			
II	Volatile metal Gas-phase combustion		Nonvolatile metal Surface combustion		Volatile Metal Gas-phase combustion		Nonvolatile Metal Surface or condensed phase combustion	
III	Soluble	Nonsoluble	Soluble	Nonsoluble	Soluble	Nonsoluble	Soluble	Nonsoluble
	Product may dilute metal during burning and cause disruption if its boiling point exceeds that of metal	No flux of product to metal	Product may build up in metal during burning	No product penetration into metal	If product returns to metal it may dilute it and cause disruption	Disruption strongly favored if product returns to metal	Metal may diffuse through growing product layer, purely condensed phase combustion possible	Product coating makes ignition difficult

F.A. Williams, "Some Aspects of Metal Particle Combustion," Physical and Chemical Aspects of Combustion: A Tribute to Irv Glassman, F.L. Dryer and R.F. Sawyer, eds., Gordon and Breach, The Netherlands, 1997, pp. 267-289.

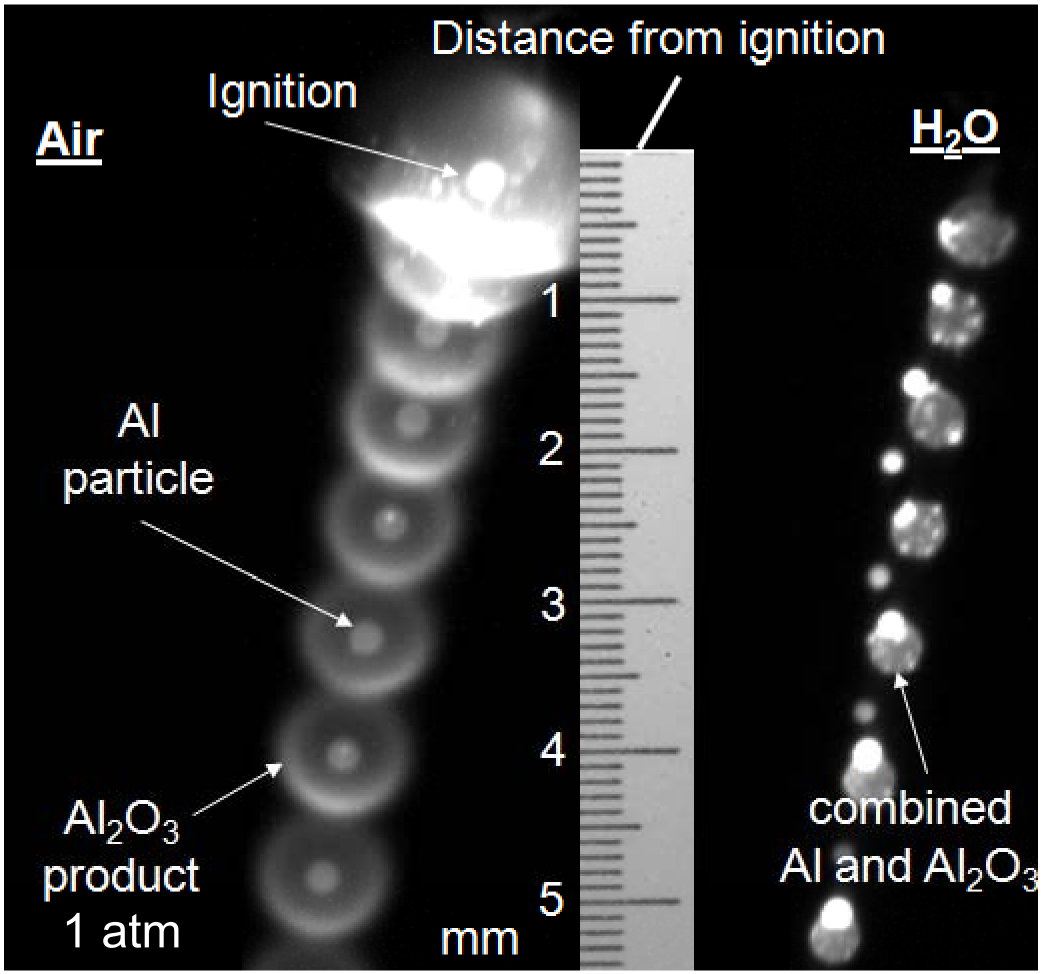
Thermodynamic Considerations – Effect of Pressure and Oxidizer



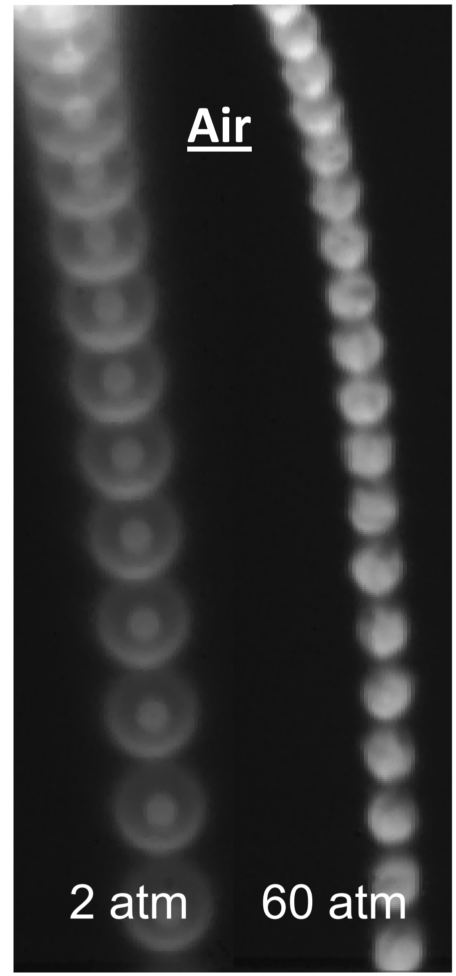
Glassman and Yetter, Combustion, Academic Press, 4th Edition, 2008

Micron Aluminum Particle Combustion

Oxidizer Effects



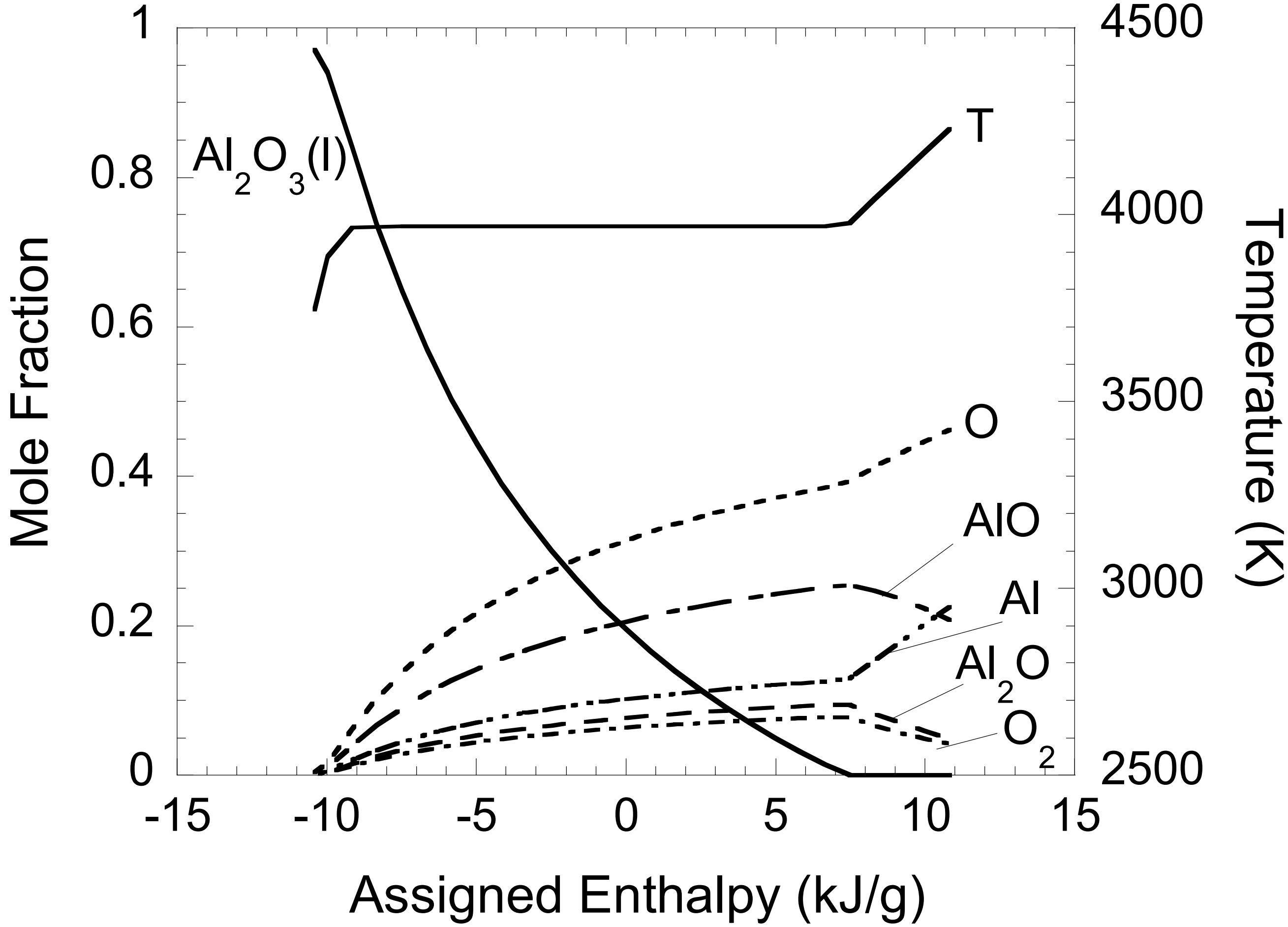
Pressure Effects



R.A. Yetter and F.L. Dryer, in Fire in Free Fall: Microgravity Combustion, H. Ross, Ed., Academic Press, Chapter 6, 2001.

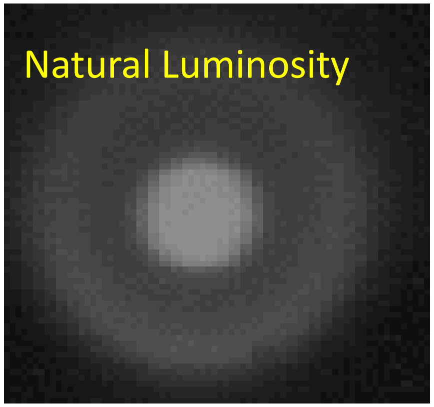
Equilibrium Product Composition and Temperature vs. Input Enthalpy

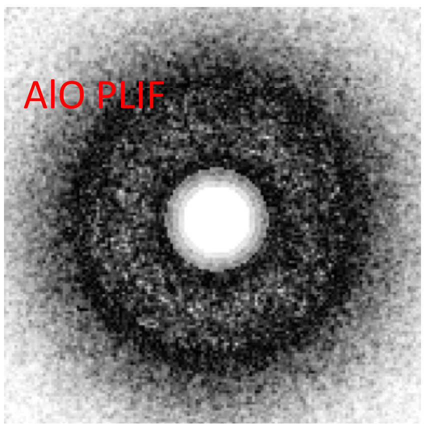
Stoichiometric Mixture of Al and O_2 at 298 K and 1 atm

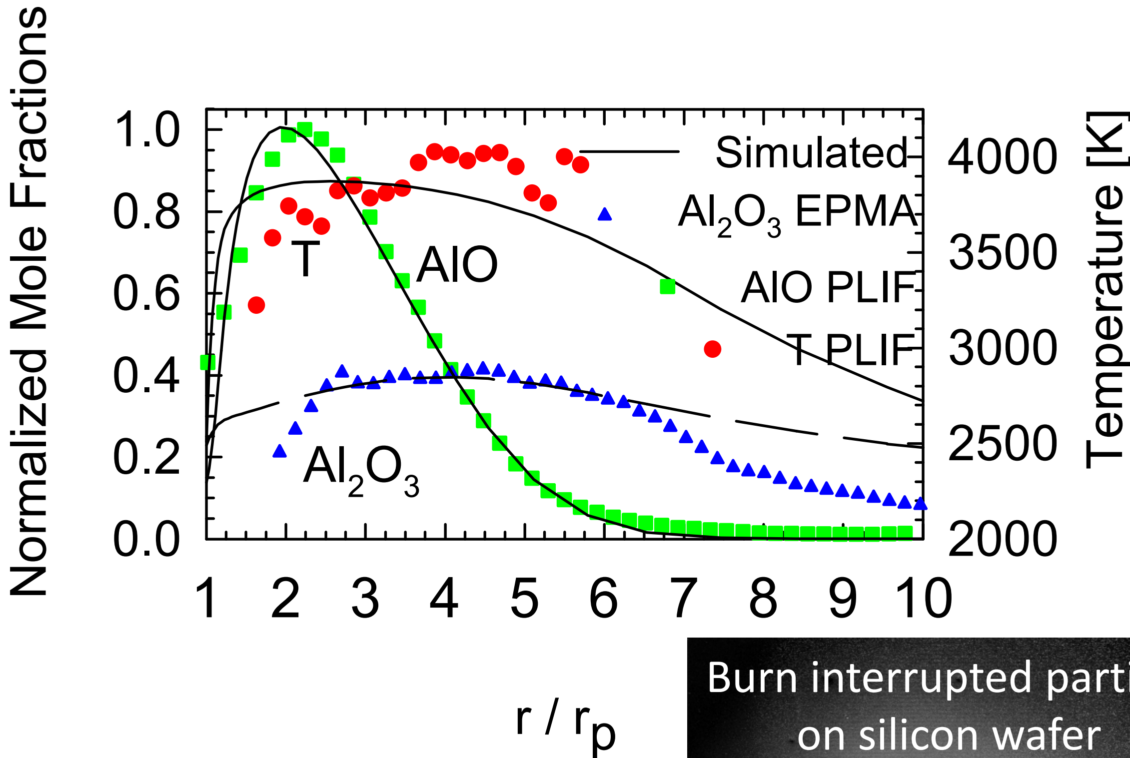


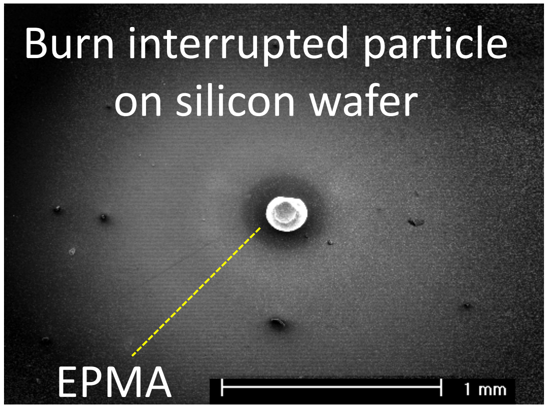
Glassman, Combustion, Academic Press, 3rd Edition, 1996

Flame Structure of Micron Aluminum Particle Burning in Air









Bucher, P., *et al*. *Proc. Combust. Inst.*, 27, 2421, 1998.

Thermodynamics of Combustion Synthesis

Heats of Formation of Chlorides		
Chloride	ΔH_f^o, 298K (kJ/mol)	Per Cl atom
CsCl	-443	-443
KCl	-437	-437
$BaCl_2$	-859	-430
RbCl	-430	-430
$SrCl_2$	-829	-415
NaCl	-411	-411
LiCl	-408	-408
$CaCl_2$	-796	-398
$CeCl_3$	-1088	-362
$AlCl_3$	-706	-235
$TiCl_4$	-815	-204
$SiCl_4$	-663	-166

$MCl_x + xNa \rightarrow xNaCl + M$

Heats of Formation of Nitrides		
Nitride	ΔH_f^o, 298K (kJ/mol)	Per Natom
HfN	-369	-369
ZrN	-365	-365
TiN	-338	-338
AlN	-318	-318
BN	-251	-251
Mg_3N_2	-461	-231
Si_3N_4	-745	-186
Li_3N	-165	-165
N_2	0	0
NaN_3	22	7

$MCl_x + xNa + (y/2)N_2 \rightarrow xNaCl + MN_y$

$M'Cl_x + nM''Cl_y + (x + ny)Na \rightarrow (x + ny)NaCl + M'M_n''$

Glassman, Combustion, Academic Press, 3rd Edition, 1996

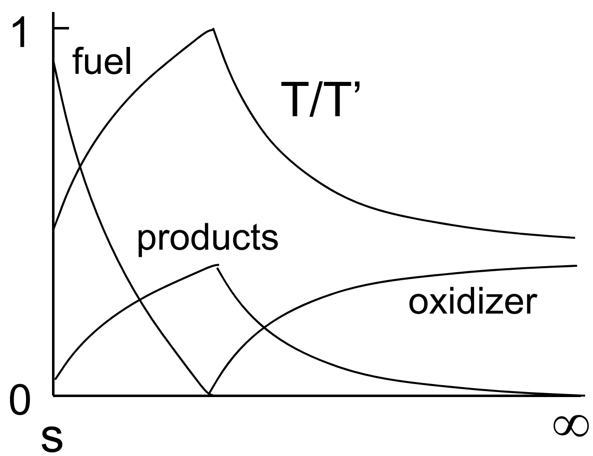
Examples of Energy Content of Thermite and Intermetallic Reactions

Reactants	Heat of Reaction		Reactants	Heat of Reaction	
	cal/g	cal/cm^3		cal/g	cal/cm^3
TNT	649	1073	TNT	649	1073
2Al + 3CuO	974	4976	Al + Ni	330	1706
2Al + MoO_3	1124	4279	Al + Pd	327	2890
2Al + 3NiO	822	4288	2B + Hf	401	3303
Si + 2CuO	762	4354	B + Ti	670	2558
3Si + 2MoO_3	720	3000	3Si + 5Ti	428	1590
Si + 2NiO	569	3420	C + Ti	736	2760
C + 2CuO	11	66	C + Zr	455	2400

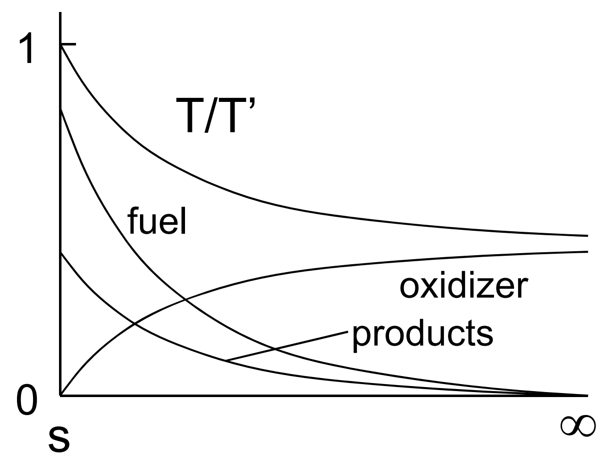
Fischer, S.H. and Grubelich, M.C., 32nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Lake Buena Vista, Fl, July 1-3, 1996.

Modes of Particle Combustion

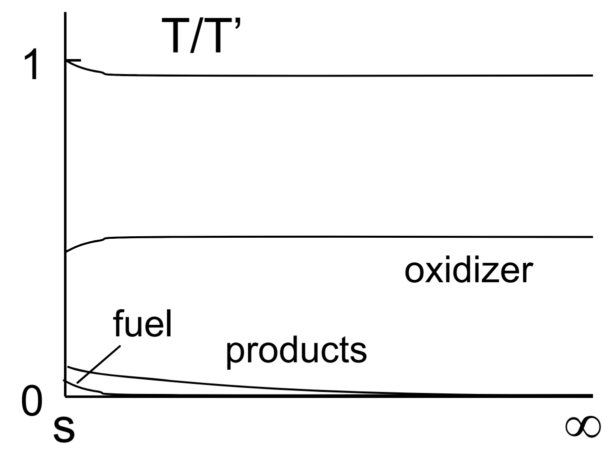
Diffusion-Controlled
with Envelope Flame



Diffusion-Controlled
without Envelope Flame



Kinetically-Controlled



Diffusion vs Kinetic Control

Diffusion controlled combustion with vaporization or surface reaction

$$t_{b,diff} = \frac{\rho_p d_0^2}{8\rho D\, ln(1+B)} \qquad t_{b,diff} = \frac{\rho_p d_0^2}{8\rho D\, ln(1+iY_{O,\infty})}$$

Kinetic controlled surface reaction

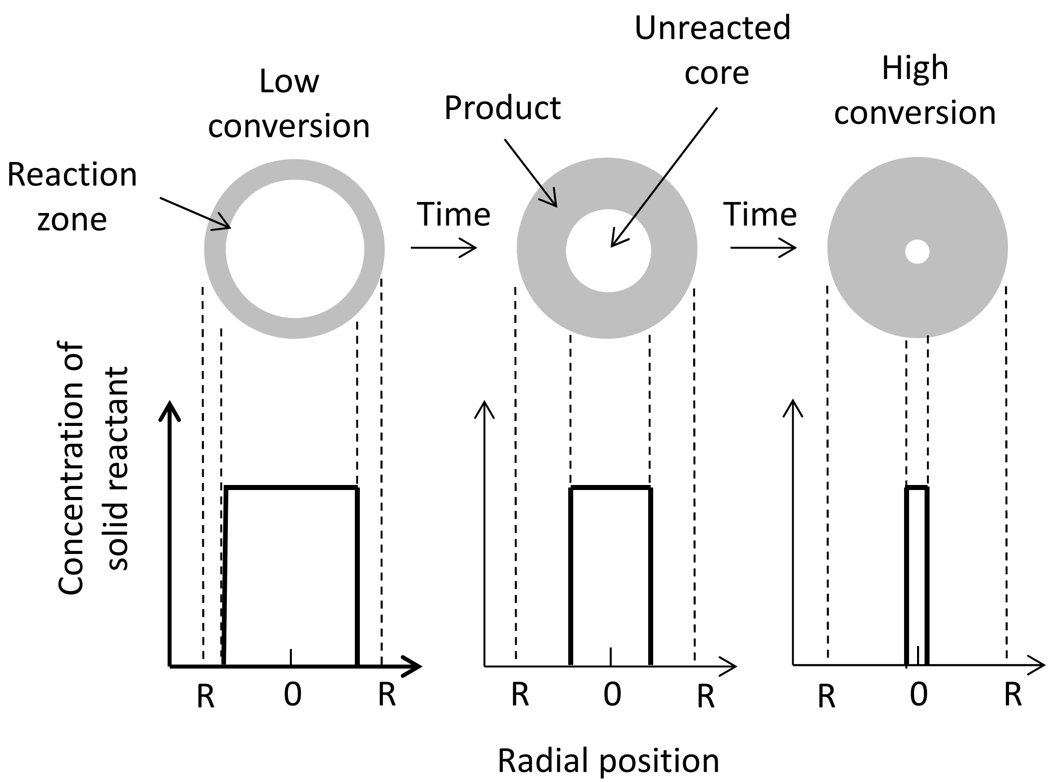
$$t_{b,kin} = \frac{\rho_p d_0}{2MW_p k P X_{O,\infty}}$$

As particle size is decreased, two conditions defined by Da =1 and Kn =1 arise

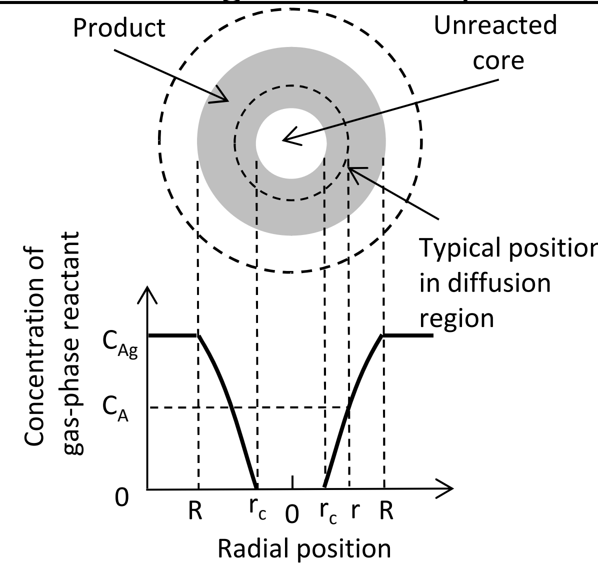
$$Da = \frac{t_{b,diff}}{t_{b,kin}} = \frac{MW_p k P d_0 X_{O,\infty}}{4\rho D\, ln(1+iY_{O,\infty})}$$

$$Kn = \frac{2\lambda}{d_p} \qquad \lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N} \qquad \lambda = \frac{2\mu}{P\left(\frac{8MW}{\pi RT}\right)^{1/2}}$$

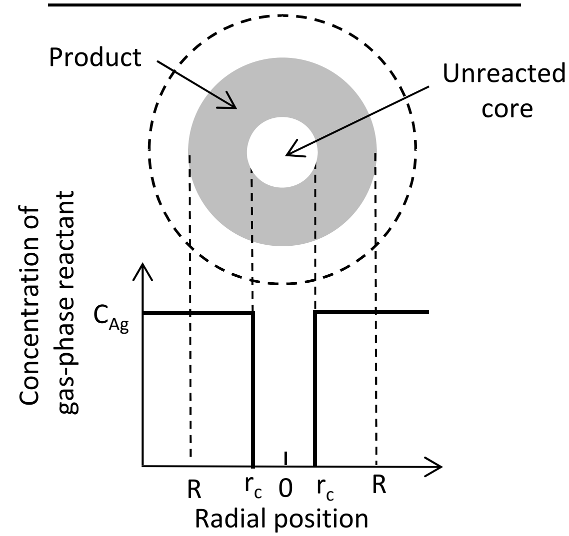
Shrinking Core Model for Spherical Particles of Unchanging Size



Diffusion through Product Layer Controls



Chemical Reaction Controls



See for example, Levenspiel, O., Chemical Reaction Engineering, Third Edition, J. Wiley and Sons, 1999

Shrinking Core Model for Spherical Particles of Unchanging Size

Diffusion through Product Layer Controls

$$\tau = \frac{\rho_p R^2}{6bDC_{Ag}}$$

$$\frac{t}{\tau} = 1 - 3\left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^3$$

$$\frac{t}{\tau} = 1 - 3(1-X)^{2/3} + 2(1-X)$$

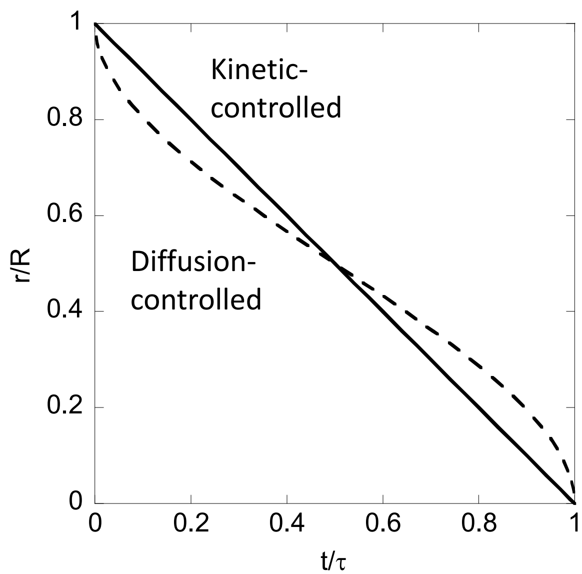
Chemical Reaction Controls

$$\tau = \frac{\rho_p R}{bkC_{Ag}}$$

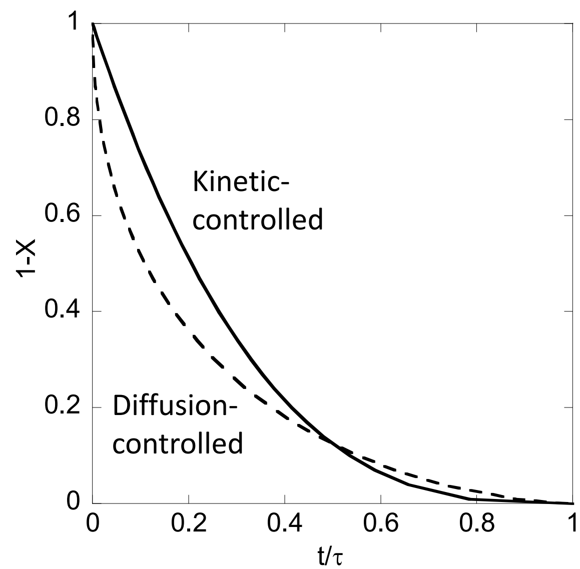
$$\frac{t}{\tau} = 1 - \frac{r}{R}$$

$$\frac{t}{\tau} = 1 - (1-X)^{1/3}$$

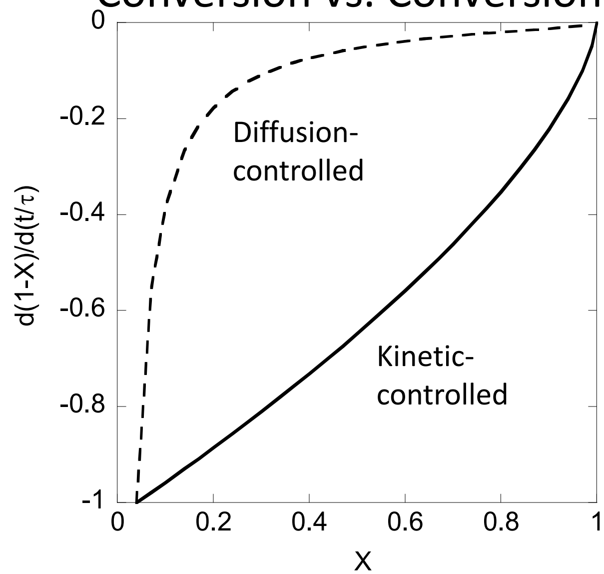
Radius vs. Time



Conversion vs. Time

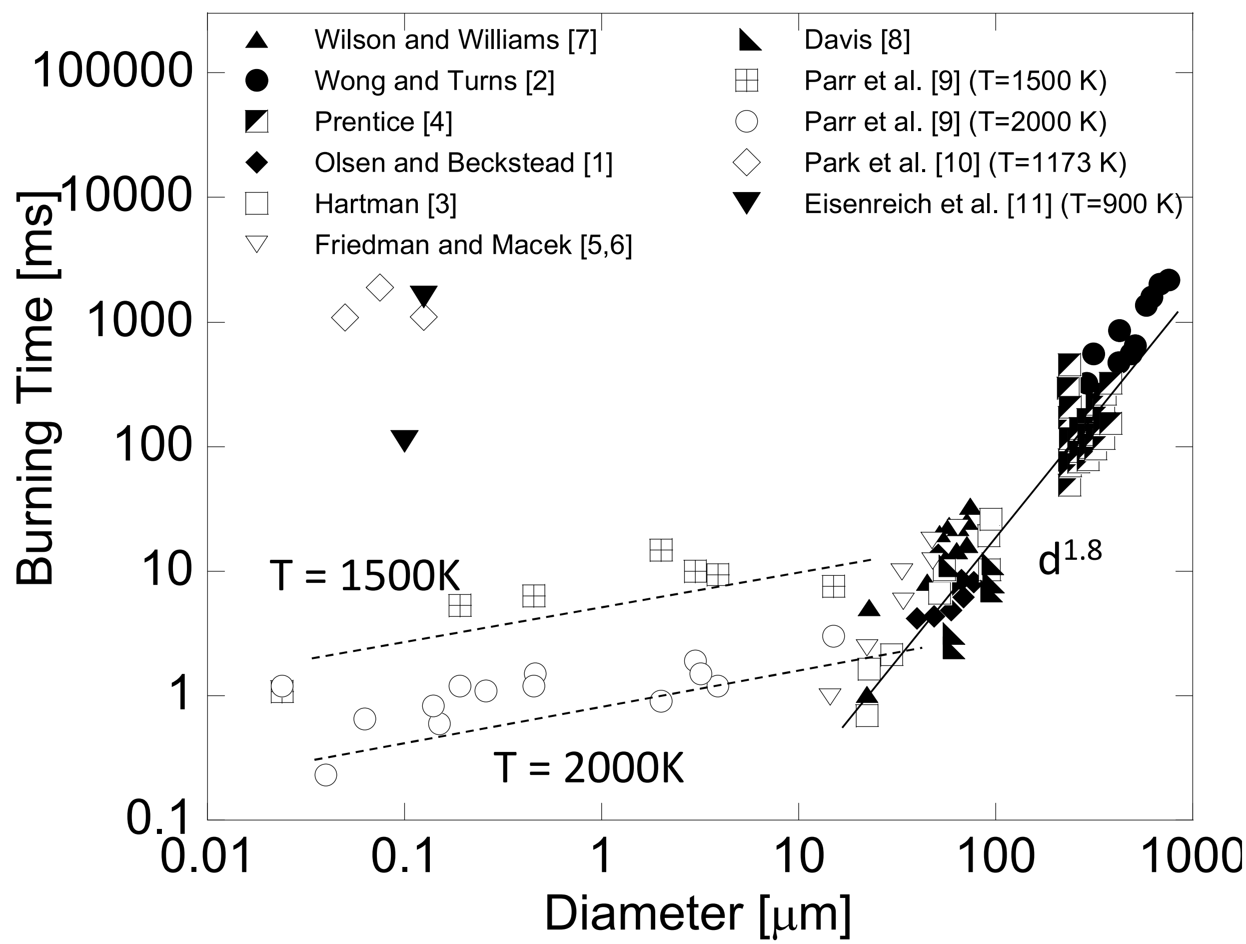


Rate of Change of Conversion vs. Conversion



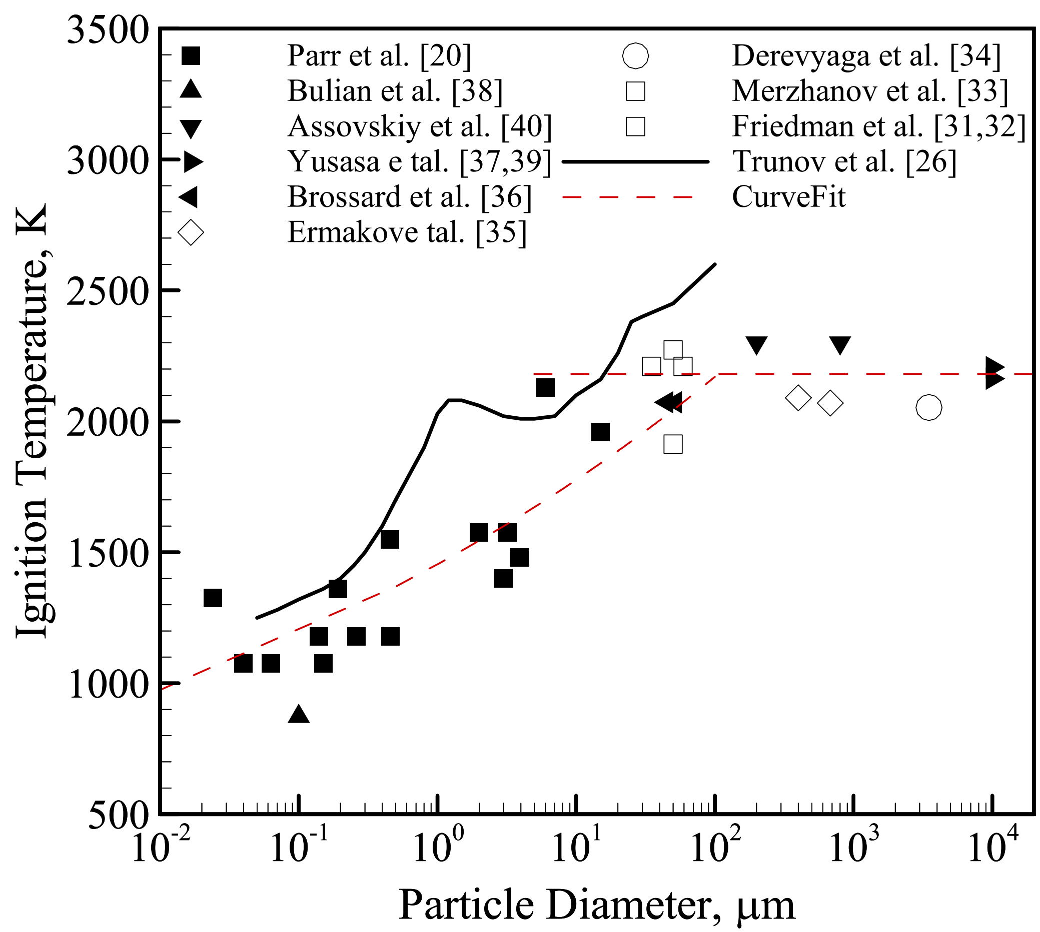
See for example, Levenspiel, O.,Chemical Reaction Engineering, Third Edition, J. Wiley and Sons, 1999

Effect of Particle Diameter on Al Burning Time

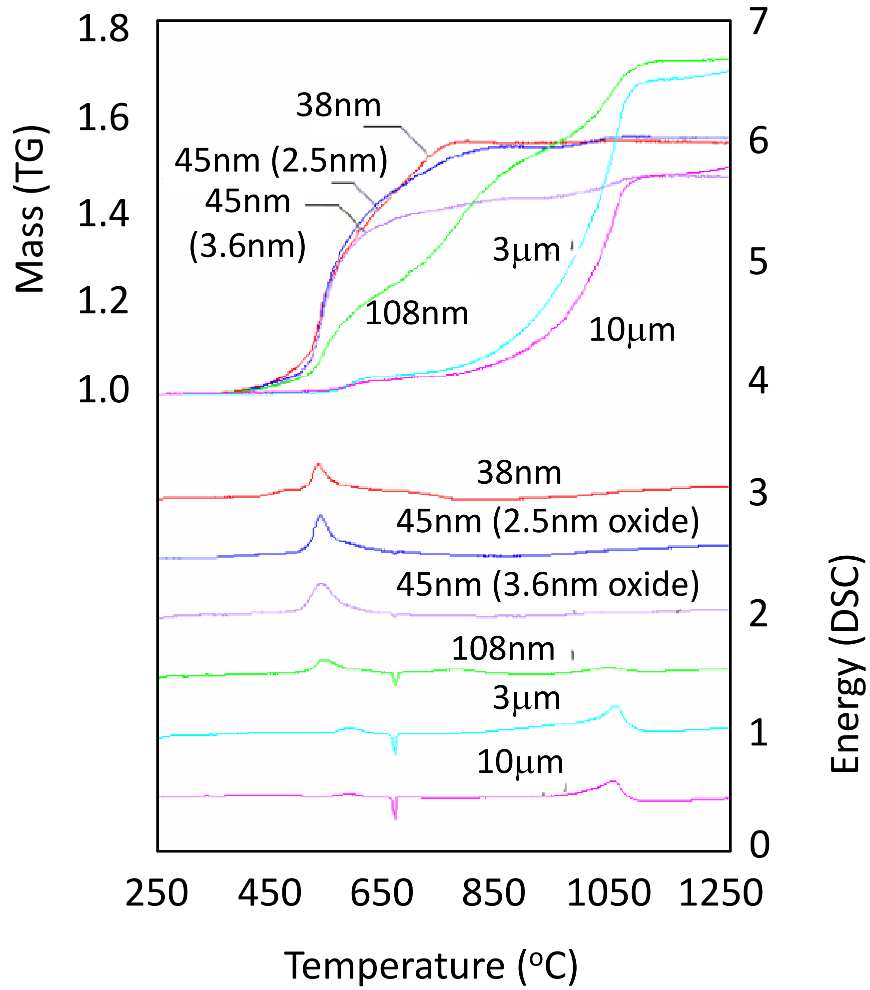


T. Bazyn, H. Krier, and N. Glumac, *Proc Combust. Inst*. 31 (2007) 2021 & *Combust. Flame* 145 (2006) 703.
Y.L. Shoshin and E.L. Dreizin, *Combust. Flame* 145 (2006) 714.

Effect of Particle Diameter on Al Ignition Temperature



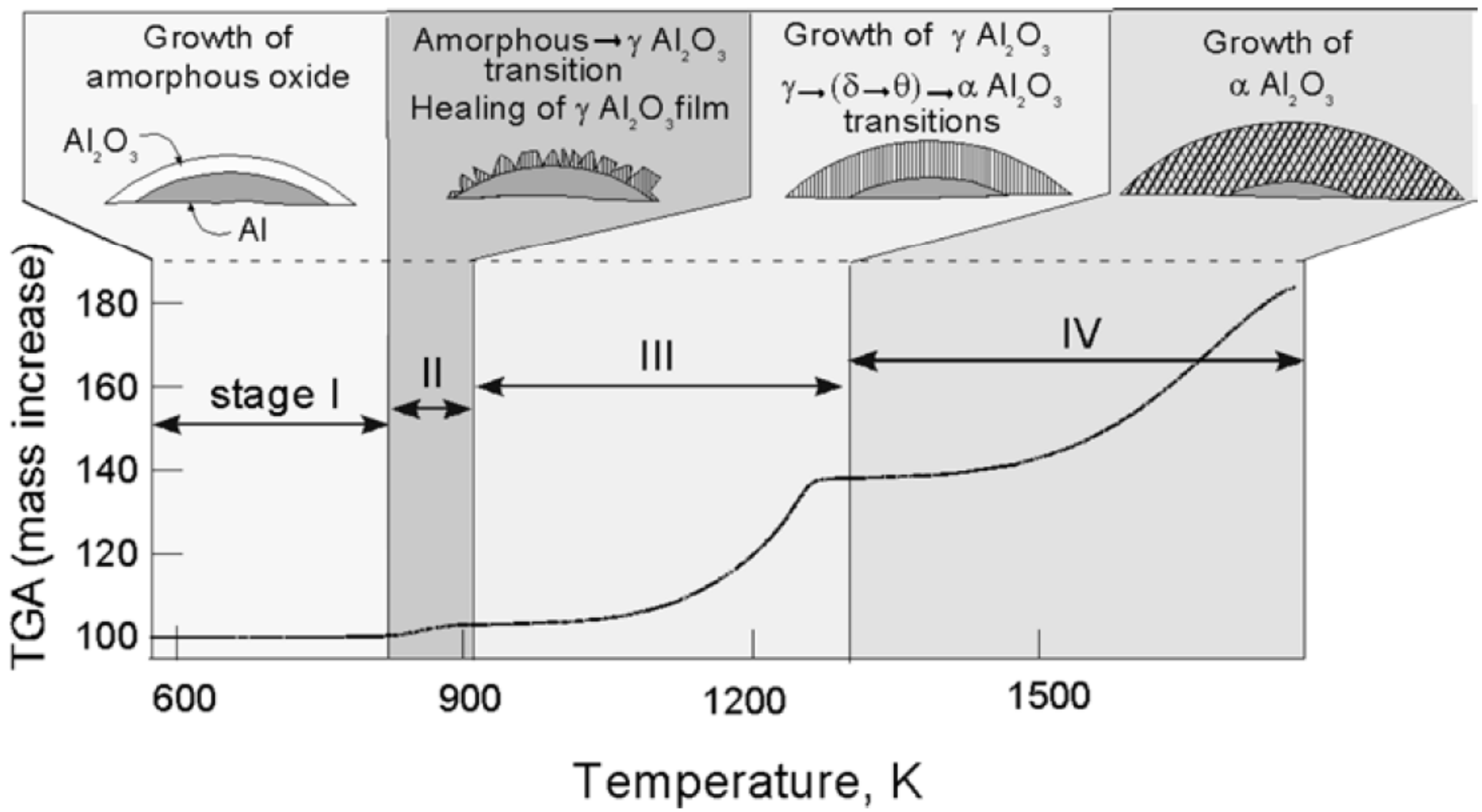
Thermal Gravimetric Analysis of Nanoaluminum with CO_2



K. Brandstadt, D. L. Frost, and J. A. Kozinski, in Advancements in Energetic Materials and Chemical Propulsion, ed. K.K. Kuo and J. de Dios Rivera, Begall House, 2007.

Il'in AP, Gromov AA, and Yablunovskii GV (2001) Combustion, explosion, and shock waves, 37 n.4: 418-422.

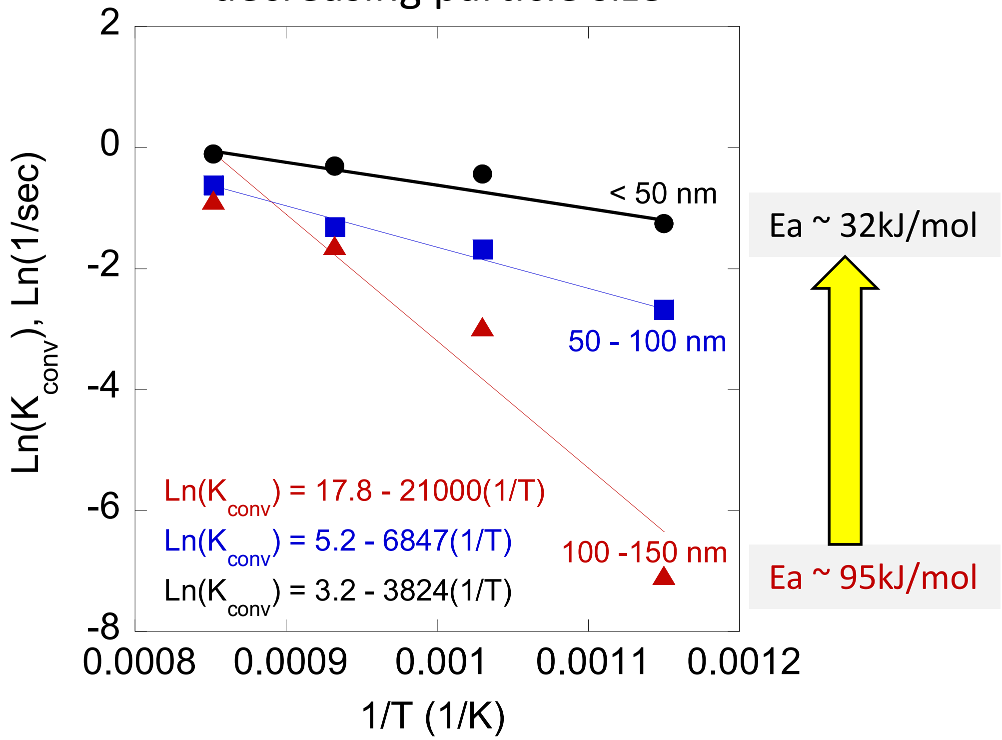
Polymorphic Phase Transformations in Al_2O_3 Layer



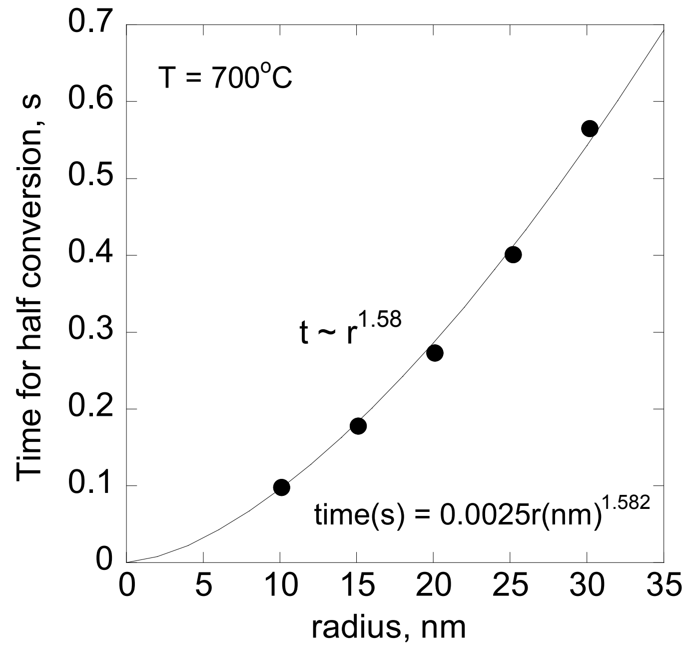
M. A. Trunov, M. Schoenitzand E. L. Dreizin, *Combustion Theory and Modelling*, 10, 2006, 603–623

Aluminum Nanoparticle Oxidation with Single Particle Mass Spectrometry

Increased rate constant with decreasing particle size



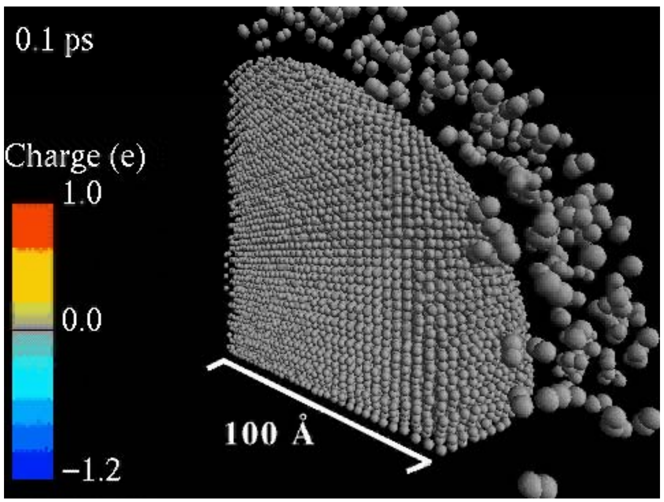
Shrinking core model

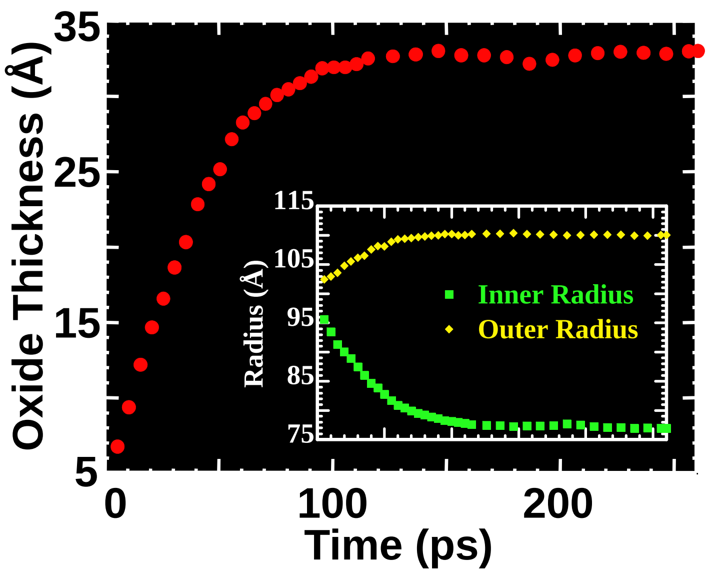


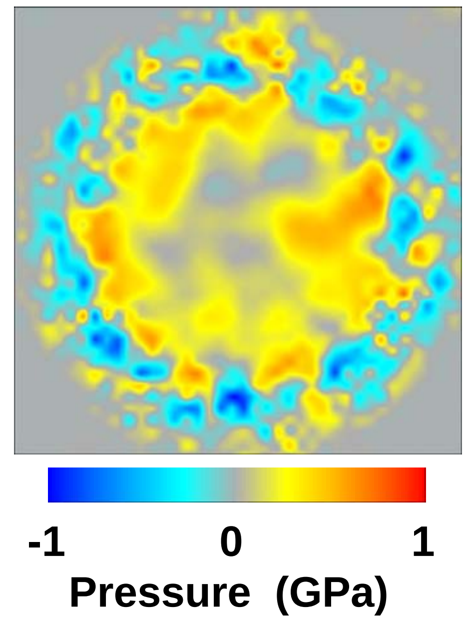
Effective diffusion coefficient (D_e) of oxygen in ash layer = 10^{-9} ~ 10^{-8} cm^2/s for < 50 nm particles
At temperatures above ~ 1000°C, hollow particles formed.

K. Park, D. Lee,† A. Rai, D. Mukherjee, and M. R. Zachariah,J. Phys. Chem. B 2005, 109, 7290-7299
A. RAI, K. PARK, L. ZHOU and M. R. ZACHARIAH, Combustion Theory and Modelling, Vol. 10, No. 5, October 2006, 843–859

Oxidation of an Al Nanoparticle by Multimillion Atom MD Simulations





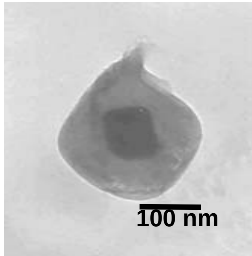


P.Vashishta, R.K. Kalia, and A. Nakano, *J. Phys. Chem. B* 2006, 110, 3727-3733

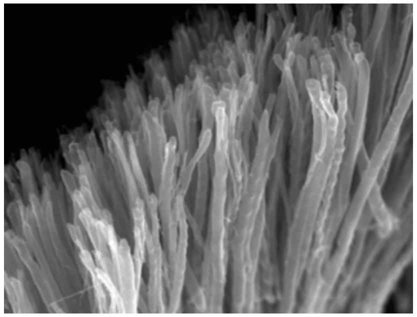
Synthesis and Assembly?

How are Nanoenergetics Made?

- The creation of nanoenergetics is still a current research area
- Many approaches taken
  – For example, Nano-Al made via:
- exploding wires
- condensation technique
- plasma methods
- wet chemistry approaches



Nano-Crystalline Explosives Encapsulated


Nitrated Carbon Tube Structures

S.F. Son and R.A. Yetter, Nanoenergetics, 2012

Synthesis Methods

- **Synthesis Group I:** Gas phase condensation based techniques for production of nanosized metal particles, e.g., wire explosion, PVD (Physical Vapor Deposition; e.g., using vacuum), CVC (Chemical Vapor Deposition), supercritical processing
    - Sun X.K, Xu J.,. Chen W.D, Wei W.D., *Nanostruct. material* , 4, 337 (1994)
    - Tohno S., Itoh M., and Takano H., *J. Aerosol Sci*. 25, 839 (1994)
    - Magnusson M.H., Deppert K., Malm J.O., Svensson S., Samuelson L., *J Aerosol Sci* 28 (Suppl1), S471, (1997)
    - Murata T., Itatani K., Howell FS, Kishioka A., and Kinosita M., *J Am Ceram Soc* 76, 2909 (1993)
    - Danen, W.C., Martin, J.A., US Patent 5266132 (1993); US Patent 5606146 (1997)
    - B.H. Kear and G. Skandan, *Nanostruct. Mater*. 8, 765 (1997)
    - Hahn H., *Nanostruct. Mater*. 9, 3 (1997).
    - Ivanov G.V., and Tepper, F.,. In Kuo, K.K., et al., Eds., *Challenges in Propellants and Combustion 100 Years after After Nobel*, Begell House, New York, (1997), p.636.
    - Jiang, W., Yatsui, K., IEEE Transactions on Plasma Science, 26(5):1498-1501(1998)

- **Synthesis Group II**: Plasma, arc, and flame synthesis
    - *Fine Particles: synthesis, characterization, and mechanism of growth*, Sugimoto T., Ed. New York, Marcel Dekker, Inc., pp. 114, 404 (2000)
    - Tomita, S., Hikita, M., Fujii, M., Hayashi, S., and Yamamoto, K., *Chemical Physics Letters* 316:361-364 (2000)
    - Chopra N.G., Luicken R.J.,Cherrey K., Crespi V.H., Cohen M.L., Louie S.G., and Zettl A., *Science* 266, 966 (1995)
    - Loiseau A., Willaime F., Demoncy N., Hug, G., and Pascard H., *Phys. Rev. Lett*. 76, 4737 (1996)
    - Ruoff R.S., Lorents D.S., Chan B., Malhotra R., and Subramoney S., *Science* 259, 346 (1993)
    - Hwang, J.-H., Dravid, V.P., Teng, M.H., Host, J.J., Elliott, B.R., Johnson, and D.L., Mason T.O., *J. Mater. Res*. 12, 1076 (1997).
    - Sun X., Gutierrez A., Yacaman M.J., Dong X., and Jin S., *Materials Science and Engineering* A286, 157 (2000).
    - Pratsinis S.E. *Progress in Energy and Combustion Science*, 24, 197 (1998)
    - Balabanova E., *Vacuum* 69, 207-212 (2002)
    - Keil, D. G., Calcote, H. F. and Gill, R. J., *Materials Research Society Symposium Proceedings* 410, 167 (1996).
    - Axelbaum R.L., Lottes C.R., Huertas J.I., and Rosen L.J., *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, (1996), p.1891.

Synthesis Methods continued

- **Synthesis Group III**: Wet chemistry, Sol-Gel, etc.
  - Hyeon-Lee, J., Beaucage, G., Pratsinis, S.E., *Chem Matter*, 9:2400-2403 (1997)
  - Tillotson, T.M., Hrubesh, L.W., Simpson, R.L., Lee, R.S., Swansiger, R.W., Simpson, L.R., *Journal of Non-Crystalline Solids* 225: 358-363 (1998)
  - Tillotson, T.M., Gash, A.E., Simpson, R.L., Hrubesh, L.W., Satcher, J.H., Jr., Poco, J.F., *Journal of Non-Crystalline Solids* 285: 338-345 (2001)

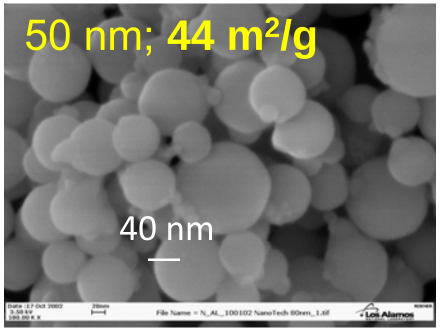
- **Synthesis Group IV**: Mechanical alloying/activation
  - Suryanarayana C., *Progress in Materials Science*, 46 (1-2): 1-184 (2001)
  - Wen, C.E., Kobayashi, K., Sugiyama, A., Nishio, T., and Matsumoto, A., *Journal of Materials Science* 35:2099 – 2105 (2000)
  - Shoshin, Y.L., Mudryy, R., S., and Dreizin, E.L., *Combustion and Flame* 128:259 –269 (2002)
  - Lu, L., Lai, M.O., Mechanical Alloying. Kluwer Academic Publ., Boston, 1998
  - El-Eskandarany, M.S., Mechanical Alloying. Noyes Publications., Norwich, NY, 2001

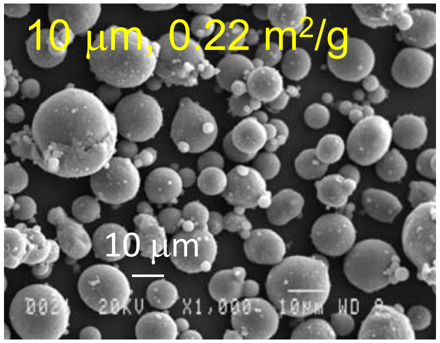
- **Synthesis Group V:** Soft Lithographic Patterning, Decal Transfer Lithography, Photolithography

Nanosized Reactive Materials

- Nanoscale powders
  - Available in large quantities now
  - Potential ingredient in propellants, pyrotechnics, and explosives
- Smaller size means larger surface area
  - Greater reactivity
  - Faster burning
  - Good for combustion efficiency
- Original nAl was ALEX (EXploded ALuminum)
  - Exploding wires
  - Still sold, good value
  - Consistency not good and size distribution broad and includes large particles (extremely spherical particles, size ranges from 50 to 250 nm, oxide layer thickness ~ 3.1 nm)
- However, some original claims of excess surface energy
  - It is true that at very small diameters there is a surface energy
  - Not significant in particles >10 nm
  - Kuo and others showed there was no excess energy in ALEX aluminum using calorimetry

The color of Al is strongly related to particle size. Typically 200 nm powder is gray (left) and 40 nm powder is black (right), from Pesiri et al., Journal of Pyrotechnics, 19, 192004

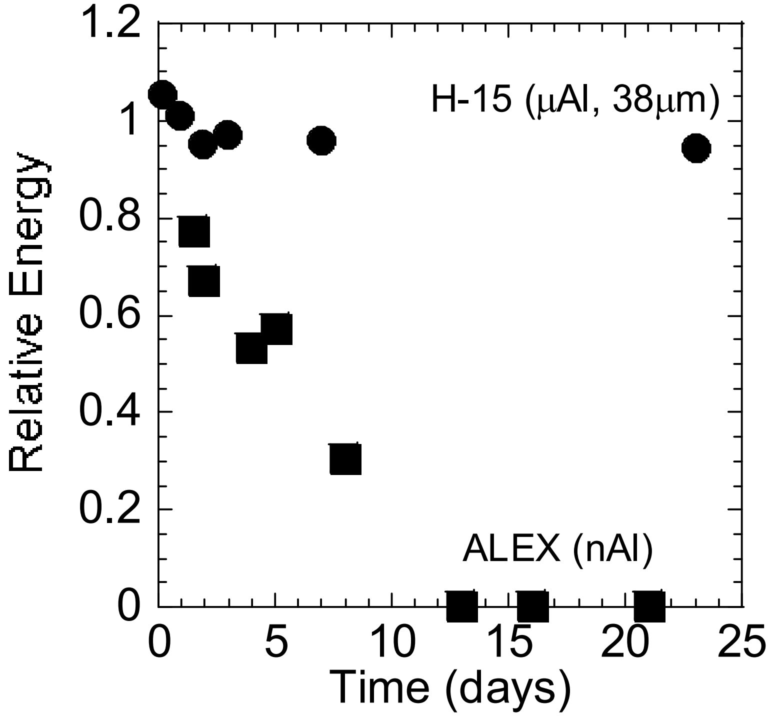




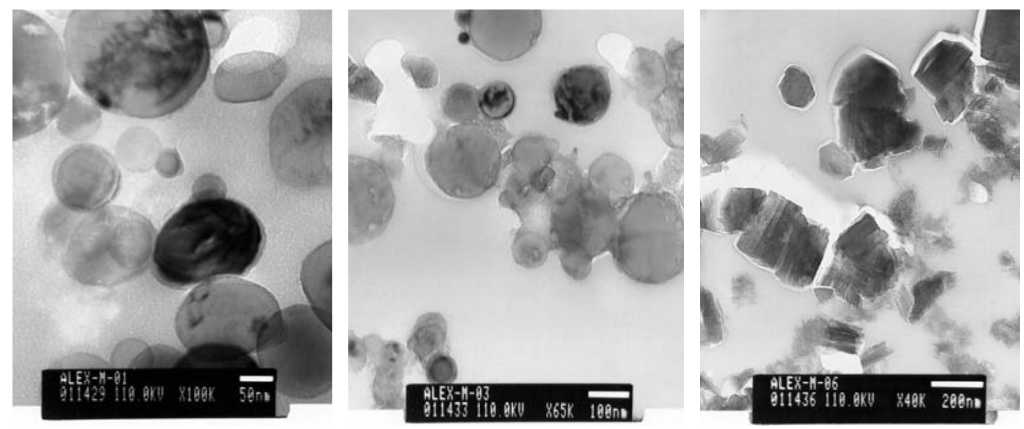
S.F. Son and R.A. Yetter, Nanoenergetics, 2012

Ageing and Coating of Particles

Accelerated Ageing,
Room Temperature,
Saturated Humidity



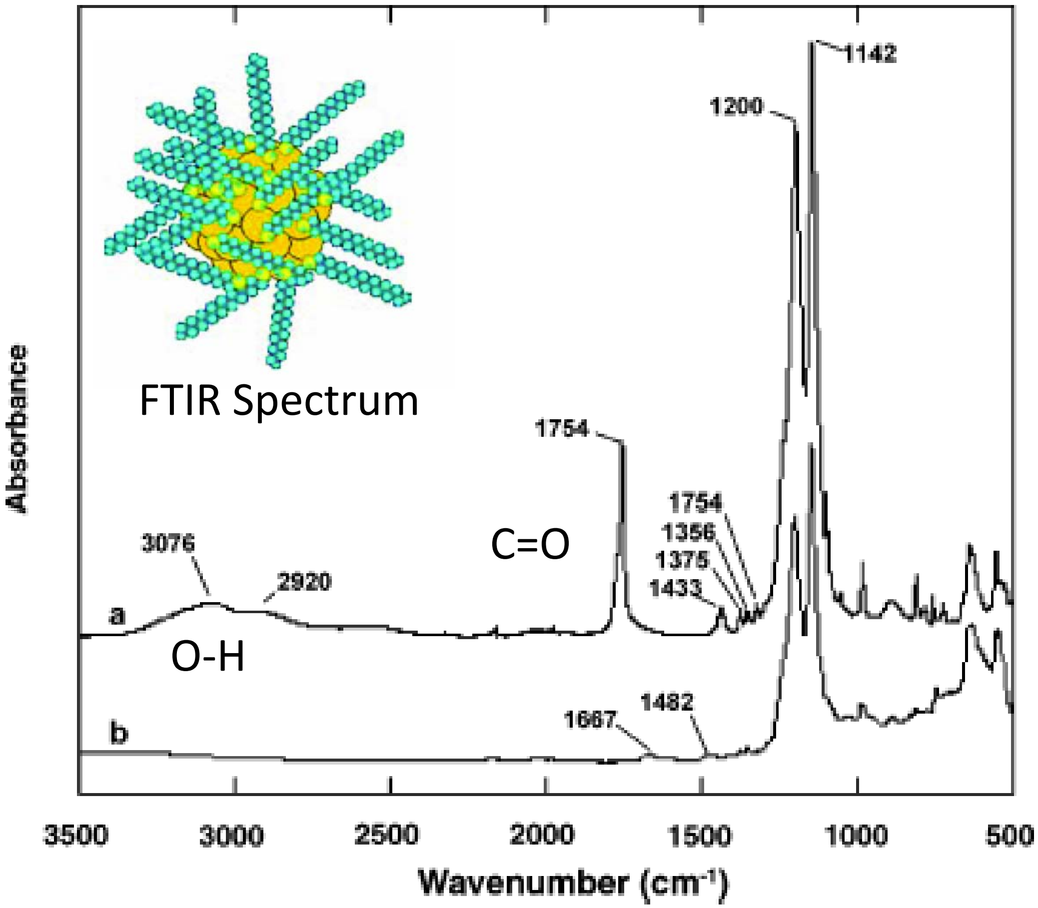
Ageing test with Alex® (air, saturated, 60 °C)

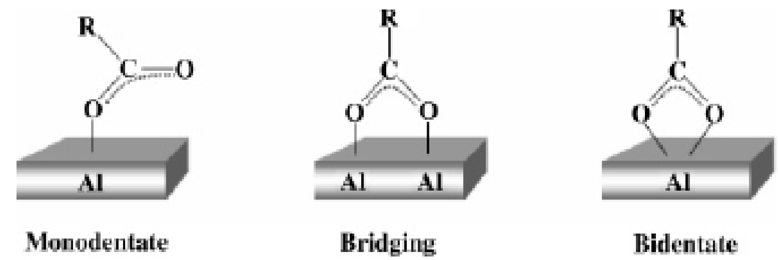


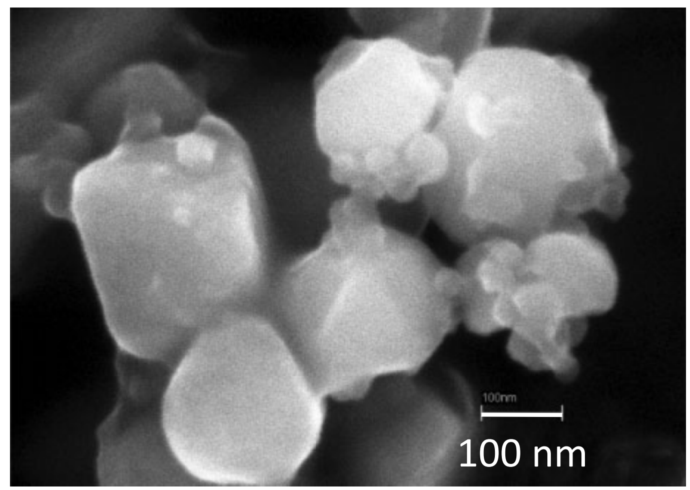
t = 0 hr t = 5 hrs t = 24 hrs

C. Dubois, P. G. Lafleur, C. Roy, P. Brousseau and R. A. Stowe, *JPP*
Vol. 23, No. 4, July–August 2007

Surface Passivation of Bare Al Nanoparticles Using Perfluoroalkyl Carboxylic Acids ($C_{13}F_{27}COOH$)







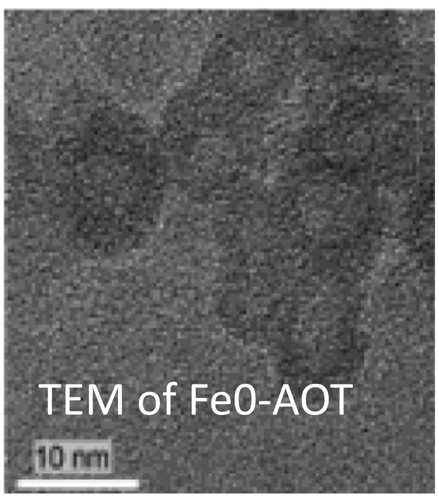
SEM (225 000 magnification) of $Al\text{-}C_{13}F_{27}COOH$

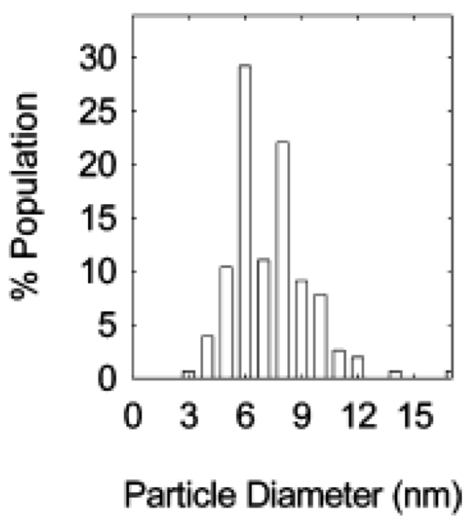
R.J. Jouet, A.D. Warren, D.M. Rosenberg, V.J. Bellitto, K. Park, and M.R. Zachariah, Chem. Mater. 17 (2005) 2987-2996.

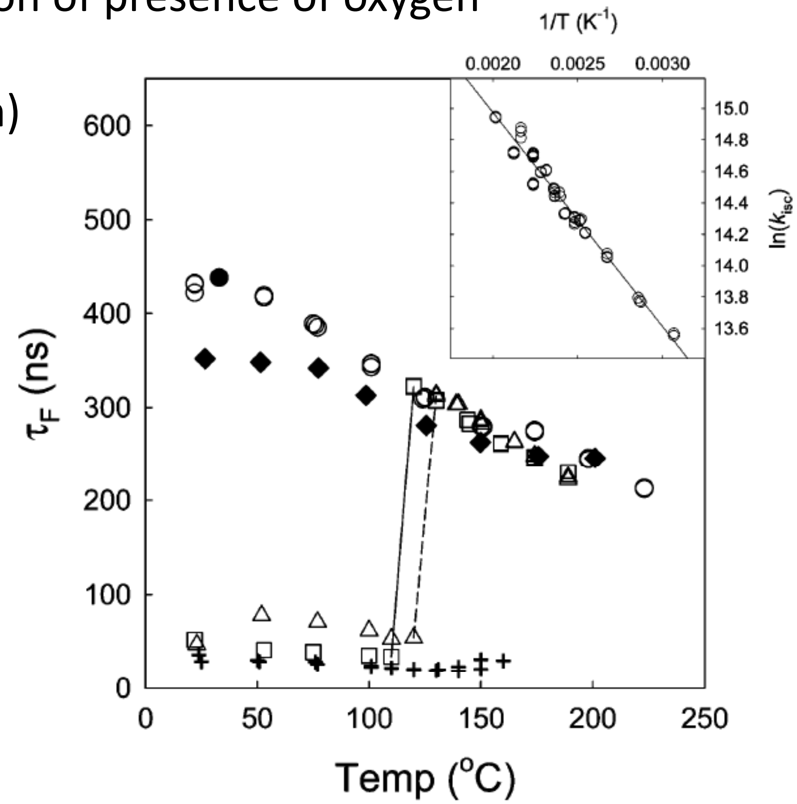
R.J. Jouet, J.R. Carney, R.H. Granholm, Sandusky, H.W. and A.D. Warren, Mater. Sci. Technol. 22 (2006) 422-429.

Low-Temperature Stability and High-Temperature Reactivity of Iron-Based Core-Shell Nanoparticles

- Iron nanoparticles made from sonochemical method
- Self-assembled monolayer of dioctyl sulfosuccinate sodium salt (AOT) or oleic acid
- Hexane solution of nanoparticles (with and without SAM), air saturated, and with pyrene
- Fluorescene lifetime of pyrene used as an indication of presence of oxygen
  ~450 ns => no oxygen
  ~20ns => oxygen (bimolecular quenching reaction)

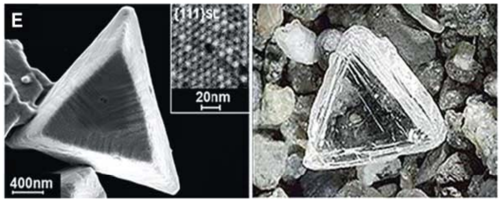






C.E. Bunker and J.J. Karnes, JACS 126, 10852, 2004

Self-Assembled Nanoscale Thermite Microspheres

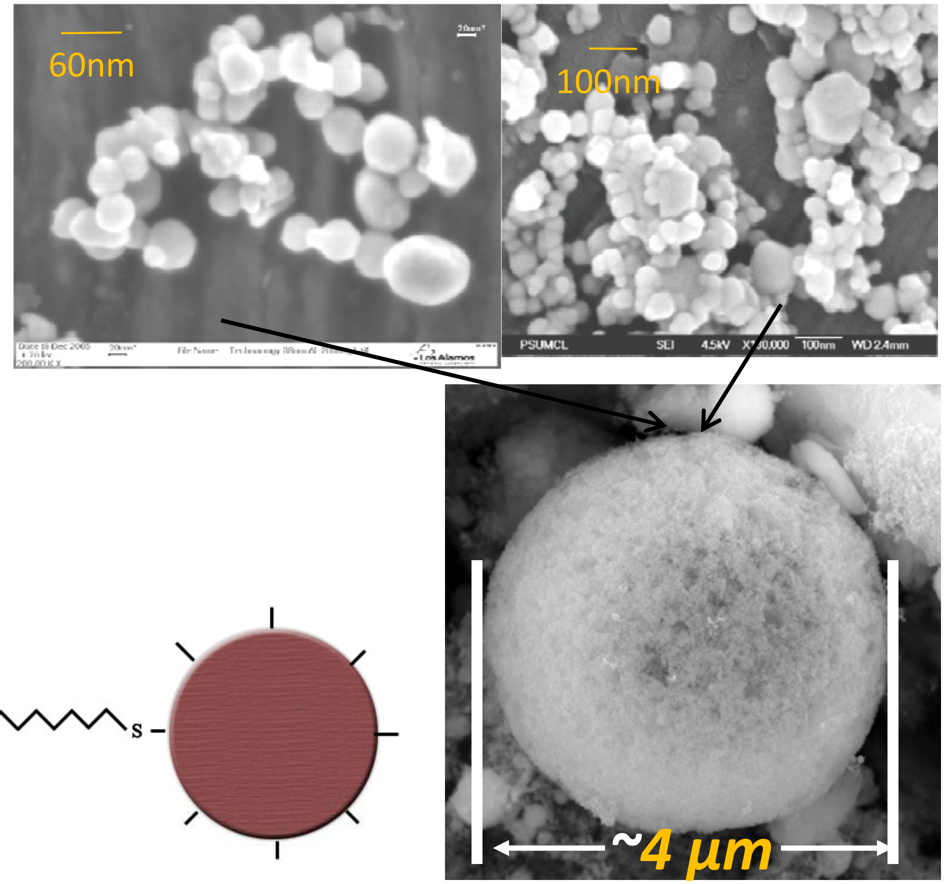


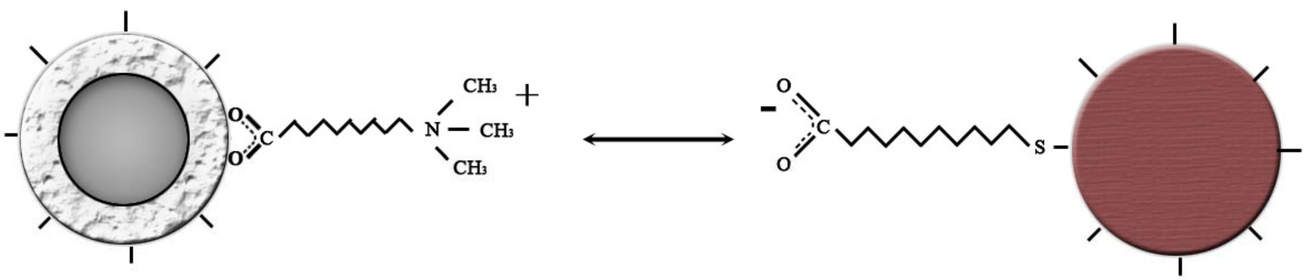
Kalsin *et al.*, *Science,* v312, 2006

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

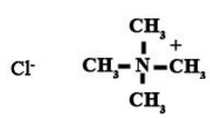
nAl (38nm)

nCuO(33nm)





nAl-TMA
(trimethyl(11-mercaptoundecyl) ammonium chloride

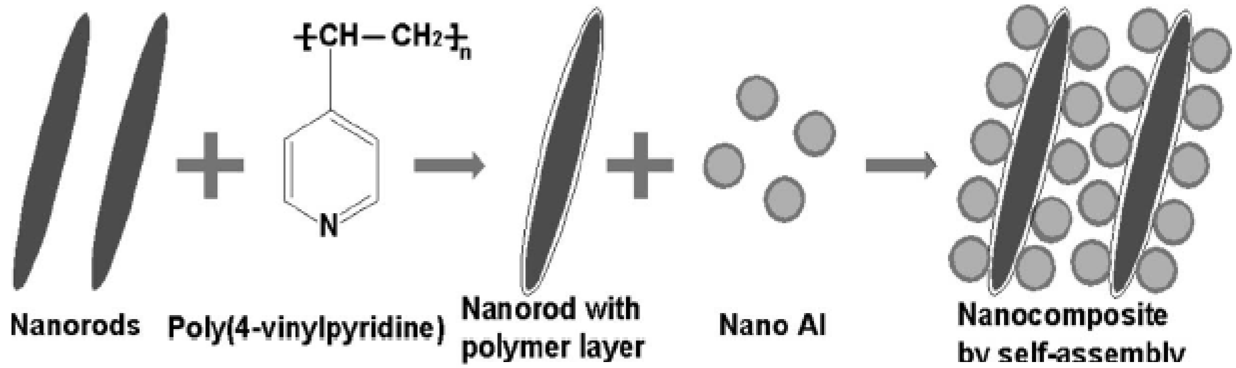


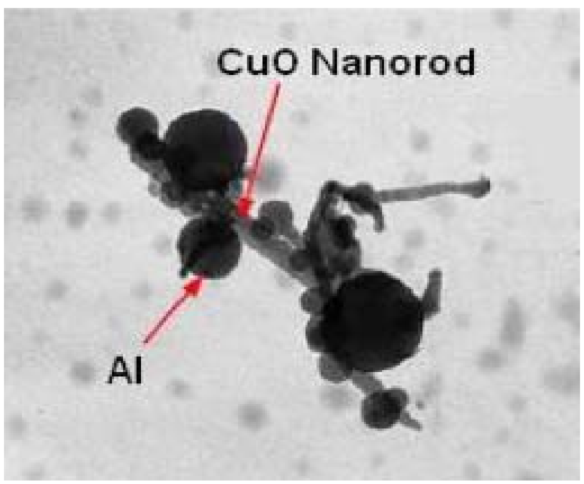
nCuO-MUA
(11-mercaptoundecanoic acid)

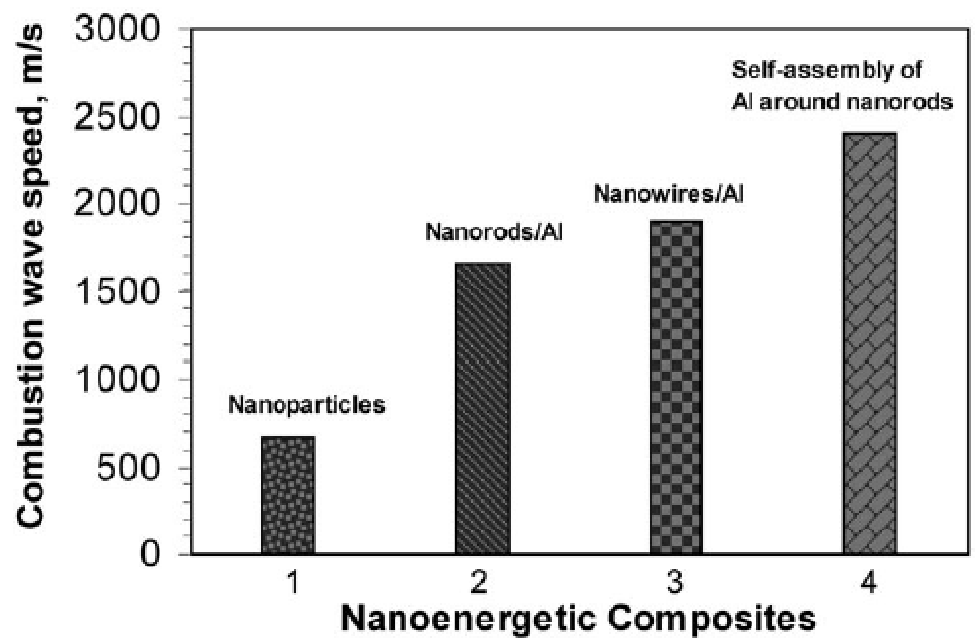
[redacted]

Malchi, J., Foley, T., Yetter, R.A., ACS APPLIED MATERIALS & INTERFACES, 1, 11, 2420, 2009

Nanoenergetic Composites of CuO Nanorods, Nanowires, and Al-Nanoparticles



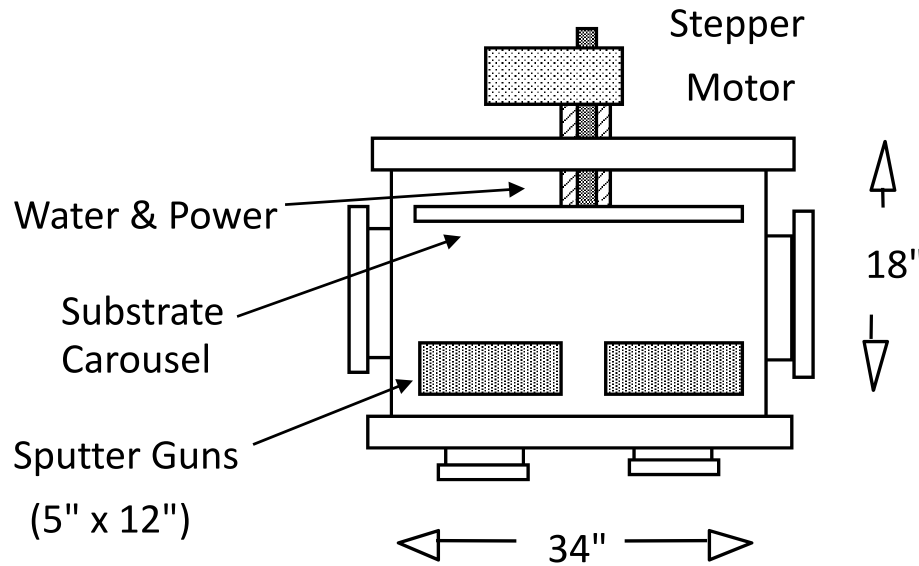


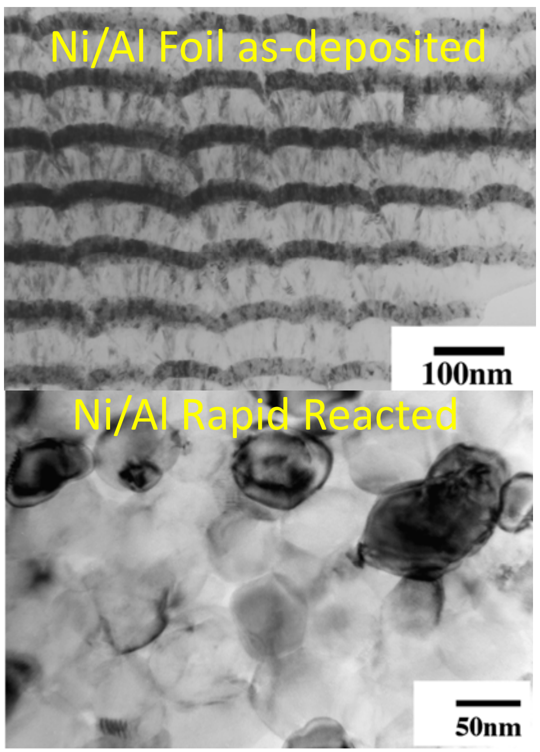


R. Shende et al., Propellants, Explosives, Pyrotechnics 33, No. 2 (2008)

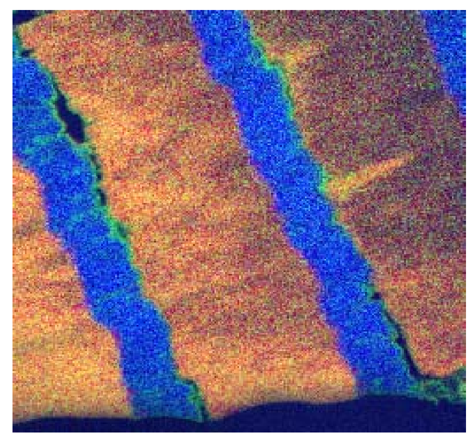
Fabrication of Reactive Multilayer Foils

- Ni/Al, Monel/Al, and Nb/Si
- Magnetron Sputter Deposited
- Free-standing Foils (10-150 µm Thick)
- Bilayer Thicknesses - 25 to 600nm
- Deposition Temperature ~ 75°C





As-Deposited CuO_x/Al Multilayer Foil Elemental Distributions

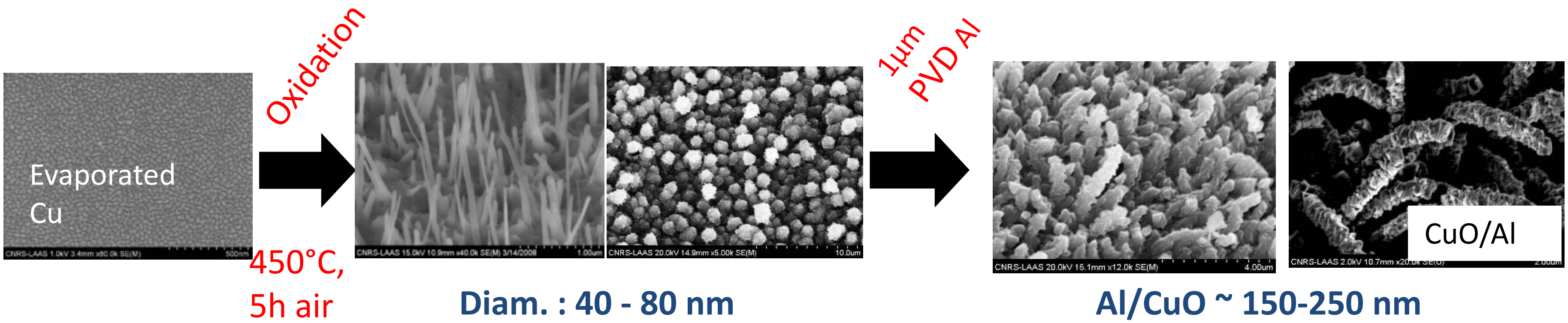


Cu Al O Cu +O

From Tim Weihs, The Johns Hopkins University

Nano Patterning of Nanosized Thermites on a Chip

- PVD based process to grow nanoscale thermites (Al/CuO and Al/NiO) on a Si / glass chip

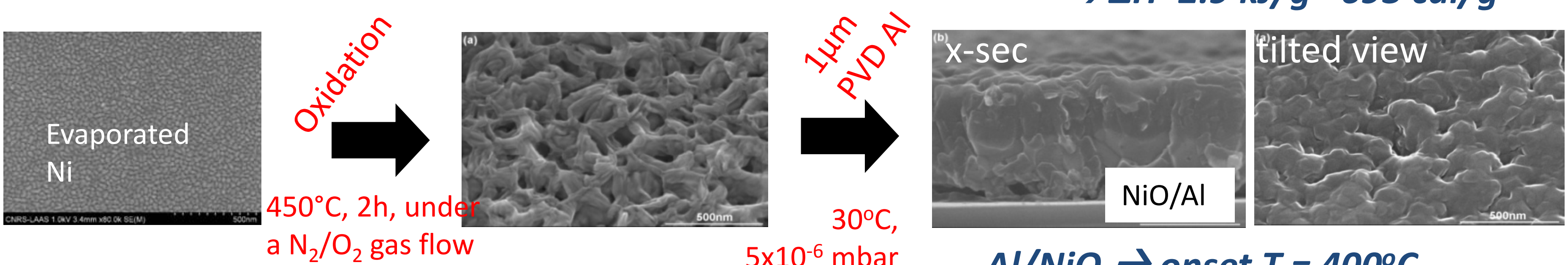


Diam. : 40 - 80 nm

Al/CuO ~ 150-250 nm

Zhang , Rossi et al, *Applied Physics Letters, 2007, 2008*
Petrantoni et al., J. Phys Chem. Of Solids, 2010

Al/CuO → onset T =500°C
→ΔH=2.9 kJ/g =693 cal/g

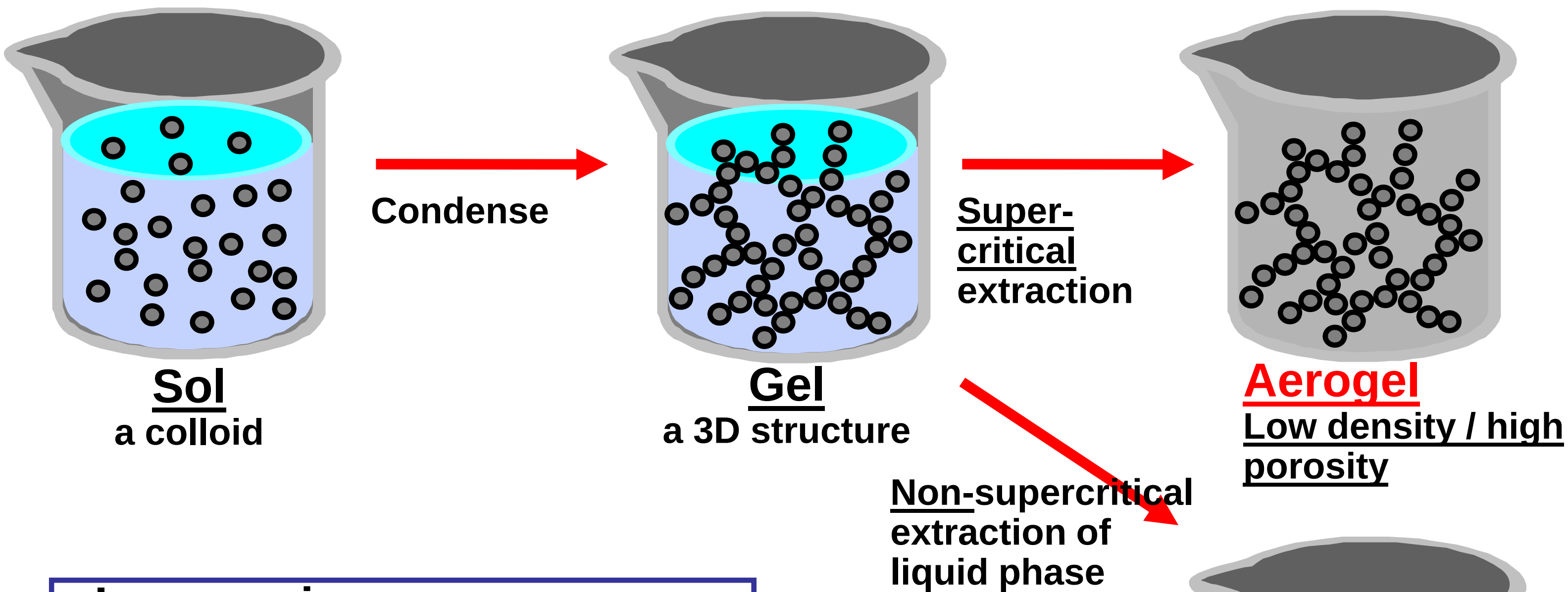


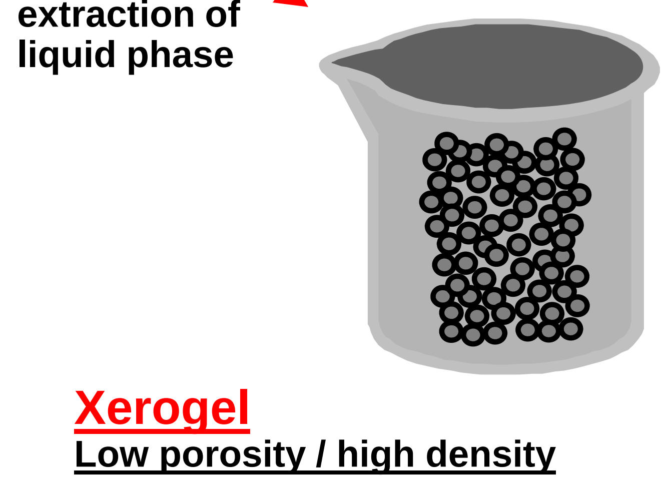
Al/NiO → onset T = 400°C
→ΔH = 2.2kJ/g = 526 cal/g

Zhang, Rossi et al *, Applied Physics A 94, 2009*

Benefits: (1) Enhanced interfacial contact and reactivity, (2) impurities and Al oxidation during fabrication small, (3) since dimensions of CuO nanowires can be tailored, the oxidizer fuel dimensions can be controlled at the nanoscale, (4) process uses standard microfabrication techniques for mass production and integration into functional devices.

The Sol-gel Methodology

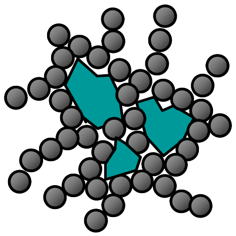




- Inexpensive
- homogeneity on nanoscale
- type and amount of components easily varied
- Cast complex shapes
- Low temp. processing

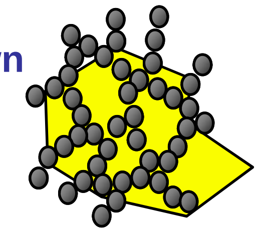
From Gash, LLNL

LLNL Developed Four Classes of Materials and Processes



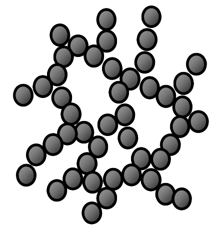
Crystallites grown in pores may be energetic

1. Solution crystallization



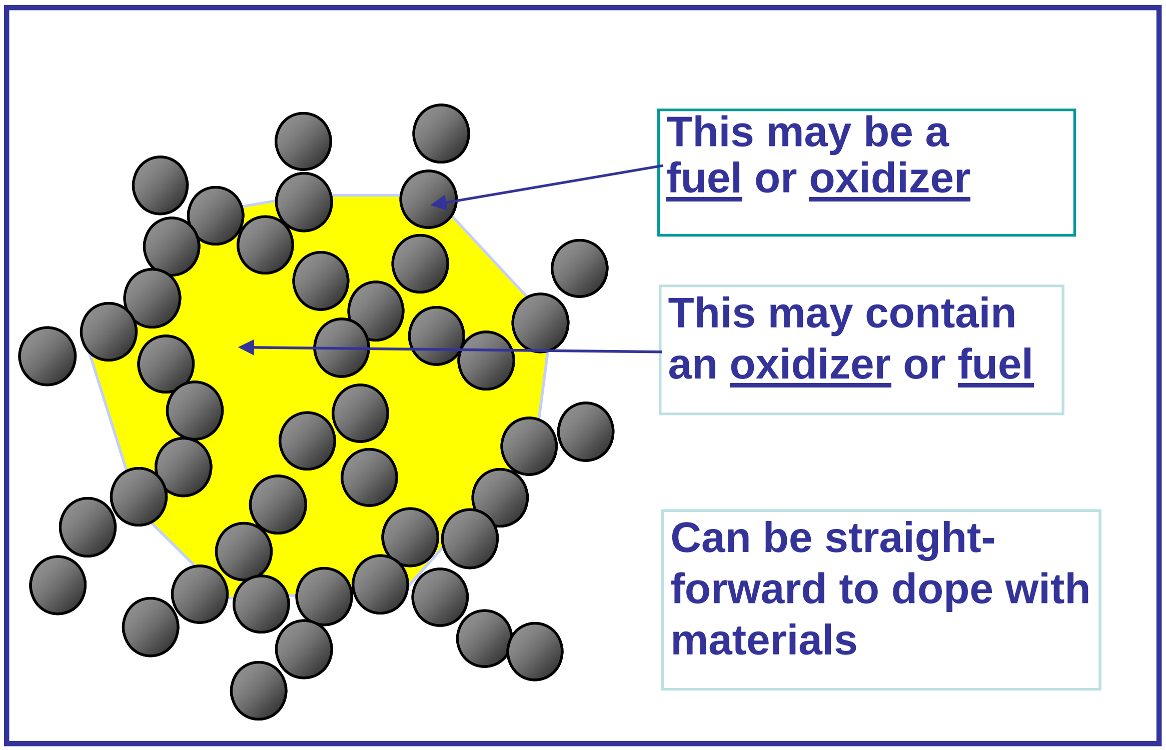
Energetic powders are added by a gel mending method

2. Powder addition



Solid skeleton may be energetic

3. Skeletal Synthesis

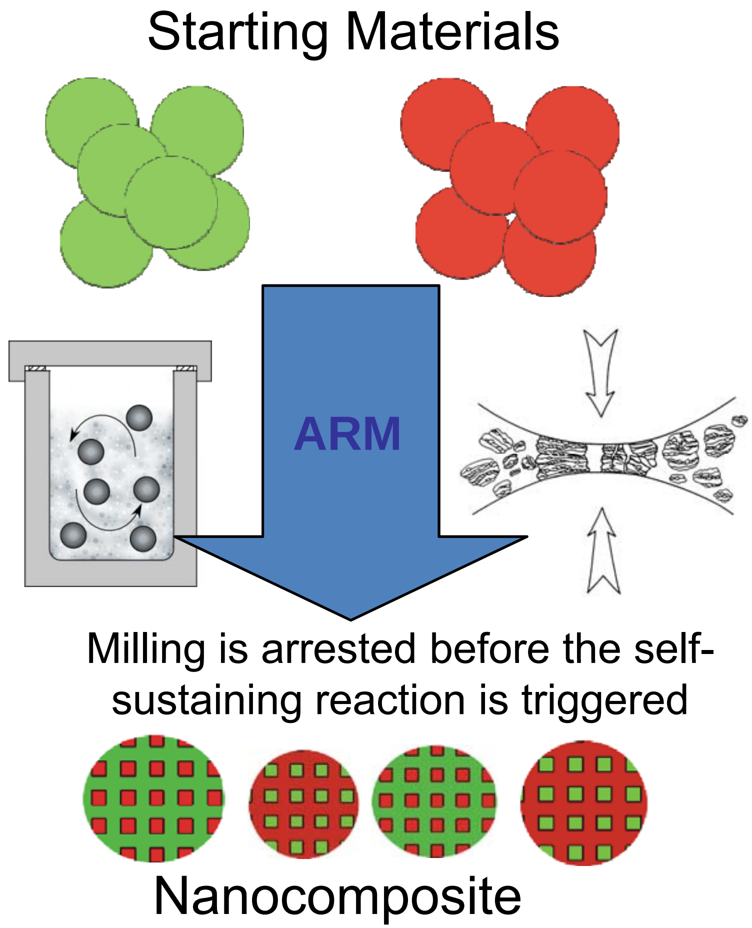


4. Nano-composites

From Gash, LLNL

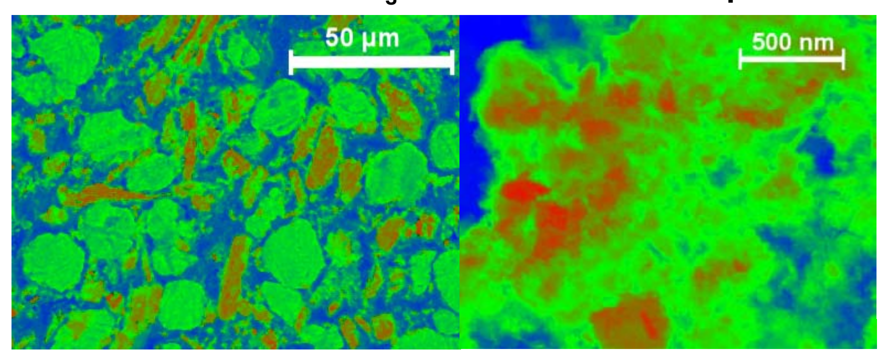
S.F. Son and R.A. Yetter, Nanoenergetics, 2012

Arrested Reactive Milling Nanocomposites



- "**Top-down**" approach to composite design
  - *vs*. "bottom-up" approach of sol-gel methods or use of nano-particles
- Micron-sized, nano-composite powders prepared by **Arrested Reactive Milling**: a high energy ball milling process
- Each individual particle
  - is subjected to pressures as high as 5 GPa during collisions
  - has the same composition as bulk
  - has near theoretical maximum density

Cross-sectioned starting mixture: 2Al + MoO_3 **ARM nanocomposite**



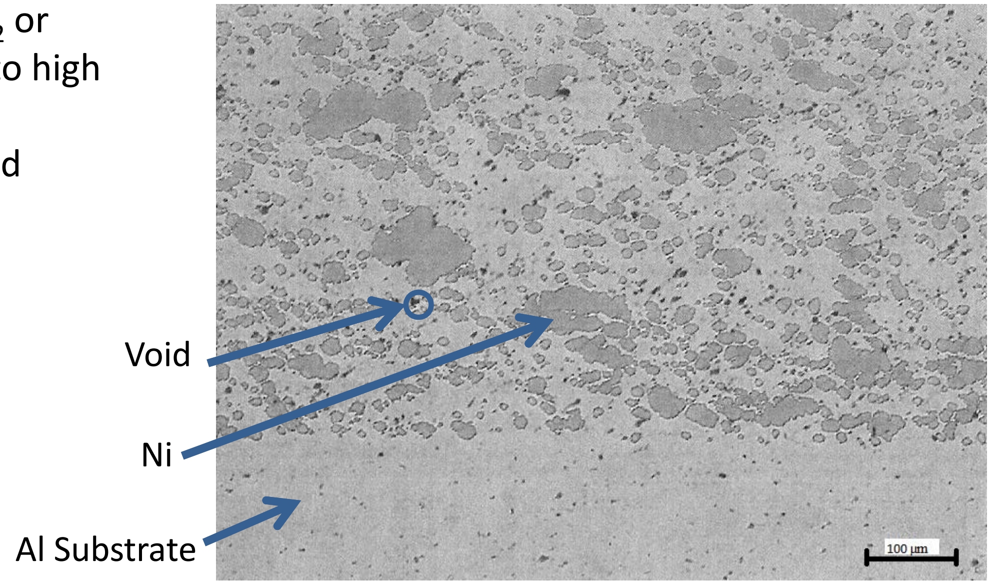
Backscattered electron SEM Images
False color maps: Al: green; MoO_3: red

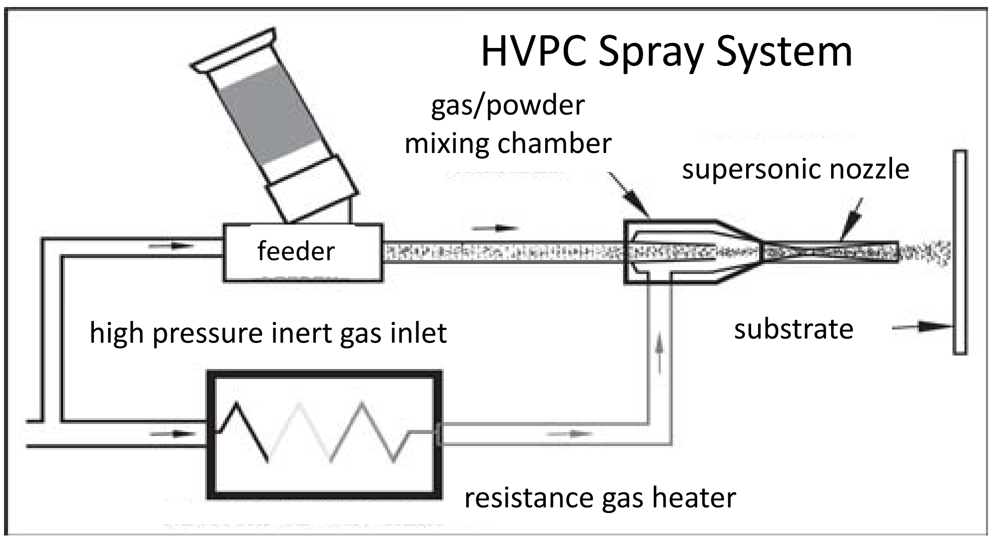
From Dreizen, NJIT

- A range of highly reactive materials produced; B/Ti, B/Mg, B/Zr, Al/Fe_2O_3, Al/MoO_3, Al/CuO, Al/Bi_2O_3, MgH_2/CuO, Al/SrO_2, Al/$NaNO_3$, Mg/MoO_3, Si/CuO, Zr/Bi_2O_3, MgH_2/MoO_3, Mg/CuO
- Liquid surfactant (hexane, kerosene) and type of grinding media are selected to adjust the **powder size** and the **degree of refinement** at which the reaction is triggered
- **Batch sizes**: 2 g – 400 g; batch synthesis time: 20 – 200 min

High Velocity Particle Consolidation (Cold Spray)

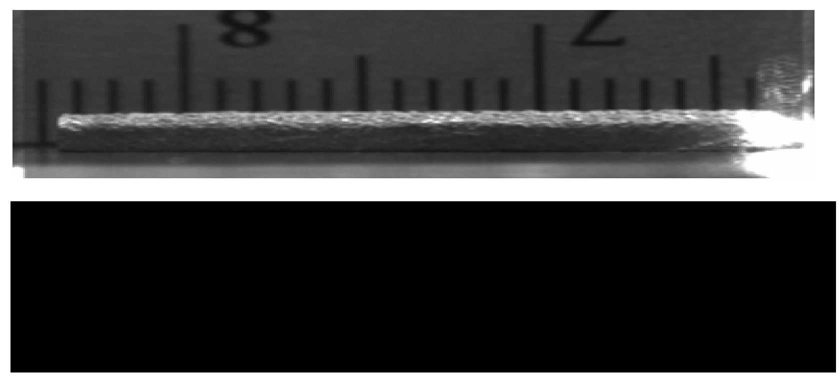
- Particles are injected into an inert gas stream (N_2 or He), then accelerated through a de Laval nozzle to high speed.
- Particles impact substrate or previously deposited material and mechanically bond with it.
- Near fully dense (<1% porosity) materials can be formed rapidly.
- Material retains significant strength and can be machined and used for structural applications.
- Particles stay below T_{mp} and are not exposed to oxygen.





Wolfe, Douglas E., et al. 2006, Journal of Thermal Spray Technology

$Ni + Al \rightarrow NiAl$ – 329 cal/g $T_{af} = 1912$ K

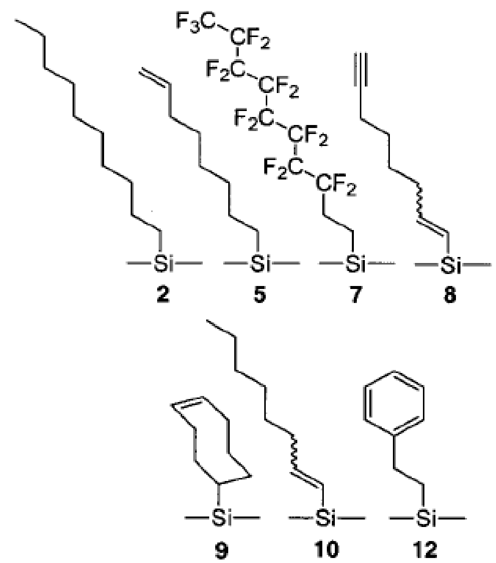


Samples ignited in ambient air 100 W Synrad 57-1 CW CO_2 laser

Silicon Reactives Can Also Be Used

Why silicon fuels?

- The oxide layer is only 1-2 nm naturally
- Aging (oxidation) likely better than Al
- Generally less sensitive than Al
- Reactives could be intimately incorporated in silicon-based microscale devices
- Tuning and switching possibilities (doping/e-field/electro-wetting)
- Some systems produce higher temperatures
- Nanoporous Si (PSi) vs. Nano-Silicon powder (nSi)
- Surface properties can be manipulated
  - Self-assembled monolayers are applied to the surface of silicon, on either nanoporous substrates or silicon particles
  - Oxide layer is stripped off with HF leaving a hydrogen terminated surface.
  - Fluorocarbon ligands are then attached to the surface by Thermally Induced Hydrosilylation producing a reactive composite devoid of unreactive oxide.

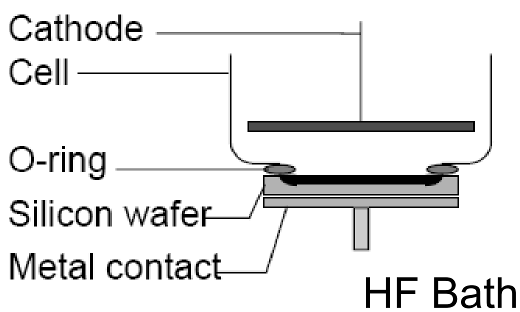


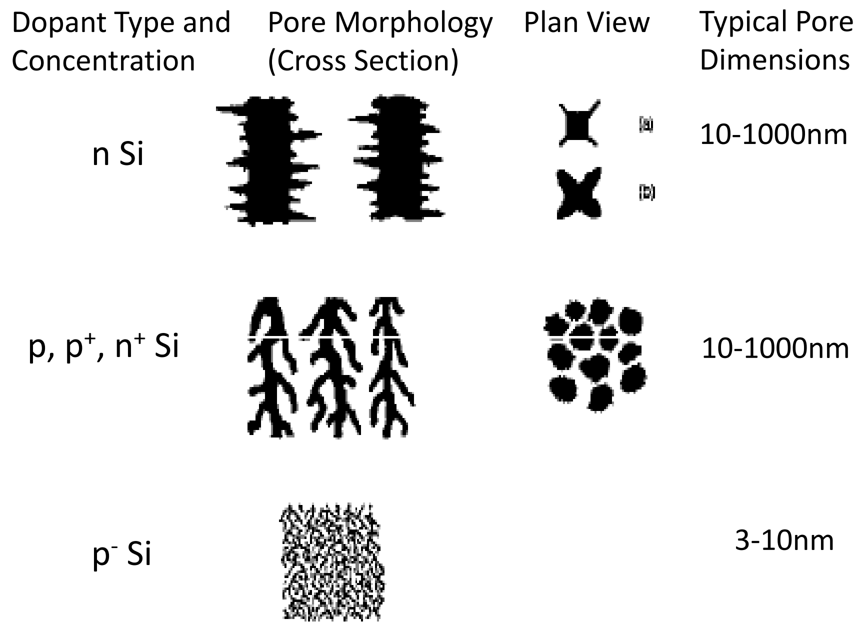
Examples of surfaces produced through white light promoted hydrosilylation reaction. M. Stewart and J. Buriak (2001).

Nanoporous Silicon Fabrication

Electrochemical Etching

- Typical etch depths of 100-200µm with reported depths of over 500µm (thickness of wafer).
- Pore diameters and % porosity can very dramatically depending on the HF concentration and current.

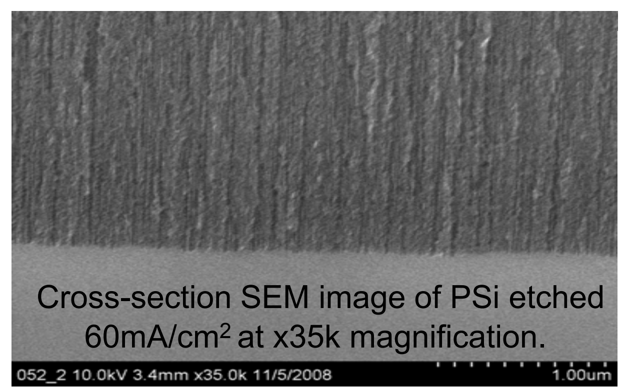




Schematic diagram illustrating the characteristic pore morphologies and typical dimensions as a function of dopant type and concentration. Searson and Macaulay (1992)

Oxidizer Loading Techniques

- Drop cast method - fill PSi by placing the PSi in an oxidizer-solvent solution and allow the solvent to evaporate (can be done under low pressure to minimize voids and with surfactant additives)
- Melt casting (e.g., sulfur)
- Supercritical fluid filling

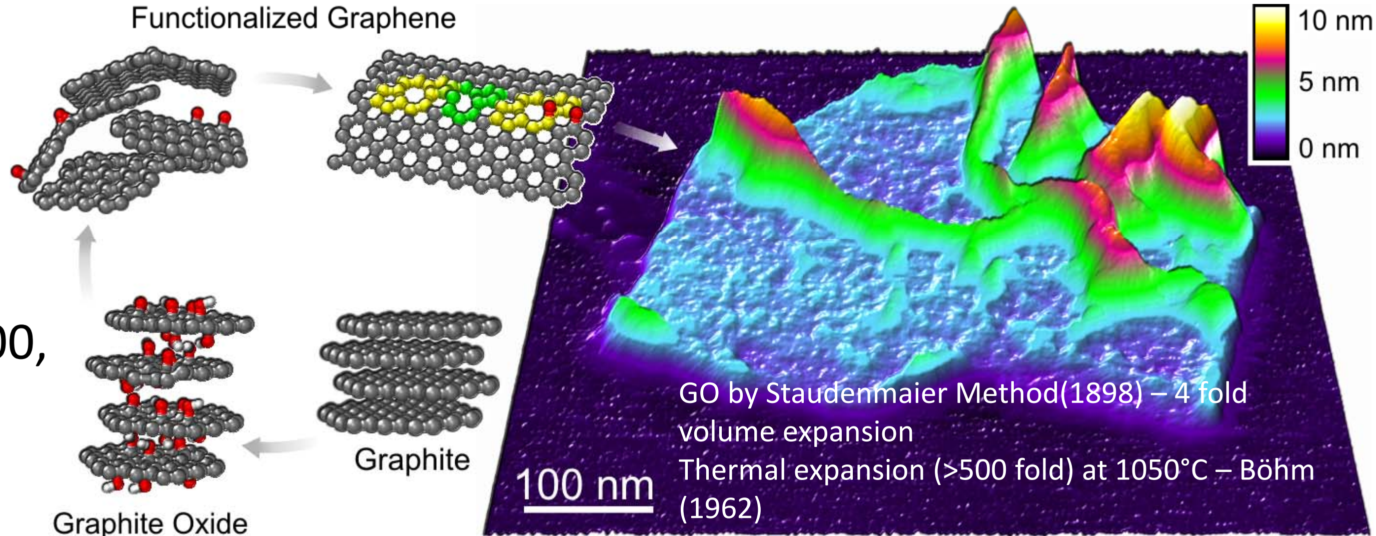


Cross-section SEM image of PSi etched 60mA/cm^2 at x35k magnification.

Functionalized Graphene Sheets as Catalysts Supports

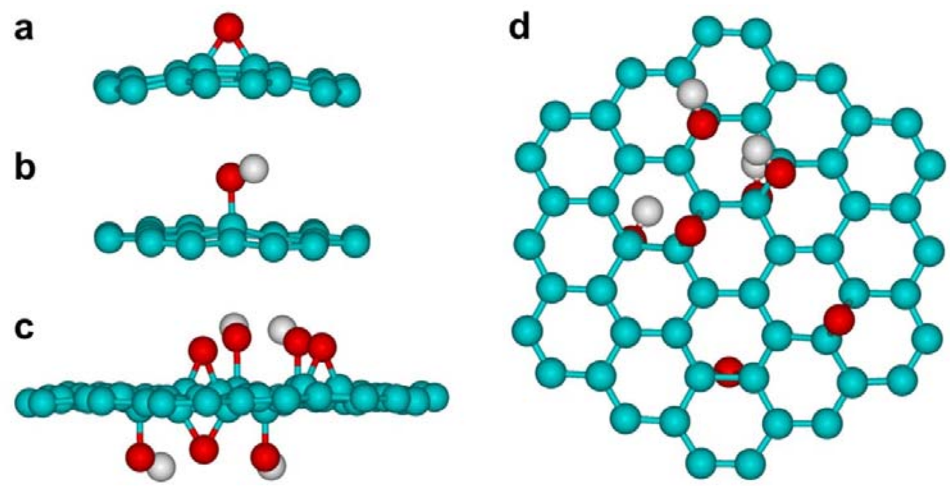
- SA ~850 m^2/g by BET & >1800 m^2/g by methylene blue adsorption in solvents
- The C/O ratio is adjustable from 2 to 500, i.e., FGS_2 to FGS_{500}.
- The edges can be carboxylated.
- Additional functional groups can be attached.
- Lattice defects can function as radical sites.
- FGS is an ideal 2D macromolecular carrier for nanoparticles.
- Exothermic surface reactions
- The particle size is below 1 μm.

Aksay, I., Princeton 2010.



H.C. Schniepp, *et al.*, *J. Phys. Chem. B* (2006)

With functional groups, thickness of graphene sheet ~ 0.78 nm

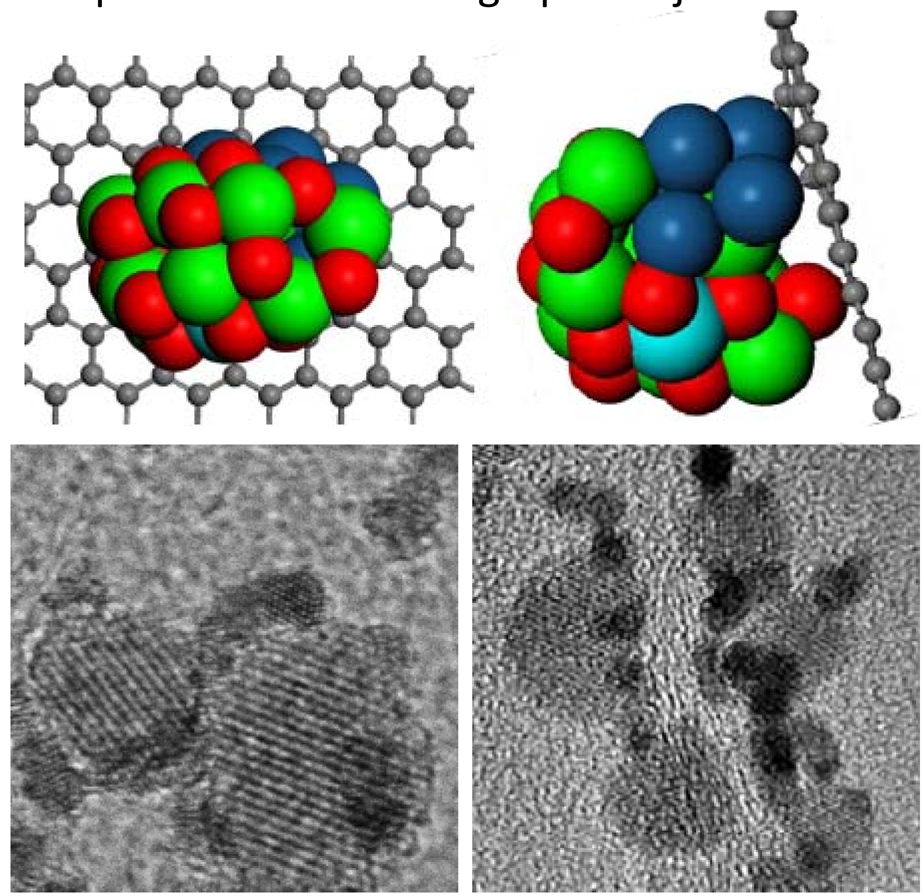


a: epoxide on graphene, b: hydroxide on graphene
c, d: in-plane and overhead view of a FGS

Metal Decorated Graphene Sheets

- Graphene as a template for nanoparticle nucleation.
- Indium-tinoxide (ITO) nanoparticles are stabilized on FGS at lattice defect sites.
- Pt nanoparticles are stabilized at the ITO graphene junctions.
- Coarsening/sintering of Pt nanoparticles is arrested due to their pinning at the ITO graphene junctions.
- The approach is suitable for other oxide/metal junctions on graphene templates.

DFT calculations show the stabilization of Pt nanoparticles at the ITO-graphene junctions.



Aksay, I., Princeton and PNNL 2010.

Polymeric Nitrogen Chains in a Graphene Matrix and Confined inside a Carbon Nanotube

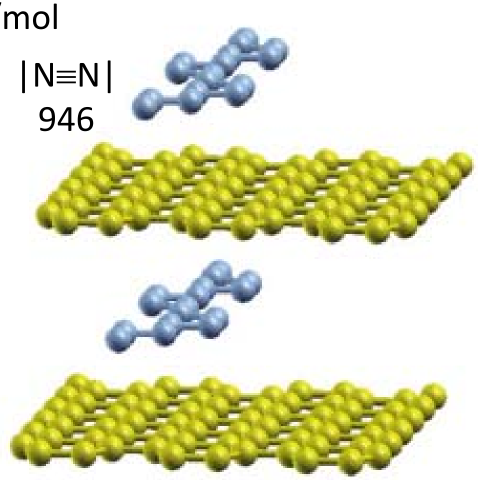
- Large energy difference between single N-N or double N=N and triple N≡N bonds.

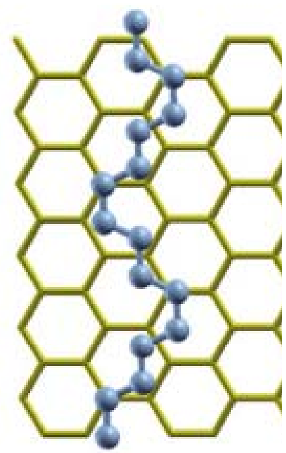
<u>Nitrogen bond enthalpies</u>

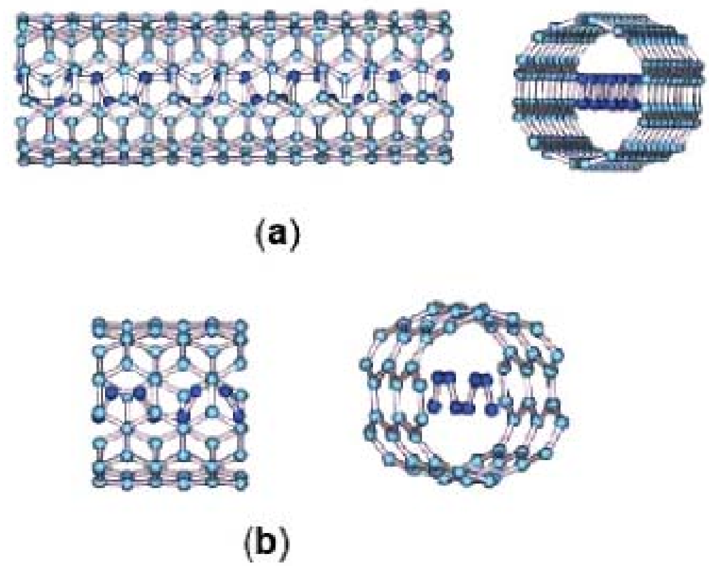
N-N	159 kJ/mol
N=N	419 kJ/mol
N≡N	946 kJ/mol

$(-N{=}N)_i-$ -368 |N≡N|

159+419   ⟶   946







- *ab initio* electronic structure and molecular dynamics calculations demonstrate stability of the nitrogen phase at ambient temperature and pressure when intercalated in a multilayer graphene matrix or using carbon nanotube confinement.
- The charge transfer from the graphene matrix to the nitrogen chain stabilizes the entire three dimensional structure.The hybridization between the nanotube and the N-chain conduction bands leads to the stability of the polymeric nitrogen.

Timoshevskii et al., Phys Review B 80, 115409, 2009; Abou-Rachid, H., et al., Phys. Review Letters, 100, 196401, 2008. Christe, K.O., PEP 32, 3, 2007, 194.

Ultra-High Pressure Supercritical Fluid Processing of Reactive Materials

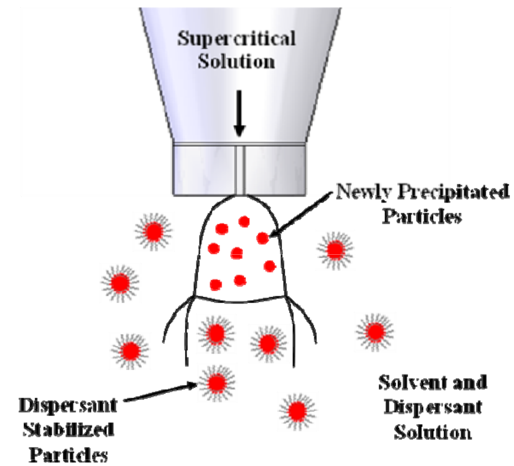
Rapid Expansion of a Supercritical Solution (RESS)

Saturation Vessel: Supercritical Solution Controlled at Selected T and P (inputs: SCF, Solute)

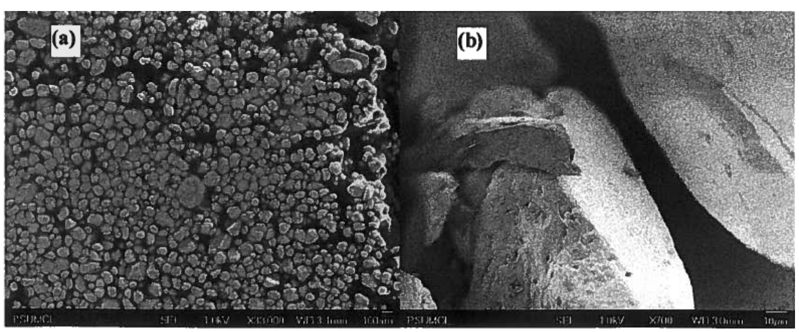
→ **Expansion Nozzle**: Rapid Expansion for Particle Formation by Homogeneous Nucleation

→ **Collection System**: Nanosized Particle Recovery

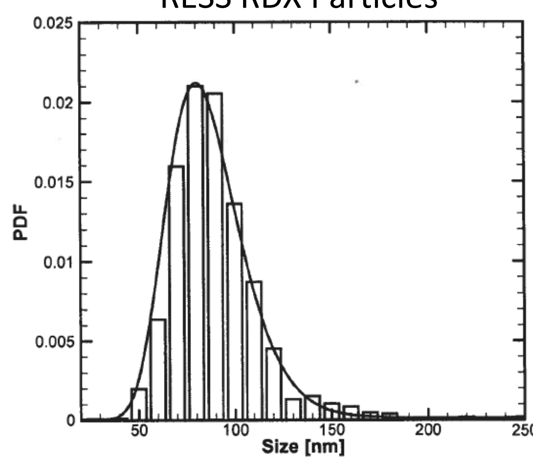
Rapid Expansion of a Supercritical Solution into an Aqueous Solution (RESS-AS)



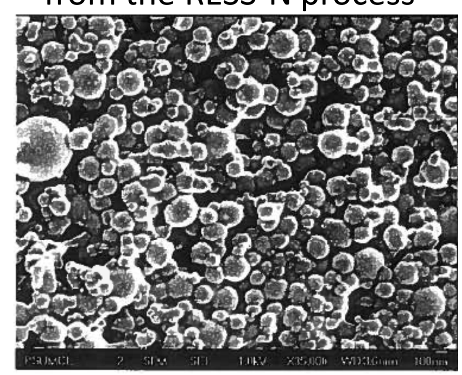
FE-SEM images of (a) RESS produced RDX particles and (b) military grade RDX



Particle Distribution of RESS RDX Particles



FE-SEM images of RDX coated ALEX nAl particles from the RESS-N process

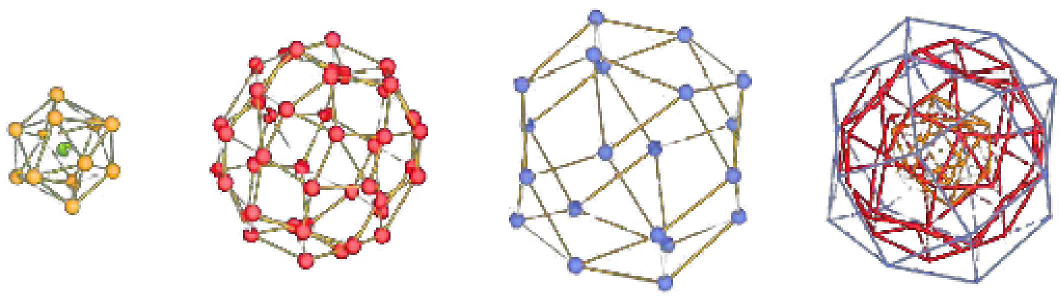


Essel, J., and Kuo, K., Penn State, 2012

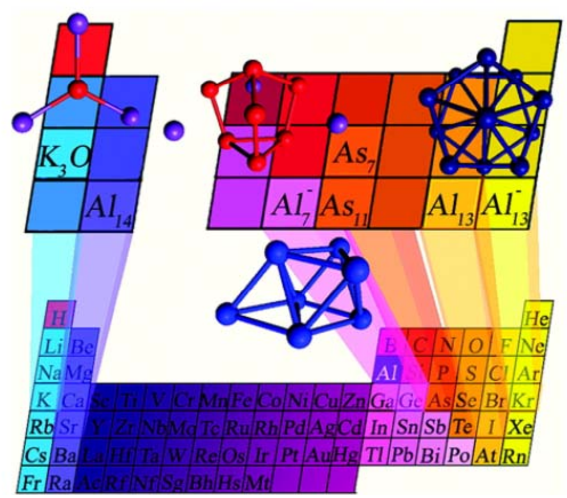
Cluster Assembled Reactive Materials

- Aluminum clusters have been studied and consist of metallic Al cores surrounded by a monolayer of a protective shell.
- Particles/clusters have between 10 and 100 aluminum atoms and diameters between 0.5 and 1.3 nm.

$$AlI + LiN(SiMe_3)_2 \rightarrow Al_{77}[N(SiMe_3)_2]_{20}^{2-}$$



Three dimensional periodic Table of cluster elements. Castleman, A. W., Jr.; Khanna, S. N. J. Phys. Chem. C 2009, 113, 2664-2675.

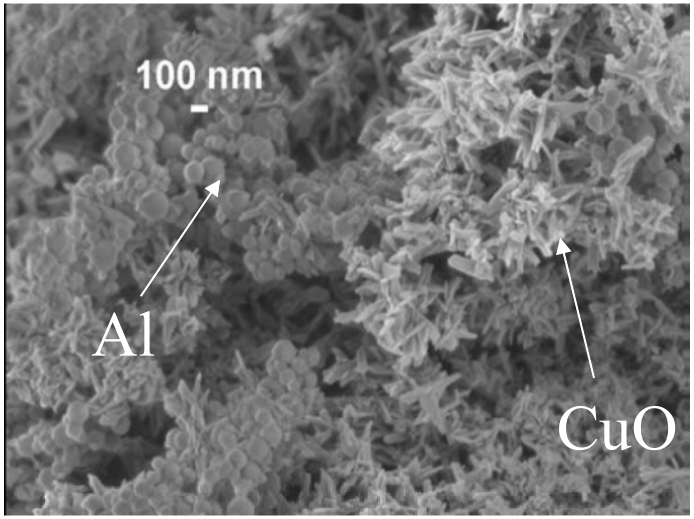


- Al cluster (far right) consists of nested shells containing (from left to right) 13, 44, and 20 Al atoms, A. Ecker, E. Weckert, and H. Schnöckel *Nature* **1997**, *387*, 379.
- Metal halide co-condensation reactor (MHCR) and metal halide chemistry enables creation of other low valent metal clusters (e.g. Ti, Hf, Si) – (B. Eichhorn, University of Maryland, 2011).
- Reactions of metal clusters with small molecules often depend on cluster size and vary discontinuously with the number of atoms and composition, rather than scale linearly with size, i.e., one atom makes a difference.
- Clusters can act as building blocks for new materials. Self assembled monolayers (SAMs) for cluster passivation and size control. Ligand-directed association for aggregate formation.

Some Examples of Nanoenergetics Combustion

Nanoscale Thermite Combustion

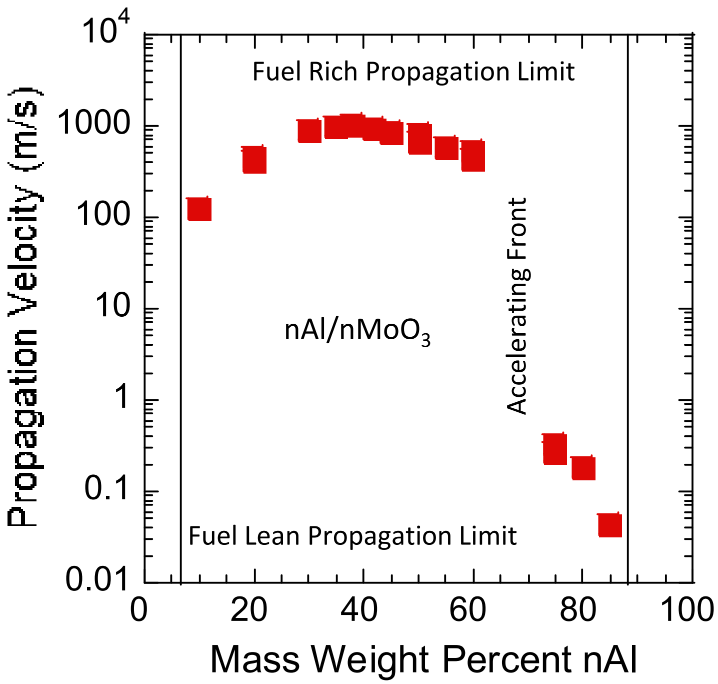
- Nanoscale thermites are prepared via sonication in a solvent (hexanes)
- Combustion propagation tested in instrumented burn tube



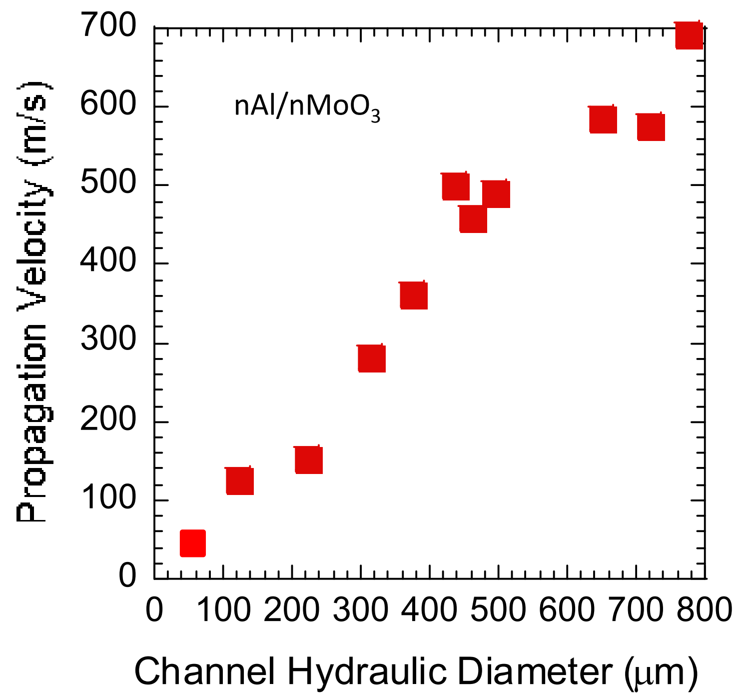
S.F. Son and R.A. Yetter, Nanoenergetics, 2012

Nanothermite Combustion

Effect of Equivalence Ratio

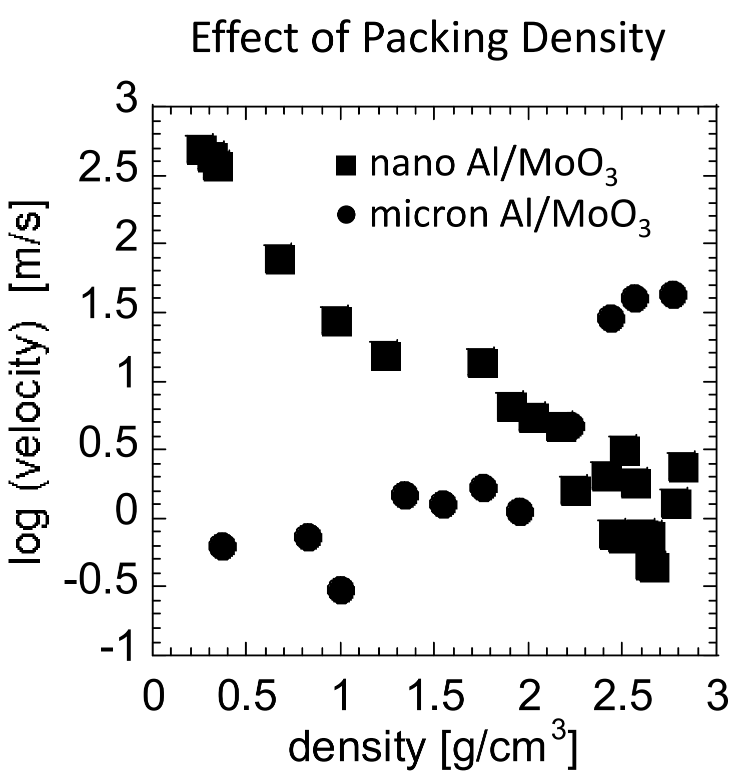


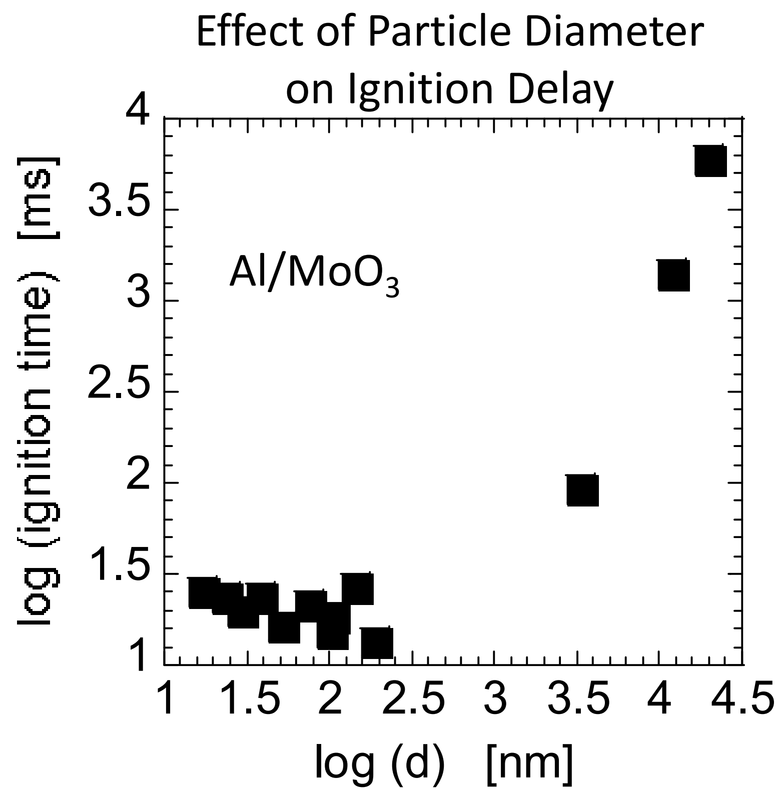
Effect of Channel Size



Dutro, G.M., Son, S.F., Risha, G., R.A. Yetter, Proceedings of the Combustion Symposium, 2009

Nanothermites



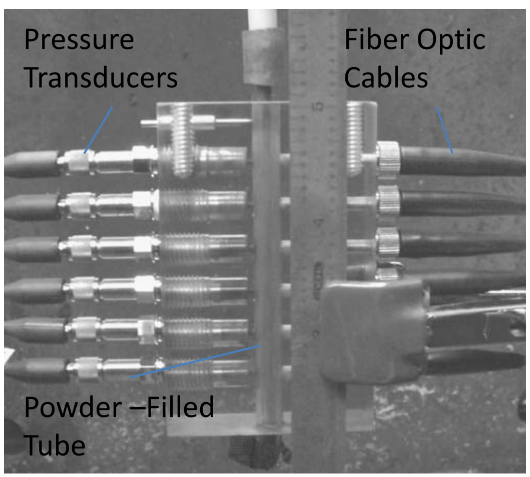


J.J. Granier and M.L. Pantoya, *Combust. Flame* 138 (2004) 373-383.
M.L. Pantoya and J.J. Granier, *Propellants Explosives Pyrotechnics* 30 (2005) 53-62.
V.E. Sanders, B.W. Asay, T.J. Foley, B.C. Tappan, A.N. Pacheco, and S.F. Son, *J. Propul. Power* 23 (2007) 707-714.

Propagation Mechanisms of Nanothermite Reactions

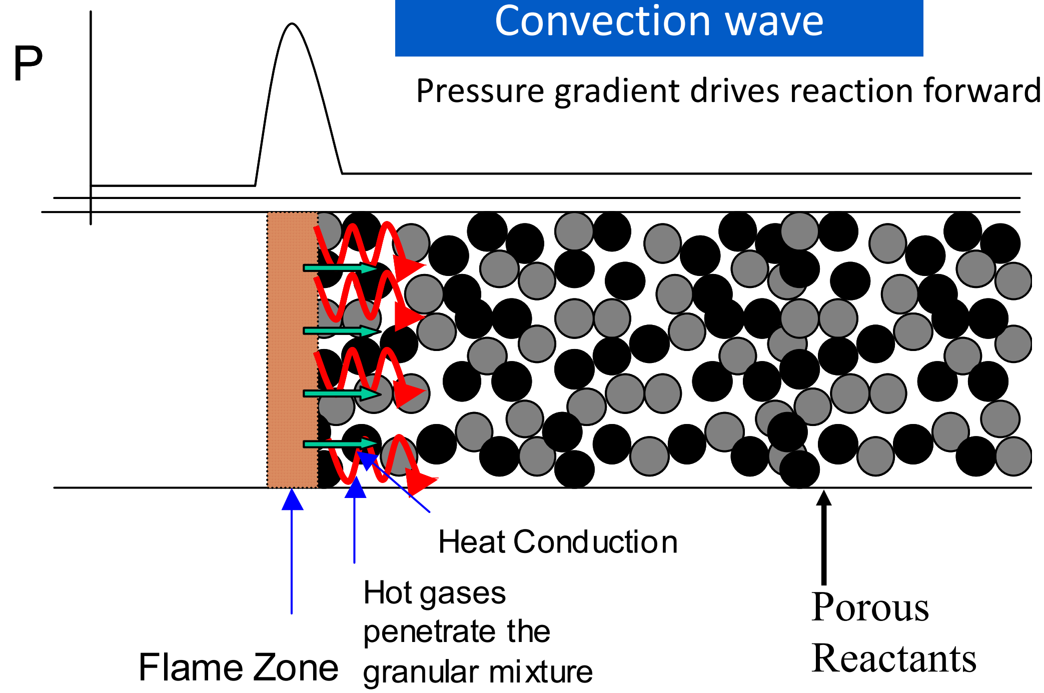
When ignited in a burn-tube, 'fast' nanothermites (Al/CuO, Al/MoO_3, Al/Bi_2O_3) react through a convective mechanism

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



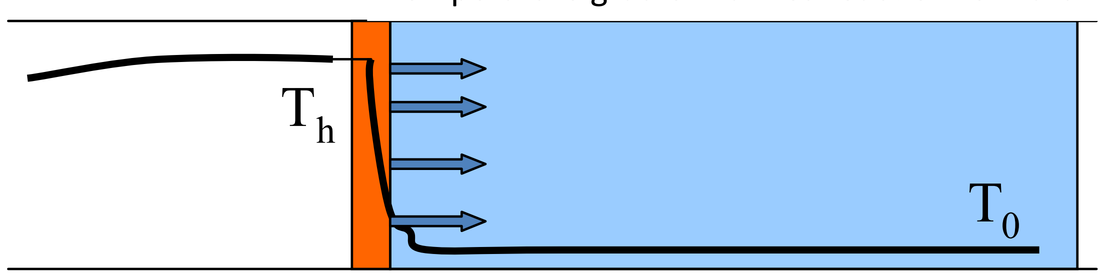
Convection wave

Pressure gradient drives reaction forward



Conduction wave

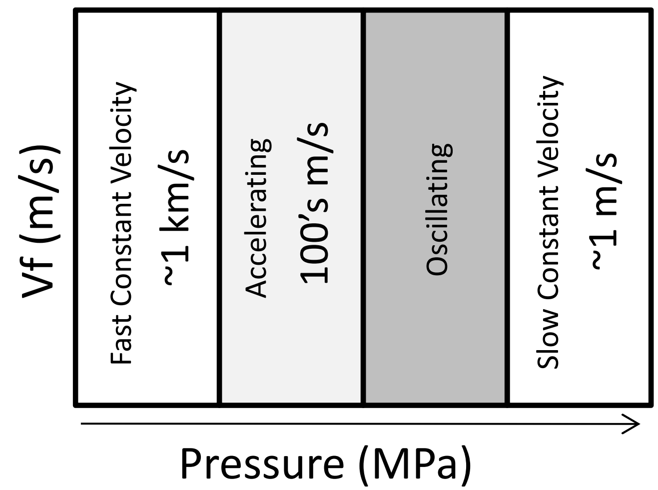
Temperature gradient drives reaction forward



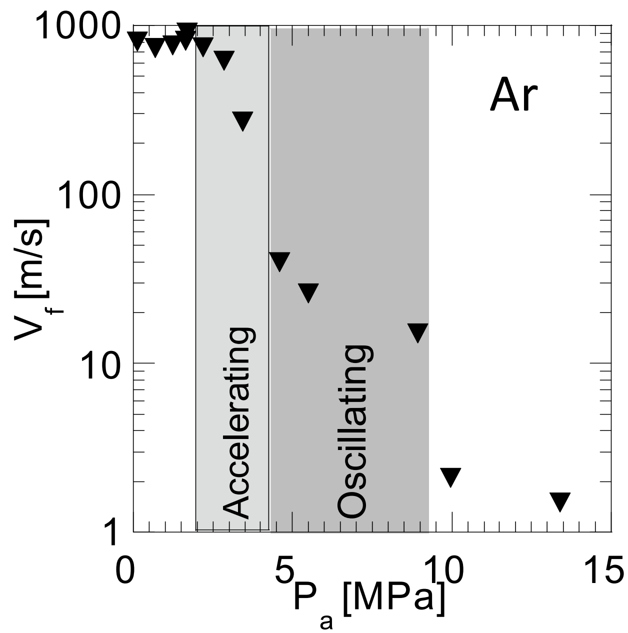
Effect of Pressure on the Propagation Rate in a Al/CuO Nanothermite

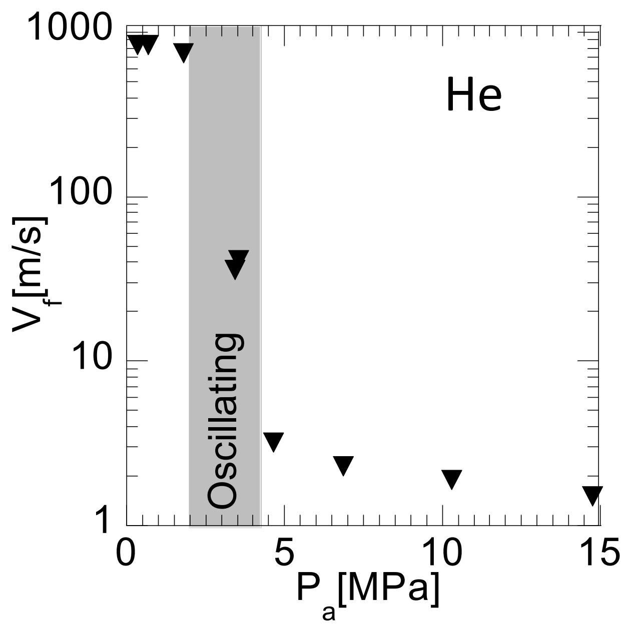
- Nano-aluminum from Novacentrix (avg. d_p=38nm)
- Nano CuO from Sigma-Aldrich (avg. d_p=33nm)
- Studies conducted in an optical strand burner (V=23 liters)
- Pressurized with 3 different gases (Ar, He, or N_2)

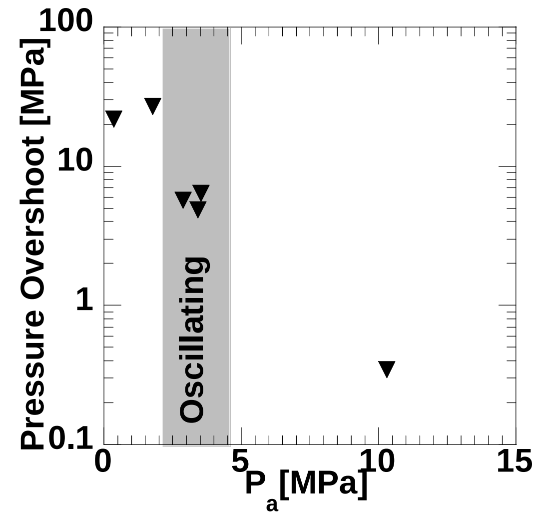
- As pressure is increased, several different modes of propagation are observed
- Pressure at which propagation mode changes depends on pressurizing gas; He has a high thermal conductivity



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



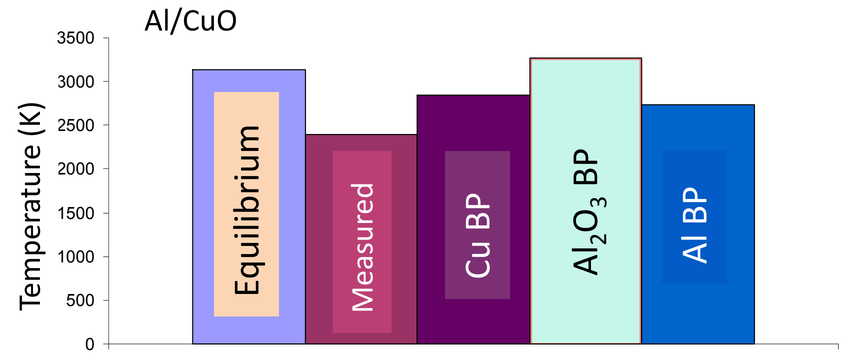




Temperature Measurements Suggest that the Final Products are not Gasified

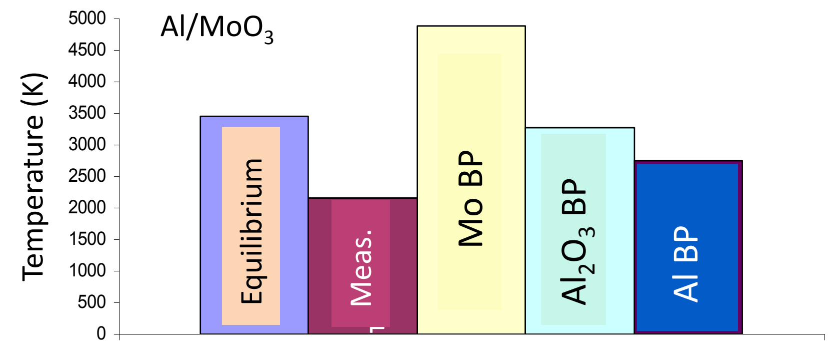
$$2\mathbf{\mathit{Al}} + 3\mathbf{\mathit{CuO}} \rightarrow \mathbf{\mathit{Al}}_2\mathbf{\mathit{O}}_3 + 3\mathbf{\mathit{Cu}}$$

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



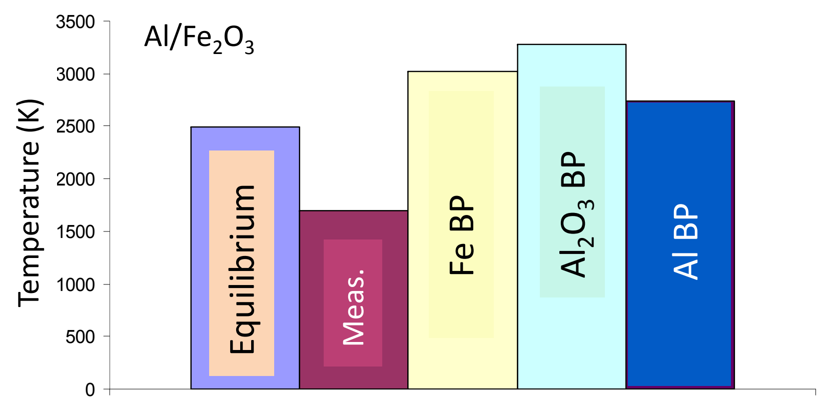
$$2\mathbf{\mathit{Al}} + \mathbf{\mathit{MoO}}_3 \rightarrow \mathbf{\mathit{Al}}_2\mathbf{\mathit{O}}_3 + \mathbf{\mathit{Mo}}$$

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



$$2\mathbf{\mathit{Al}} + \mathbf{\mathit{Fe}}_2\mathbf{\mathit{O}}_3 \rightarrow \mathbf{\mathit{Al}}_2\mathbf{\mathit{O}}_3 + 2\mathbf{\mathit{Fe}}$$

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

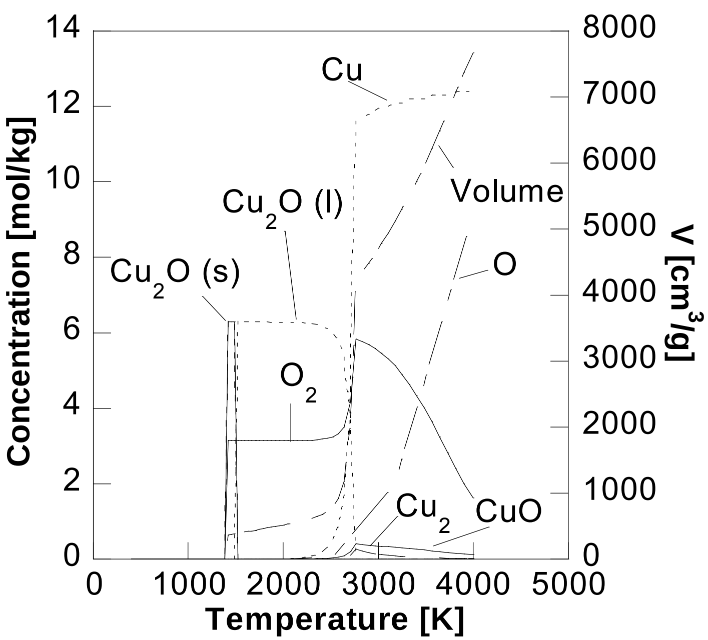


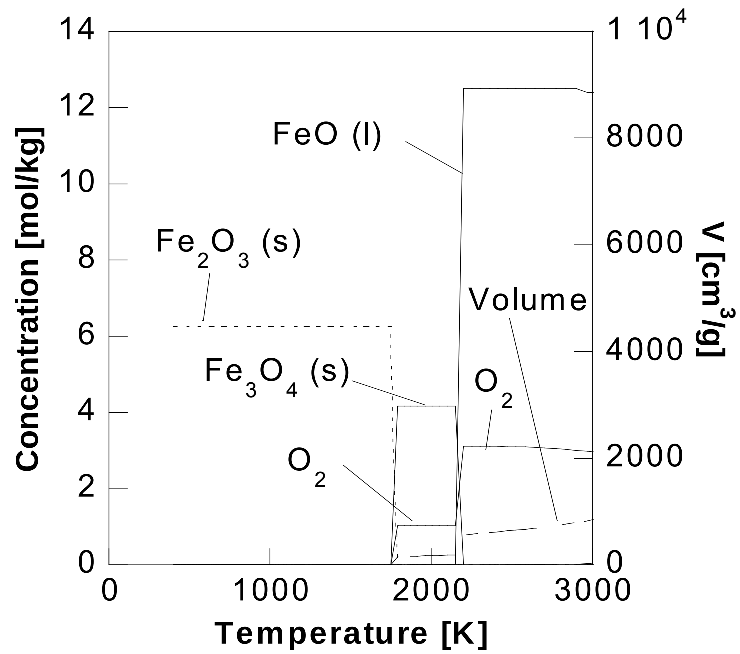
Metal Oxides Vaporize or Decompose at Low Temperatures

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

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

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





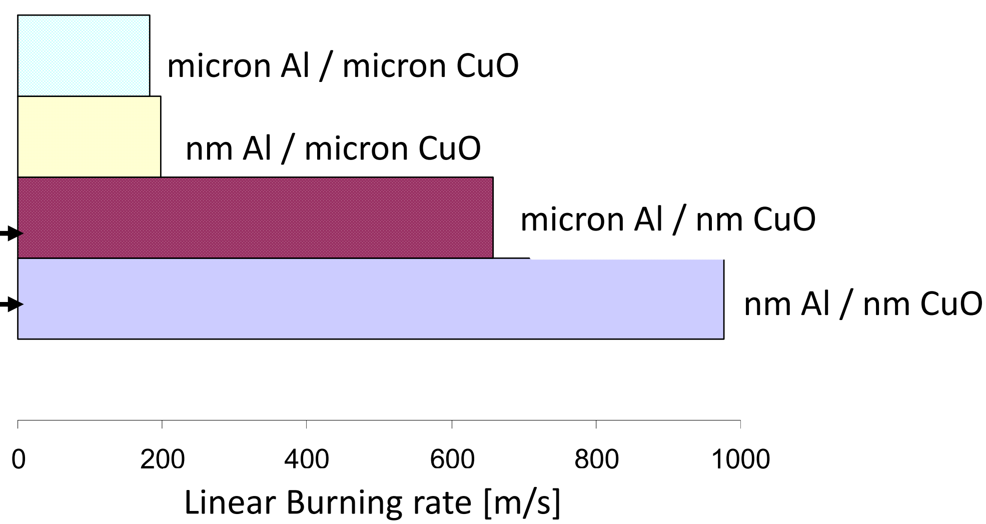
Effects of Oxidizer vs Fuel Particle Size

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

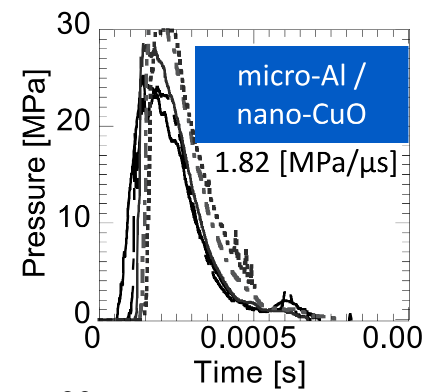
	Linear Burning Rate [m/s]	Mass Burning Rate [kg/s]	Energetic Mass Burning Rate [kg/s]	Avg. mass per run [g]	% mass Al_2O_3
Nano Al/ Nano CuO	977	3.79	3.14	0.31	17.1
Micron Al/Nano CuO	658	4.77	4.72	0.58	1.0
Nano Al/Micron CuO	197	1.31	1.08	0.53	17.1
Micron Al/Micron CuO	182	2.02	2.00	0.89	1.0

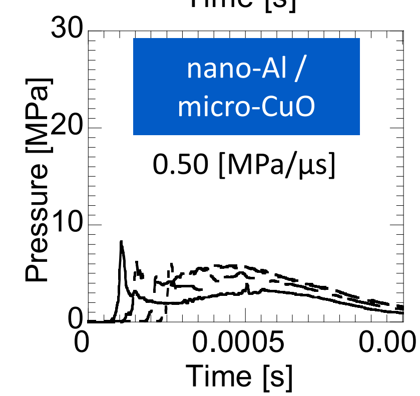
Linear propagation rate was more dependant on the CuO particles size

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



Evidence that the oxide decomposition drives convective burning

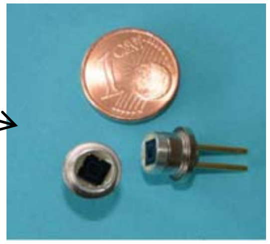




Silicon Reactives Background

- Previous work:
  - Silicon powders have been used in pyrotechnic formulations since the 19th century, however it's combustion has been relatively unstudied
  - The fast reaction of nanoporous silicon first reported in 1992 by McCord et al
  - In 2002 Mikulec et al reported the first solid-state explosive using porous silicon and a $Gd(NO_3)_3x6H_2O$
  - Clément and co-workers developed an airbag igniter using oxidizer filled nanoporous silicon wafers
  - Examples of pore fillers: $NaClO_4$ x $1H_2O$, $Ca(ClO_4)_2$ x $4H_2O$, Magnesium Perchlorate, Sulfur, PFPE
- The combustion of silicon-based composites has not been adequately studied

Prototype of Porous Si-based Airbag Igniter (Clément et al., 2007)

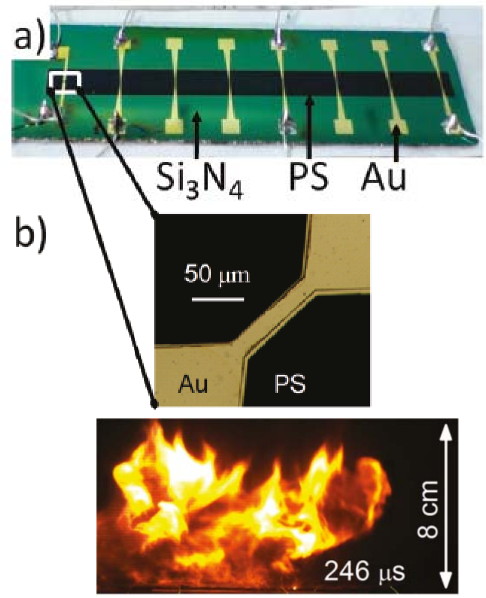


S.F. Son and R.A. Yetter, Nanoenergetics, 2012

Psi $NaClO_4$ Burning Rates > 3000 m/s

- Porous silicon films 65-90 μm thick were fabricated using galvanic etching approach that does not require an external power supply as well as electrochemical etch.
- 3.2 M solution of NaClO4 in methanol dropcast on the chip
- ΔH_R = 9.9 kJ/g in N_2 and 27.3 kJ/g O_2.
- Energy output and initiation are dependent on the hydrogen termination of the Psi.

Becker C.R., Apperson, S., Morris, C.J., Gangopadhyay, S., Currano, L.J., Churaman, W.A., and Stoldt, C.R., NanoLetters, 2011
Currano and Churaman, J. MEMs, 18, 2009.



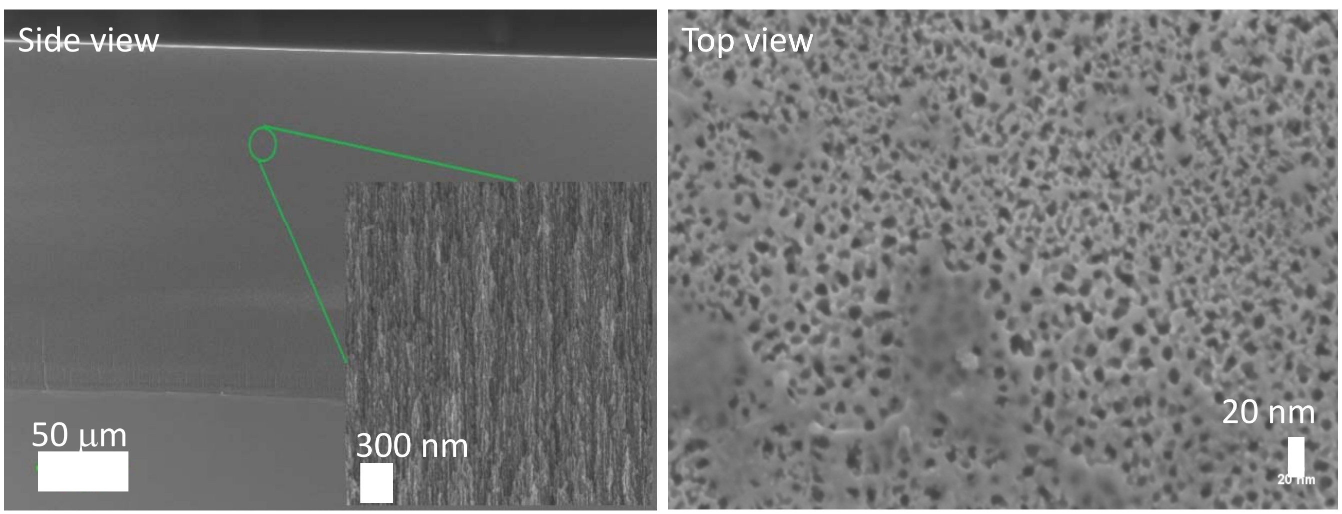
- Psi $NaClO_4$ reaction used to drive flyer plate:
- Plate force ~ 67mN, Equivalent pressure on plate area ~ 3.4kPa

Properties and flame propagation velocities

Electrolyte (HF;EtOH)	Thickness (μm)	Pore size (nm)	Porosity (%)	Surface area (m^2/g)	Velocity from video (m/s)	Velocity from wires (m/s)
20:1	65-95	2.4-2.5	65-67	830-850	3050	3100
3:1	65-95	2.8-2.9	79-83	890-910	2170	2150

Reaction Tuning using Ordered Multi-scale Structures with nPS: The Reference Case

- Degenerately doped (1 – 5 mΩ-cm) substrates were used for reference Si
  - Substrates with lower dopant concentrations yield fragile porous layers
  - Equivalence ratio of the composite cannot be accurately determined
- Experimental procedure:
  - Porous layers were etched on 4” wafers using electrochemical process
  - The process was tuned to yield mechanically stable thick porous layers whose surfaces can be cleaned even after impregnation with the oxidizer
  - Porosity determined gravimetrically by dissolving porous layers in aqueous NaOH
  - 5 mm wide samples were scribed soaked in $Mg(ClO_4)_2$ – methanol solutions
  - Varied compositions were prepared using solutions of different concentrations.
  - Equivalence ratio was determined gravimetrically after cleaning the surfaces



FE-SEM images of porous layers etched on degenerately doped substrates. BET measurements indicate a surface area ~ 350 m^2/g

V.K. Parimi, S.A. Tadigadapa, and R.A. Yetter

Propagation Rates and Temperatures for Degenerately Doped Substrates

- Samples ignited with 10 ms pulse from 200W CO_2 laser.
- Propagation rate obtained from x-t plots using high speed video
- Reaction temperature estimated using multi-wavelength pyrometry with a spectrometer and wavelengths between 475-615 nm.

No.	$\boldsymbol{\Phi}_{th}$	$\boldsymbol{\Phi}_{measured}$	Speed (m/s)	Temperature (K) ε = const	$\varepsilon \sim 1/\lambda$	$\varepsilon \sim 1/\lambda^2$
1	3.8*	1.2-1.24	5-7.7	2044	1897	1769
2	4.6*	1.2-3.8	2.6-7.7	1869-2184	1747-2018	1639-1876
3	5.6	3.3-4.6	4.1-4.5			
4	6.7	2.4-3.4	2.5-3.3	1844-1930	1723-1798	1617-1683
5	8.3	4.7-5.1	3.9-4.9	1706-2043	1824-1897	1647-1771
6	13.5	3.9-5.2	2.4-2.8	1792-1870	1677-1746	1577-1637
7	16.5	10.3-19.5	3.2-4	2002	1862	1740
8	33.1	20.4-20.8	2.6 -3	1886-1993	1760-1853	1650-1732

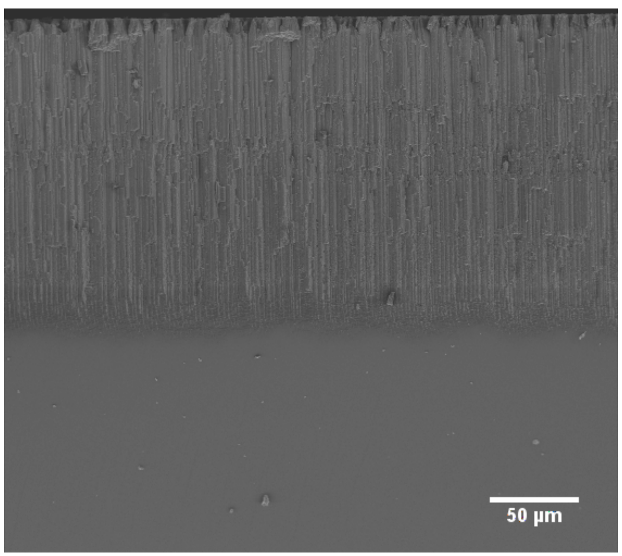
- Fuel rich flame extinction limit:
  - Samples soaked in 0.1 M solution ($\boldsymbol{\Phi}_{th}$ = 80) did not ignite
  - Samples soaked in 0.15 M solution ($\boldsymbol{\Phi}_{th}$ = 56, $\boldsymbol{\Phi}_{measured}$ = 39) ignited but did not propagate

V.K. Parimi, S.A. Tadigadapa, and R.A. Yetter

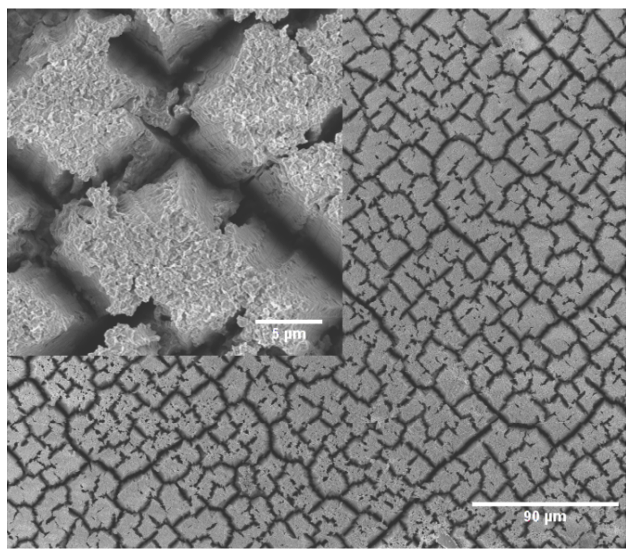
Electrochemical Etch of Silicon Wafers with Different Doping Produces Different Structures

- Higher speeds reported with moderately doped p-type substrates (1 – 20 Ω-cm)
- Moderately doped (2-5 Ω-cm boron) substrates were tested to verify higher rates
- Reaction front propagations between 300-1,000 m/s were observed for these substrates
- Micrometer scale cracks were observed in the porous layer
- Porosity and equivalence ratio estimates are believed to be incorrect ($P \approx 0.54$, $\boldsymbol{\Phi}_{th} \approx 9.6$)
- Porosity cannot be determined gravimetrically due to the high sensitivity

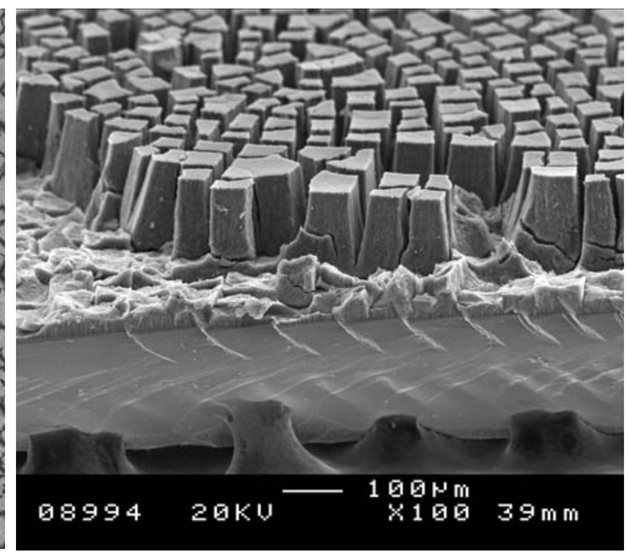
2-5 Ω-cm nPS (side view)



2-5 Ω-cm nPS (top view)



1-20 Ω-cm nPS



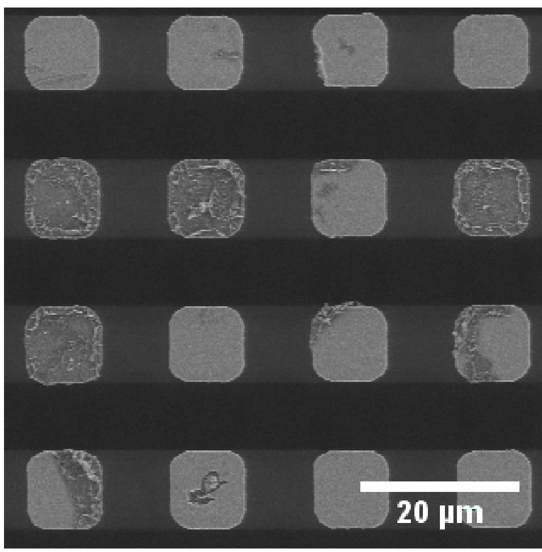
(from Physical Optics Corporation)

V.K. Parimi, S.A. Tadigadapa, and R.A. Yetter

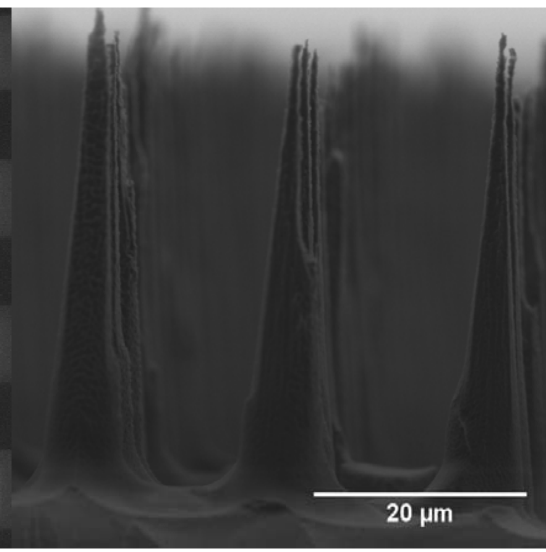
Ordered Structures Fabricated on Degenerately Doped Substrates

- Si wafers (highly doped 0.001-0.005 Ω-cm) were photolithographically patterned using thick layers of photo-resist (KMPR or SPR-220-7)
  - An RF RIE process was used to etch pillared structures
  - Height of the structures is limited to ~ 35 µm by sidewall profile and photo-resist properties
- Using thicker photo-resist layers affects feature sizes
- The photo-resist was stripped and nanopores were etched using the electrochemical process
  - Thick porous layers are etched below the surfaces

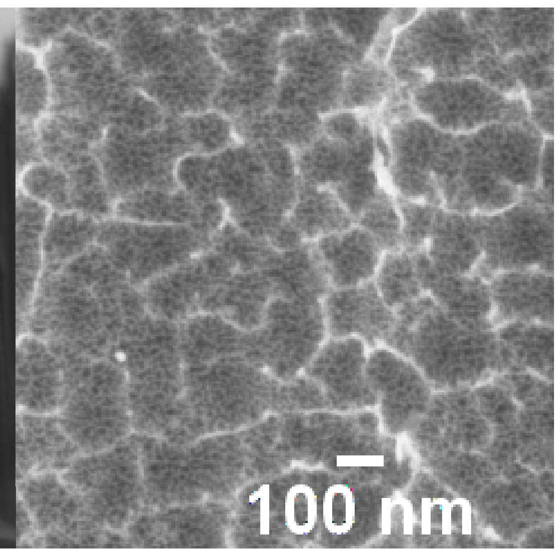
Top view



Side view



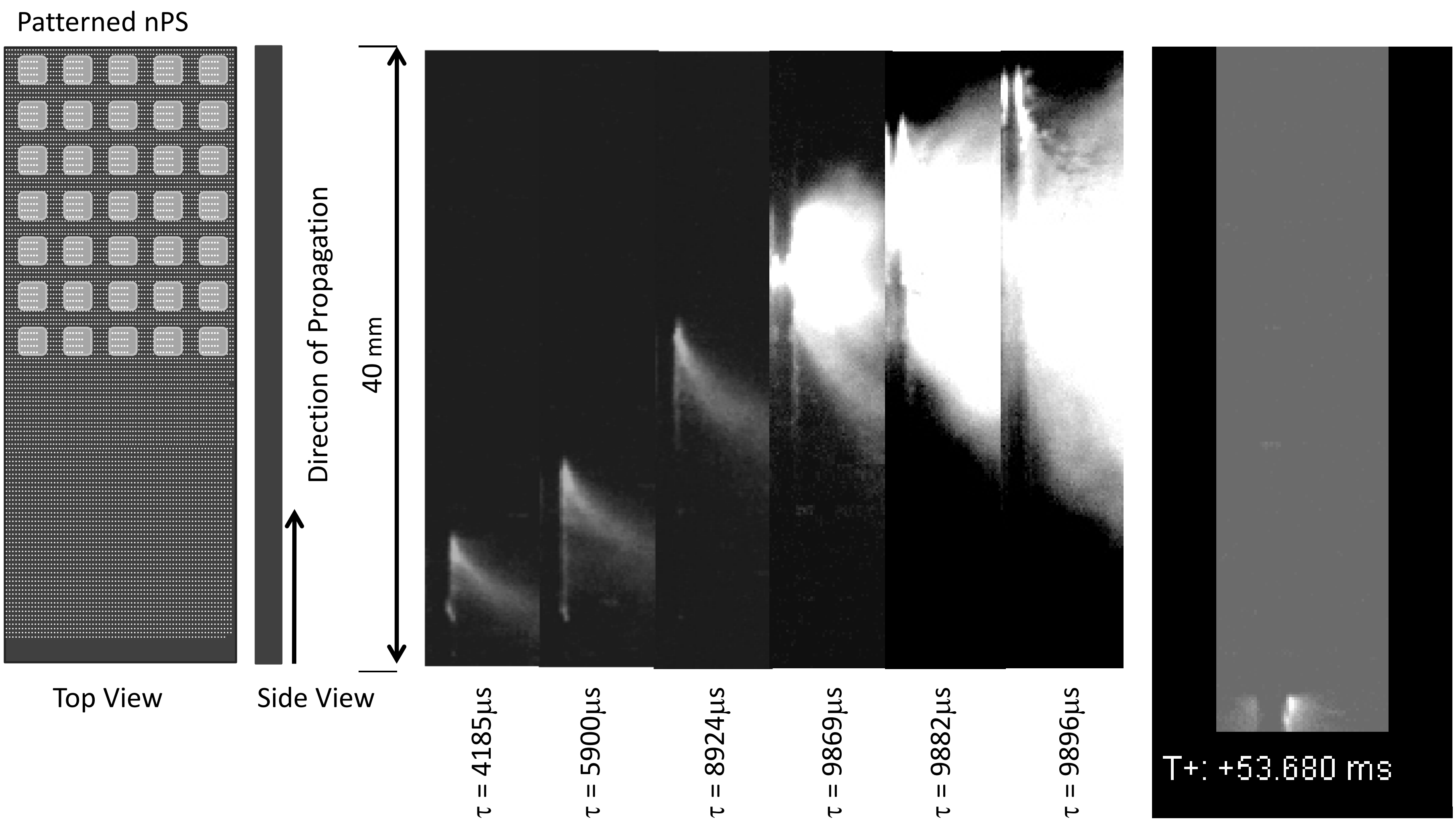
Surface of Pillars



The pillars are ~ 35 µm tall and have 8µm square bases separated by ~8µm. The pore diameters on the pillars and the substrate are ~ 20nm.

V.K. Parimi, S.A. Tadigadapa, and R.A. Yetter

Reaction Propagation through Patterned nPS/$Mg(ClO_4)_2$ Composite



The pillars are ~ 35 μm tall and have 8μm square bases separated by ~8μm. The pore diameters on the pillars and the substrate are ~ 20nm.

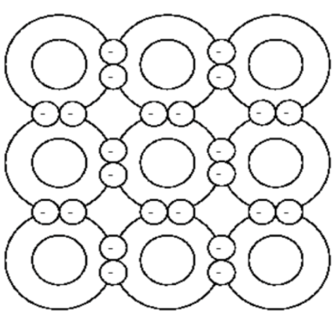
V.K. Parimi, S.A. Tadigadapa, and R.A. Yetter

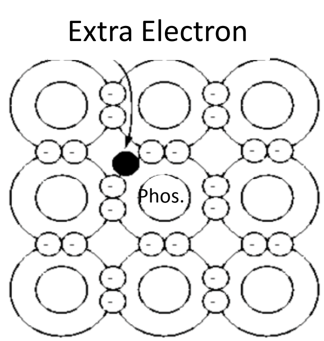
Effect of Doping Silicon Reactives?

- Why could doping make a difference?
  - **Oxidation-reduction reaction needs the transfer of electrons**, like *np* semiconductor
  - Reducing agent is the electron donor, oxidizer is the electron acceptor
  - Therefore, an **n-type reducing agent** and **p-type oxidizer** should be more reactive (McClain (1982))
  - Schwab & Gerlach (1967) **demonstrated this with the thermite reaction**,

$$Ge + 2MoO_3 \rightarrow GeO_2 + 2MoO_2$$

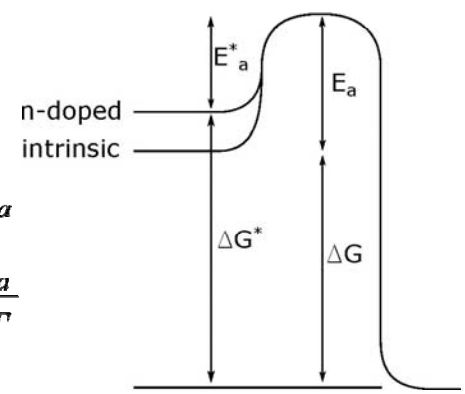
  - n-type Ge accelerated reaction, p-type Ge slowed reaction
  - Effect on oxidizer doping also shown by McClain & Schwab to improve oxidizer reactivity





$$\delta\Delta G = \delta E_a$$

$$\frac{\delta\Delta G}{RT} = \frac{\delta E_a}{RT}$$



G.M. Schwab, J. Gerlach. The Reaction of Germanium with Molybdenum(VI) Oxide in the Solid State, Z. Physik Chem., 56:121, 1967.

Doped Si Powders – Production and Characterization

- Doped powders were produced by milling silicon wafers in a planetary ball mill for 3 hours

Powder Designation	Dopant	SSA (m^2/g)
intrinsic	N/A	10.1
low p-doped	boron	10.6
n-doped	arsenic	8.9
high p-doped	boron	10.2

Powder Type	Dopant	Resistivity (Ω-cm)	Conductivity (S/m)	wt% dopant
intrinsic	N/A	80	1.25	N/A
low p-doped	boron	0.015	6.67×10^{3}	$7.9\times10^{-5} – 2.13\times10^{-4}$
n-doped	arsenic	5×10^{-3}	2.0×10^{4}	6.54×10^{-2}
high p-doped	boron	3.5×10^{-3}	2.86×10^{4}	$1.55\times10^{-2} – 4.35\times10^{-2}$

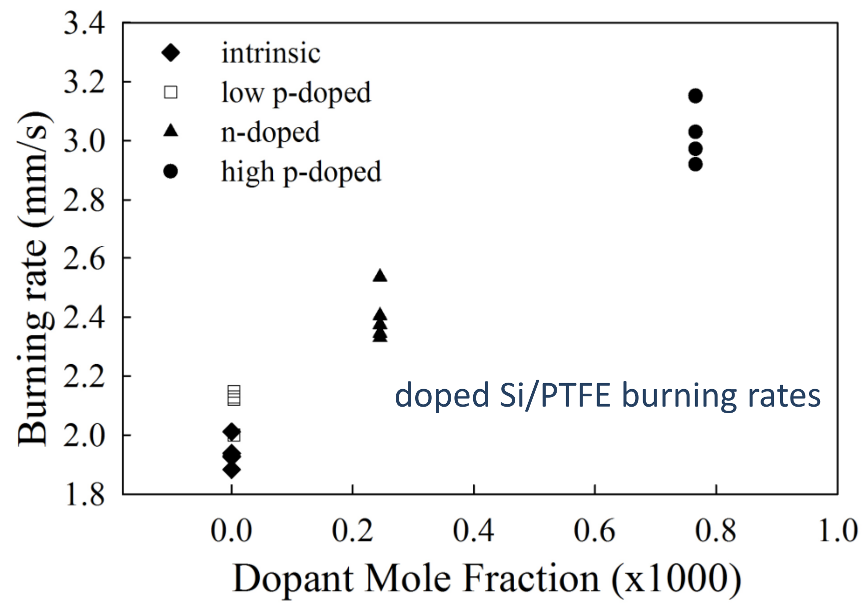
- Particle sizing carried out by laser diffraction – uniform particle sizes were measured by Malvern mastersizer 2000
- XRD analysis performed with Bruker D8 x-ray diffractometer - No crystalline impurities detected

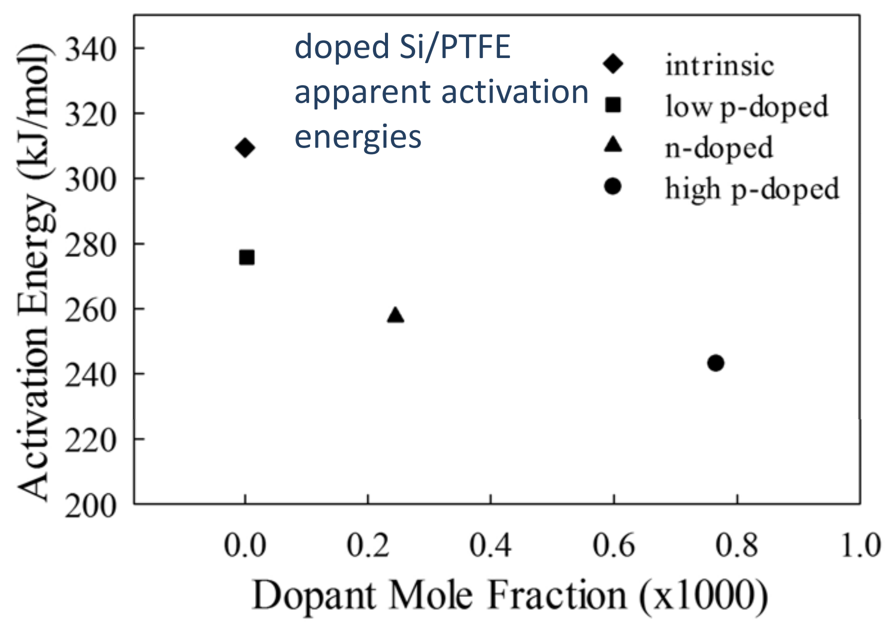
- BET analysis shows SSA should not affect burning rates
- SEM images show that all powders have similar morphologies
- Agree well with particle sizing results
- Fracture surfaces on all particles

S.F. Son, Purdue, 2011

Doped Powders – Reaction Characterization

- Burning rates of pressed pellets of doped Si/PTFE at 200 psi were analyzed
  - Doping has a large apparent effect
  - The effect contradicts the theory
- Differential thermal analysis supports burning rate data
  - Apparent activation energy measured by the Kissinger method
  - Higher burning rate samples correlate with lower activation energy samples
  - **The effect may be kinetic, but not according to the original hypothesis!**
  - Thermal properties verified by TPS method to be nearly identical
- Could the very small amount of dopant have the same effect as doping of the Si crystals?
  - Thermodynamically the amount of dopant has a negligible effect on energy or temperature
  - Could there be a catalytic effect?

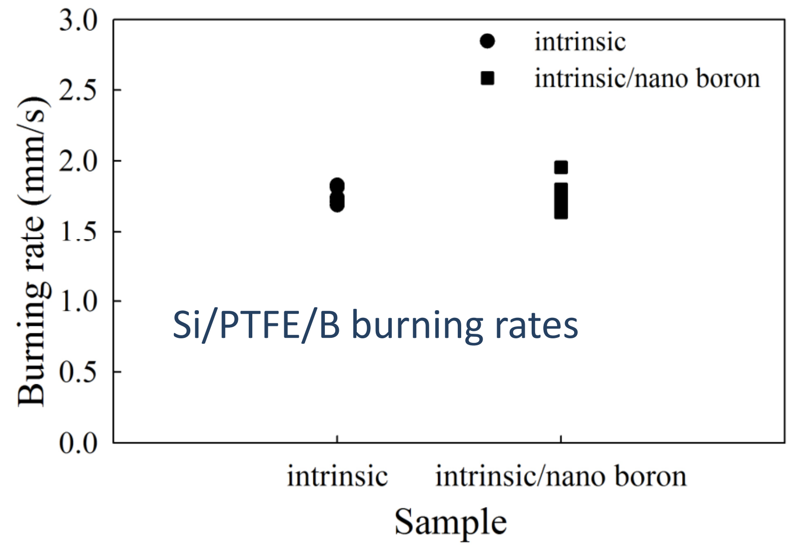


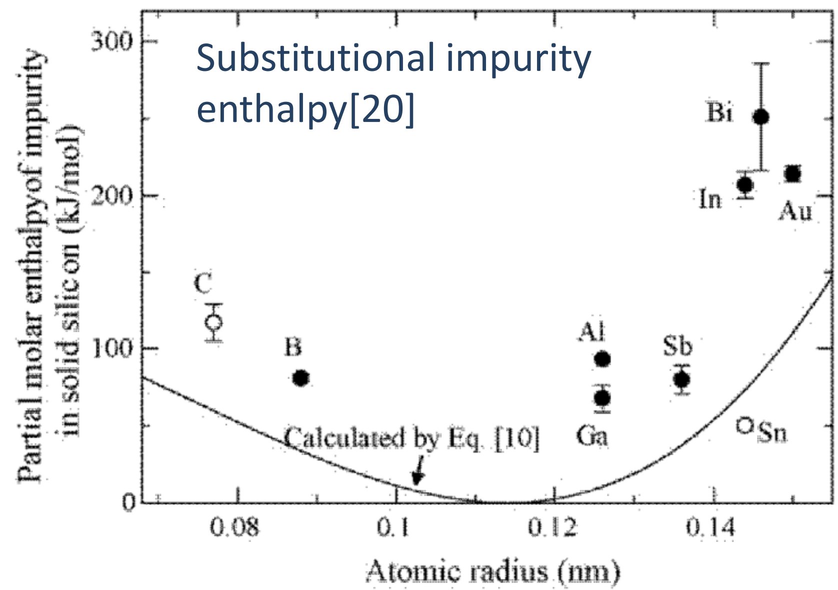


S.F. Son, Purdue, 2011

Doped Powders – Summary

- Small amount of boron powder added to intrinsic Si/PTFE during processing
- **Nano boron did not affect burning rates**
- How can observed results be explained? New hypotheses - lattice defects or electron mobility affects kinetics:
  - Electron mobility
    - Proportional to dopant concentration
  - Lattice defect and strain energy due to substitutional impurities
    - Proportional to dopant concentration
  - Ge doped Si needed to eliminate one of the above

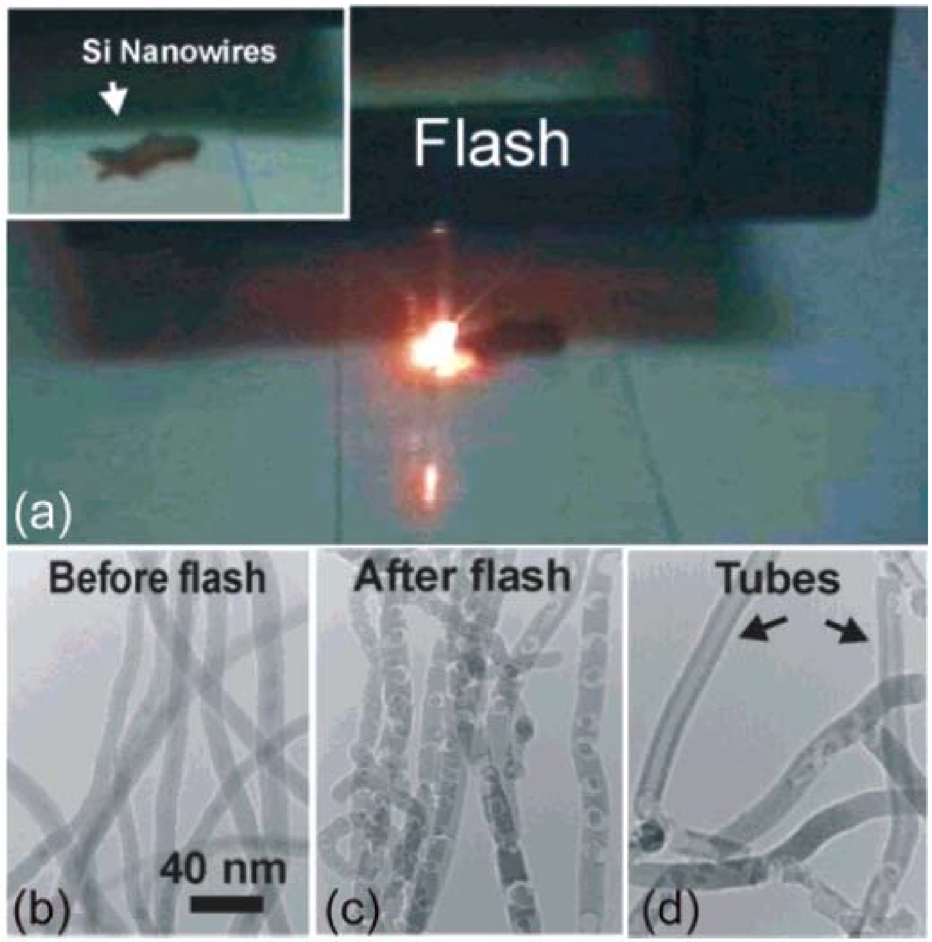




[20]T. Yoshikawa, K. Morita, S. Kawanishi, and T. Tanaka, Thermodynamics of Impurity Elements in Solid Silicon, Journal of Alloys and Compounds, Vol. 490, 2010, pp. 31-41.

S.F. Son, Purdue, 2011

Like Carbon Nanotubes and Nanothermites, Nanosilicon can be Light Activated for Ignition



N. Wang,* B. D. Yao, Y. F. Chan, and X. Y. Zhang, Nano Letters, 2003, 3, 475n

Coal Direct Chemical Looping Process: Reaction Mechanisms of Solid Fuels with Metal Oxides

Reduction

Indirect reduction with aid of gaseous intermediates

$$CO + MO \rightarrow CO_2 + M$$

$$CO_2 + C \rightarrow 2CO$$

With coal, volatiles may initiate the reaction

$$\text{Coal} \rightarrow \text{coal volatiles } (CO, H_2, \text{etc})$$

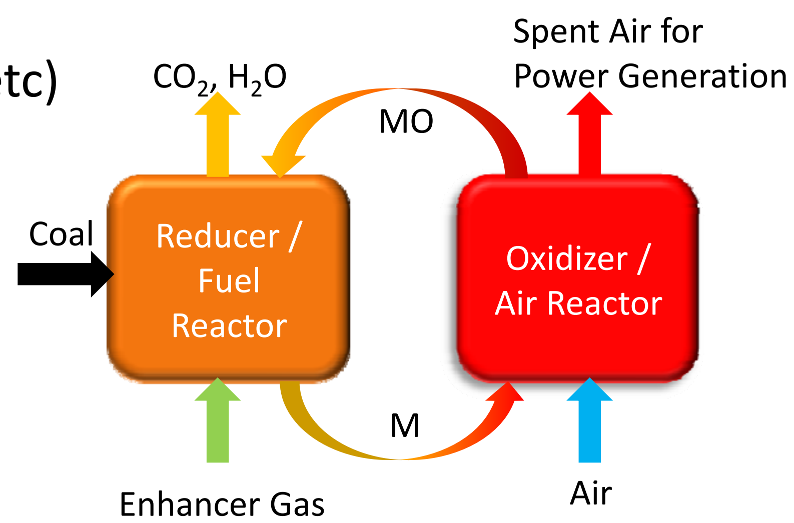
Chemical looping oxygen uncoupling process

$$MO \rightarrow M + ½\, O_2$$

$$C + O_2 \rightarrow CO_2$$

Direct solid-solid reactions

$$C + 2MO \rightarrow CO_2 + 2M$$



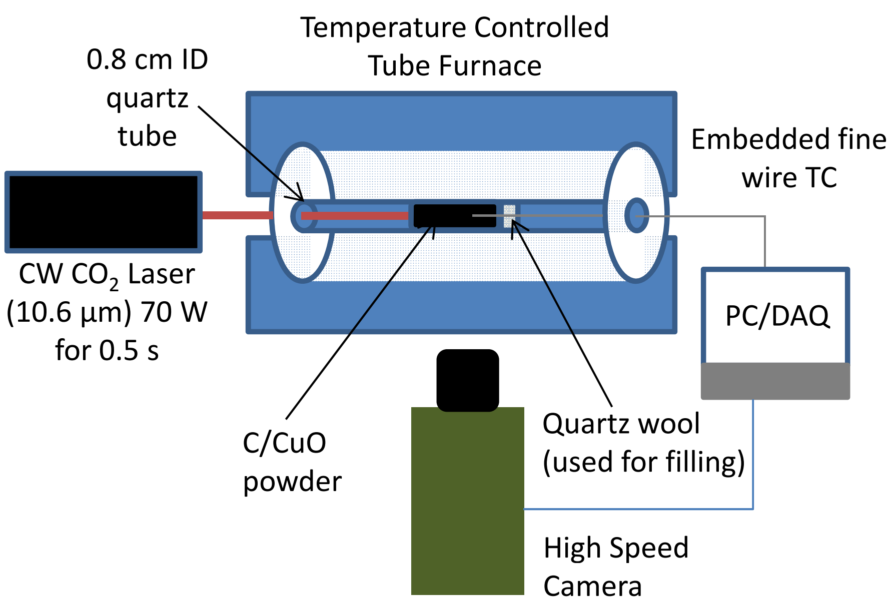
Oxidation

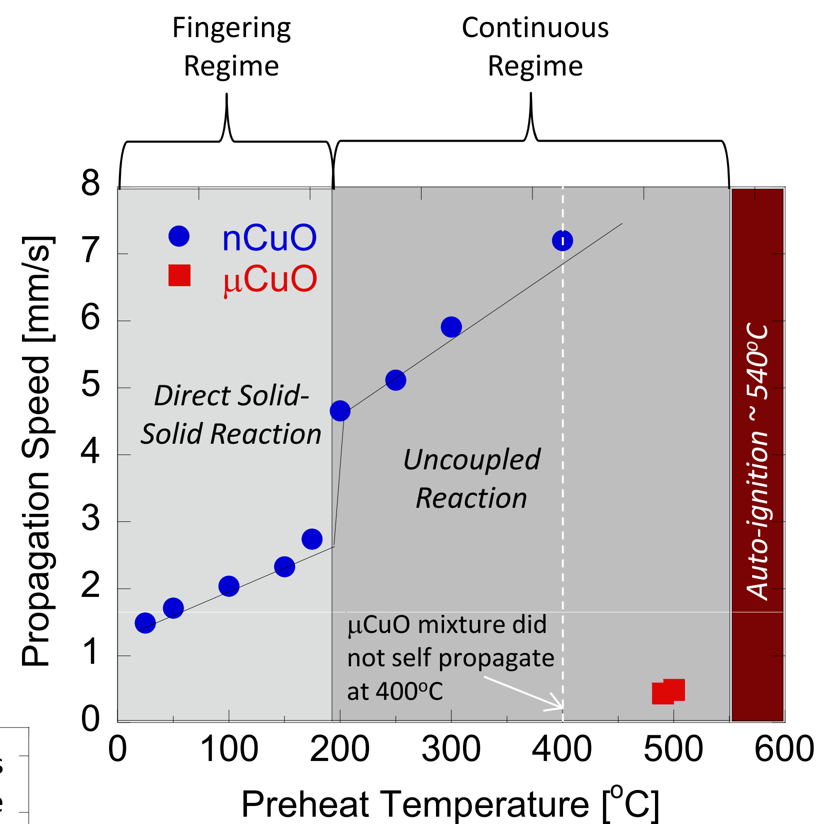
Heterogeneous versus vapor phase combustion

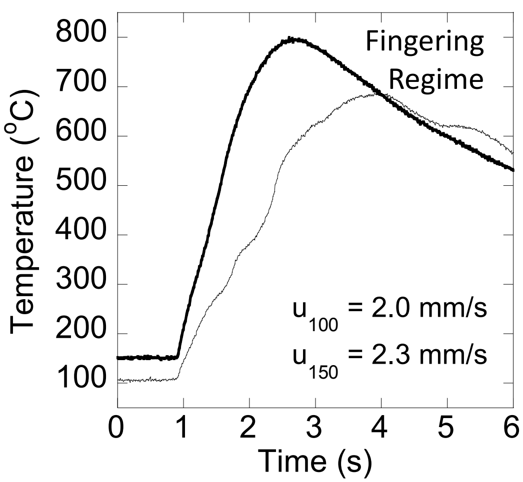
$$M + ½\, O_2 \rightarrow MO$$

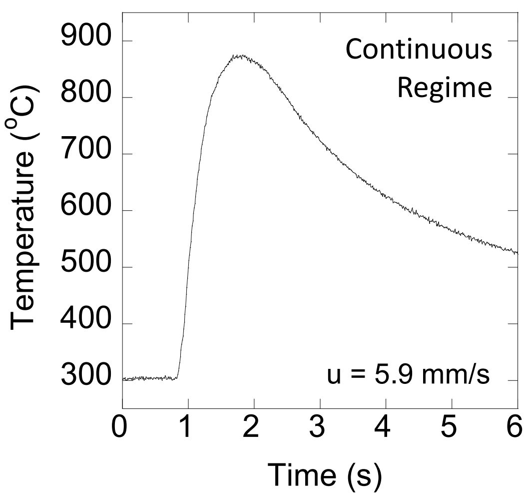
$$M + H_2O \rightarrow MO + H_2$$

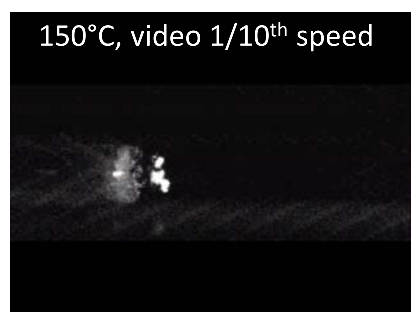
Ignition and Flame Propagation of Carbon – Copper Oxide Mixtures

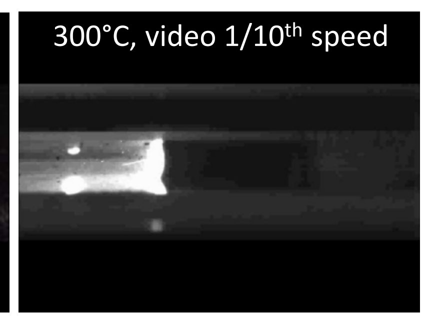










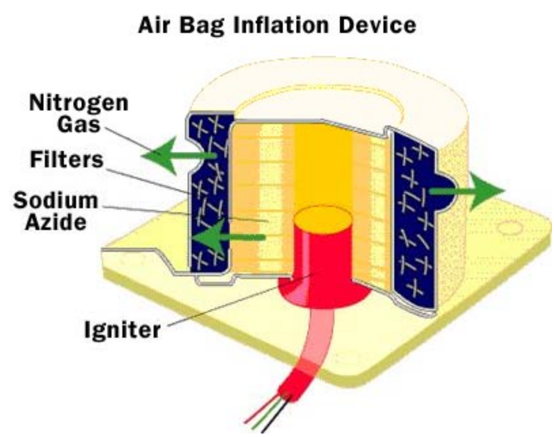


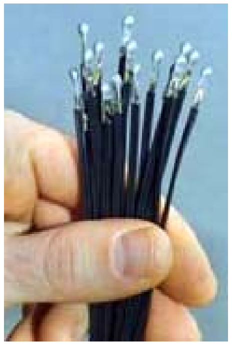
Weismiller and Yetter, PSU

How are nano reactive systems being applied?

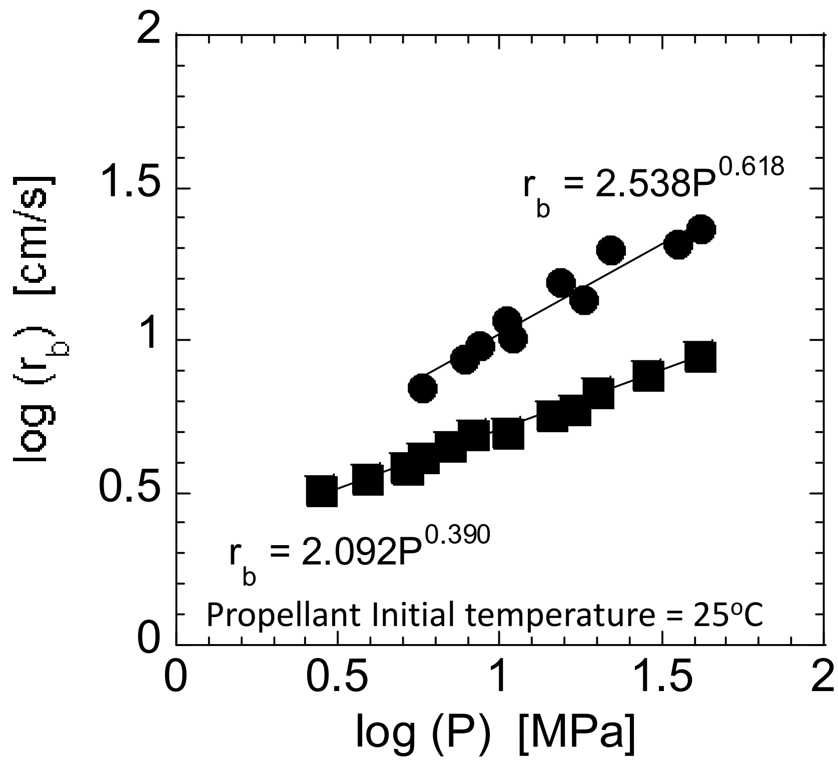
Some Examples of Nanoenergetics Applications

- Ingredients in propellants and explosives
- In-situ soldering and welding
- Gun primers, detonators, electric matches
- Airbags
- Micro-actuators
- Micro-pumps
- Micro-thrusters
- Micro-switches
- Micro-valves
- Dispersed catalysts
- Drug injection
- Visible light emission
- Active denial
- Chemical looping particles
- and, many others





Applications of Nano Aluminum (nAl)



■ Composite propellant with 18% μAl

● Composite propellant with 9% nAl (ALEX) / 9% μAl

- Nano Aluminum (nAl) has been used in propellants, explosives, and pyrotechnics
- Propellants
  - Al could ignite near/on the surface
  - Would improve heat feedback ⇒ faster burning
- Explosives
  - React in the reaction zone and affect detonation
  - Mixed results
- Pyrotechnics
  - Can possibly extend applications of composites, such as thermites (metal/metal-oxide reaction, redox reactions) or intermetalic (such as Al + Ni → AlNi)
  - Reactive structures

Mench, M.M., Yeh, C.L., and Kuo, K.K., "Propellant Burning Rate Enhancement and Thermal Behavior of Ultra-fine Aluminum Powders (ALEX)," in Proc. of the 29th Annual Conference of ICT, 1998, pp. 30-1 – 30-15.

G. V. Ivanov, and F. Tepper, Challenges in Propellants and Combustion 100 Years after Nobel, pp.636-645, (Ed. K. K. Kuo et al., Begell House, 1997).

Nano-Aluminum/Ice Propellants for Replacement of Cryogenic Hydrogen

Motivation

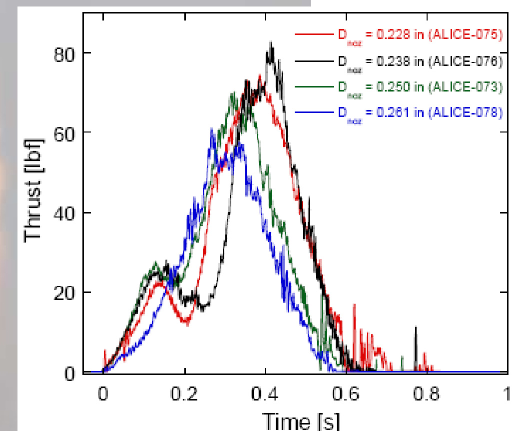
- Cyro-propellant performance without cryo shortcomings
- Nanotechnology for designing and assembling future propellants
- Multi-functionality for both propulsion and power applications

$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

1.5” dia. x 1.5” long center perforated 80nAl-ice grain

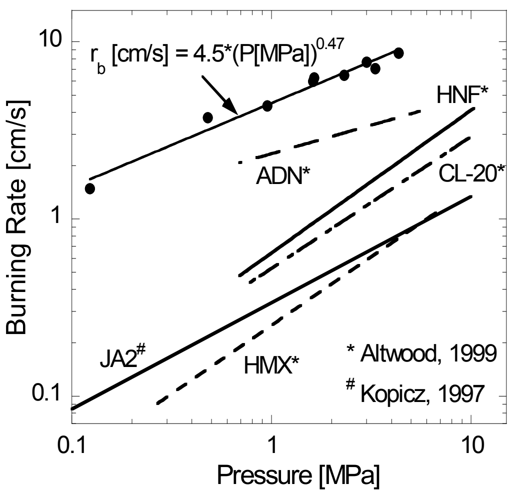
Research

- nAl-H_2O composites are studied as a means to generate hydrogen at high temperatures and at fast rates
- Composites have high energy density and low sensitivity
- Combustion occurs without heat releasing gas phase reactions & thus many flame spreading and instability problems of conventional propellants are eliminated.

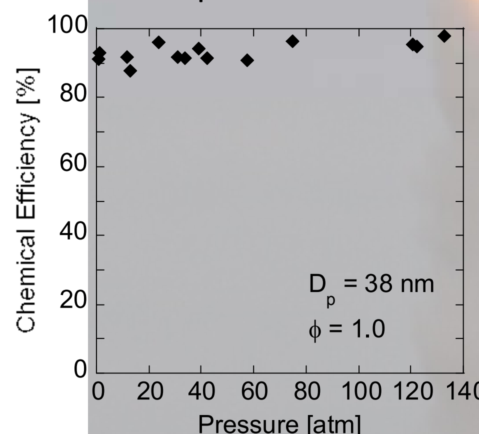


nAl-ice grain in phenolic tube

Burning rates of 38 nAl & liq. H_2O



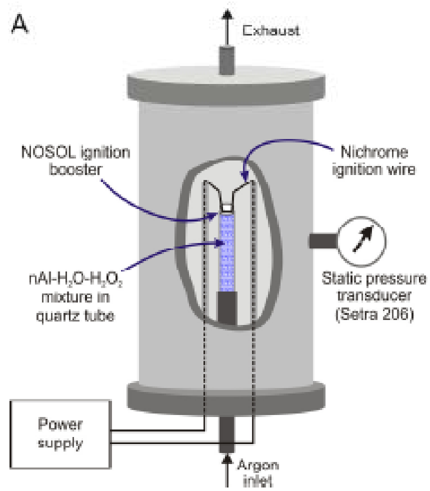
Efficiency of H_2 production

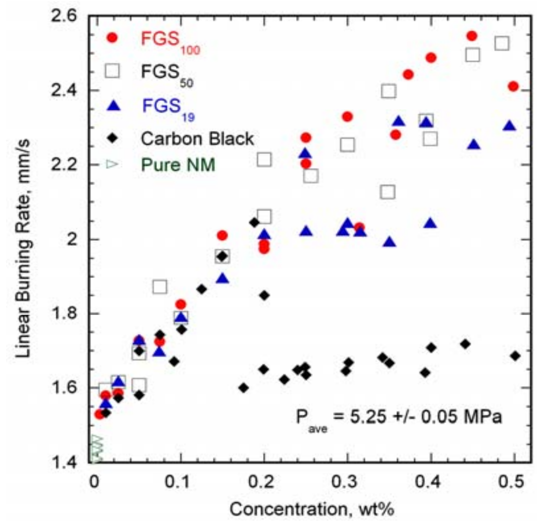


Risha, G.A., Son, S.F., Yang, V., & Yetter, R.A., 2008

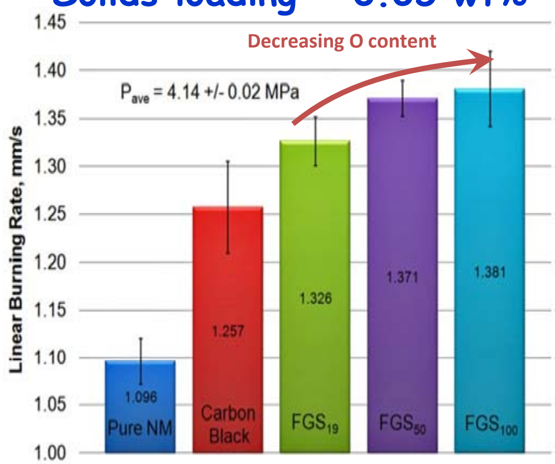
FGS Colloids for Enhanced Combustion

Liquid Strand Burner: NM gas-phase chemistry well understood; liquid-phase chemistry not important at low pressures





Solids loading ~ 0.05 wt%

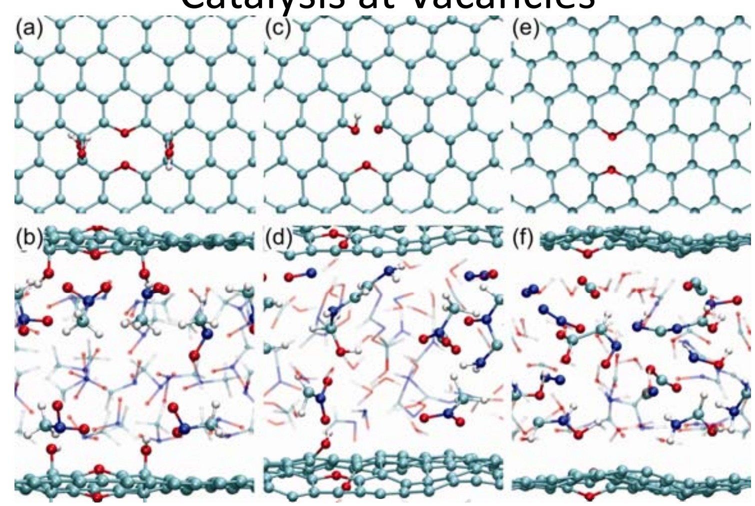


- More reduced FGS is a better accelerant than carbon black or FGS of low C/O (mol/mol).
- Lower deflagration pressure-limit with carbon additives.
- Reduced performance of carbon black and FGS_{19} at ~0.2wt% may be due to particle aggregation at liquid/vapor interface, preventing passage of particles into vapor phase.
- At low FGS concentrations, the loss of surface defects/surface area lowers the burning rate.

J. Sabourin, R.A. Yetter, D. M. Dabbs, I. A. Aksay, and F.L. Dryer, 2010.

ab-initio **molecular dynamics simulations show that only vacancies functionalized with groups, such as hydroxyls, ethers, and carbonyls greatly accelerate thermal decomposition of nitromethane through reaction pathways in which protons or oxygens are exchanged between the functional groups and nitromethane or its products**

Catalysis at Vacancies

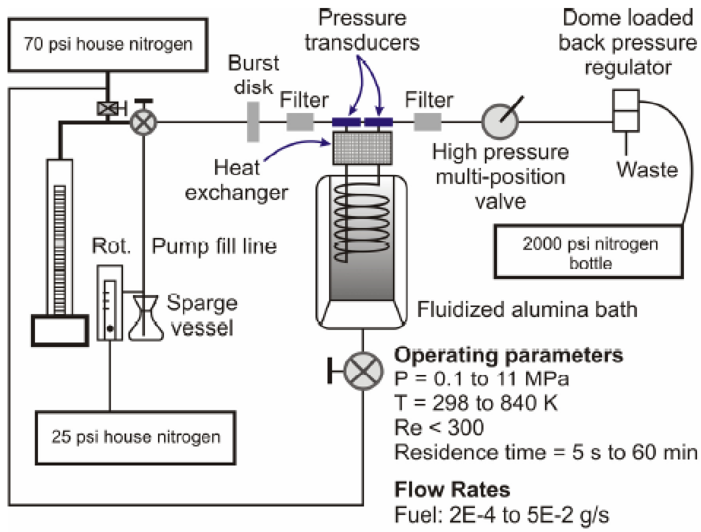


(a) and (b) initial configuration; (c) and (d) after 10 ps; (e) and (f) final configuration

L-M. Liu, R. Car, A. Selloni, D. M. Dabbs, I. A. Aksay, and R. A. Yetter, 2012.

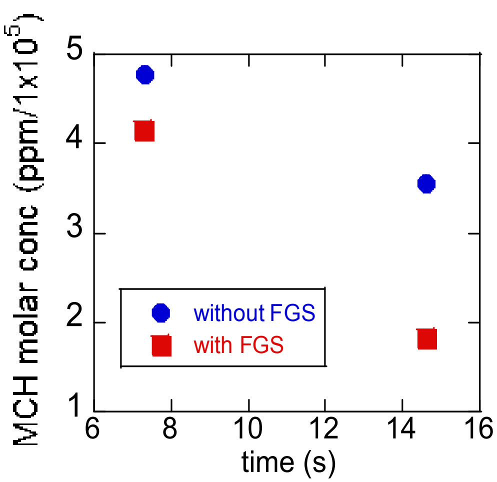
FGS Colloids for Enhanced Fuel Decomposition

Liquid Sub/Supercritical Reactor



Liquid Fuel/Particles Mixtures: 0.005wt% FGS in methylcyclohexane (MCH)

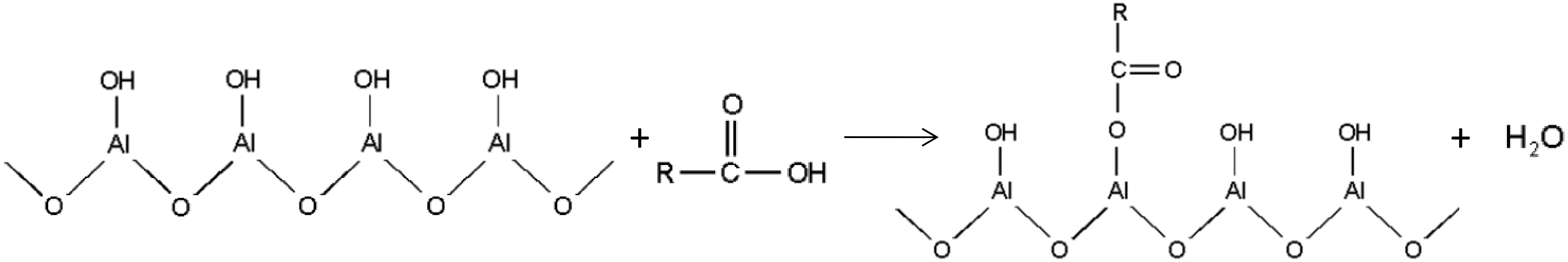
Reactor Temperature	820 K (Tr = 1.4)
Reactor Pressure	4.7 Mpa (Pr = 1.3)
Reactor Coil Length	6.4 m
Pump flow rate	0.5 mL/min
Reynolds Number	844
Residence time	14.9 sec



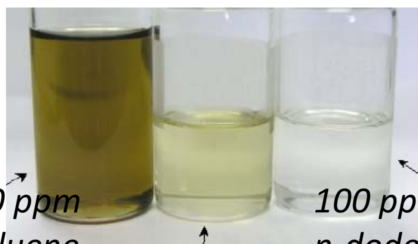
- **MCH was ~20 % more decomposed with 0.005wt% FGS than without FGS at above conditions. Gaseous products increased by ~ 20%.**
- **Identified components in gaseous products and condensed phase: similar to those without FGS; however, methane (32% increase), ethane (39% increase), ethylene (18% increase), propane (38% increase), propylene (25% increase) all increased.**

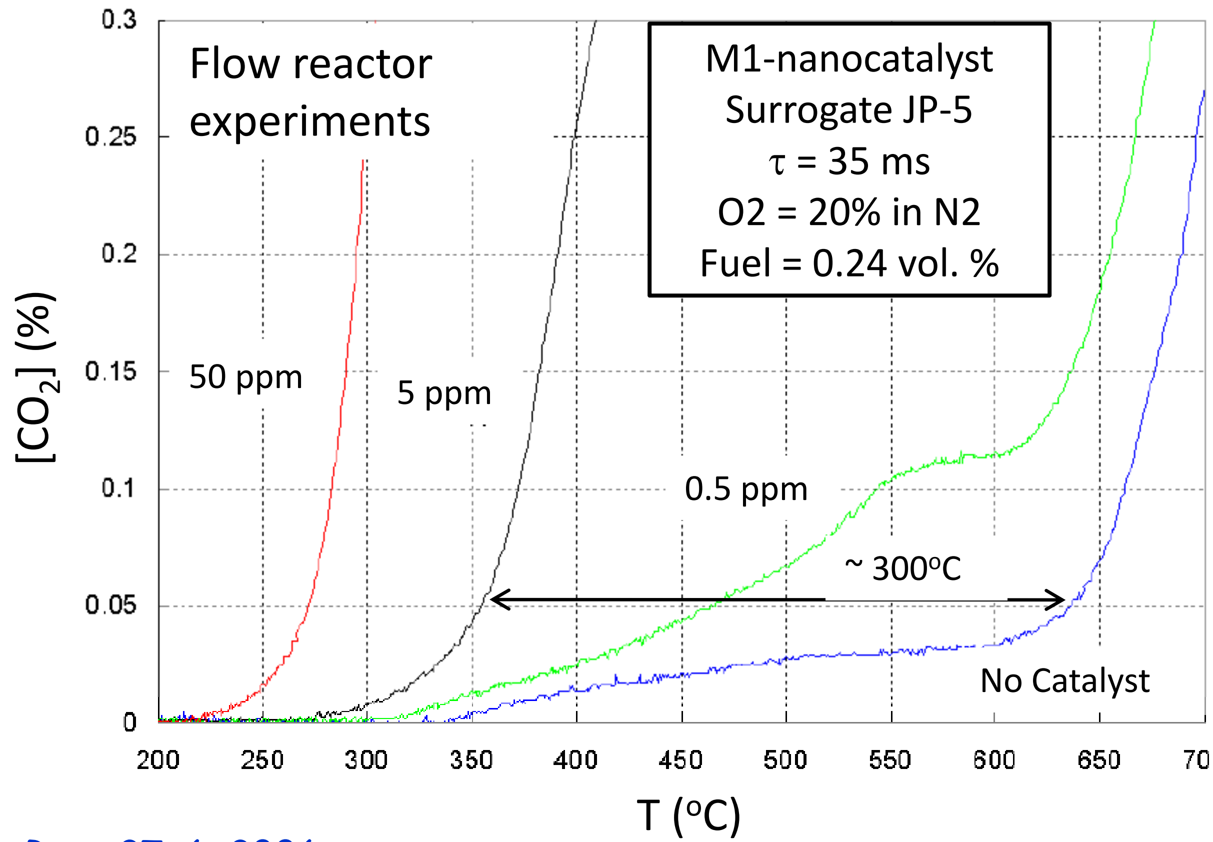
Disperable Nanocatalysts

Boehmite Particle — Carboxylato-alumane Particle



M_1/Al_2O_3 Catalyst





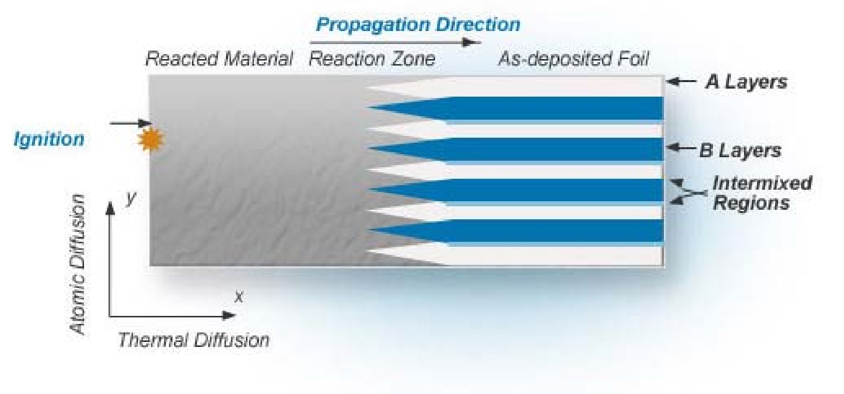
Metal exchange reaction to replace aluminum cations (in the boehmite particle) with metal cations of acetylacetonates, e.g., Pd, Pt, lanthanum, cerium, etc.

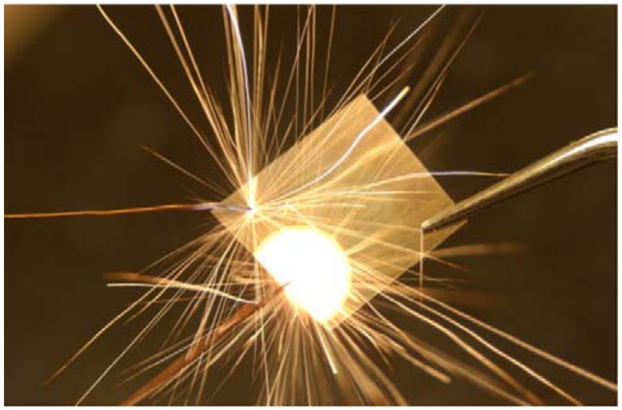
Wickman, D.T. et al., J. Russ. Laser Res., 27, 6, 2006

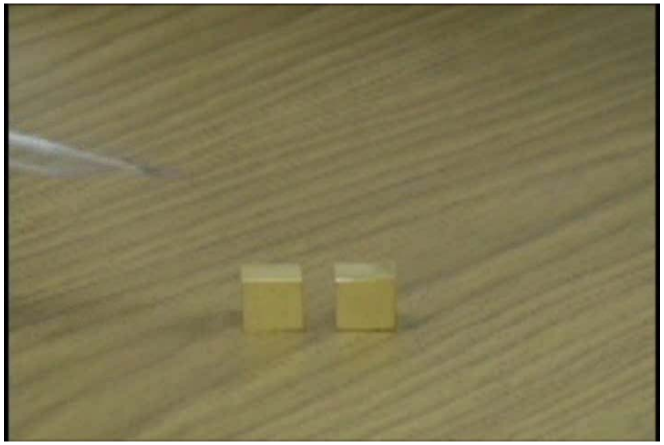
Reactive Foils for Soldering and Brazing

NanoFoil® (Indium Corporation – formerly Reactive Nanocomposites)is a new class of nano-engineered material. It is fabricated by vapor-depositing thousands of alternating nanoscale layers of Aluminum (Al) and Nickel (Ni). When activated by a small pulse of local energy from electrical, optical or thermal sources, the foil reacts to deliver localized heat up to temperatures of 1500°C in fractions (thousandths) of a second. Today, this localized heat is used in many bonding applications ranging from the bonding of sputter targets to backing plates, to the attaching of a component such as an LED to a circuit board.
http://www.indium.com/nanofoil/#ixzz1xQC55sjc

NanoFoil® Properties	
Size - thickness	40-150µm in free-standing forms
Composition Before Reaction	Alternating layers of Ni and Al
Composition After Reaction	$Ni_{50}Al_{50}$
Foil Density	5.6-6.0 g/cm^3
Heat of Reaction	1050-1250 J/g
Reaction Velocity	6.5-8 meters/second
Maximum Reaction Temperature	1350°-1500°C (2460°-2730°F)
Thermal Conductivity	35-50 W/mK
RoHS Compliant	Pb-free



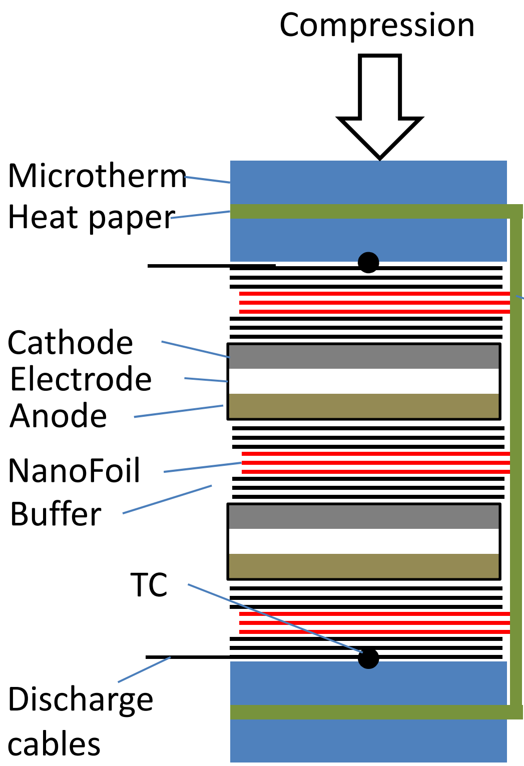




Thermal Batteries

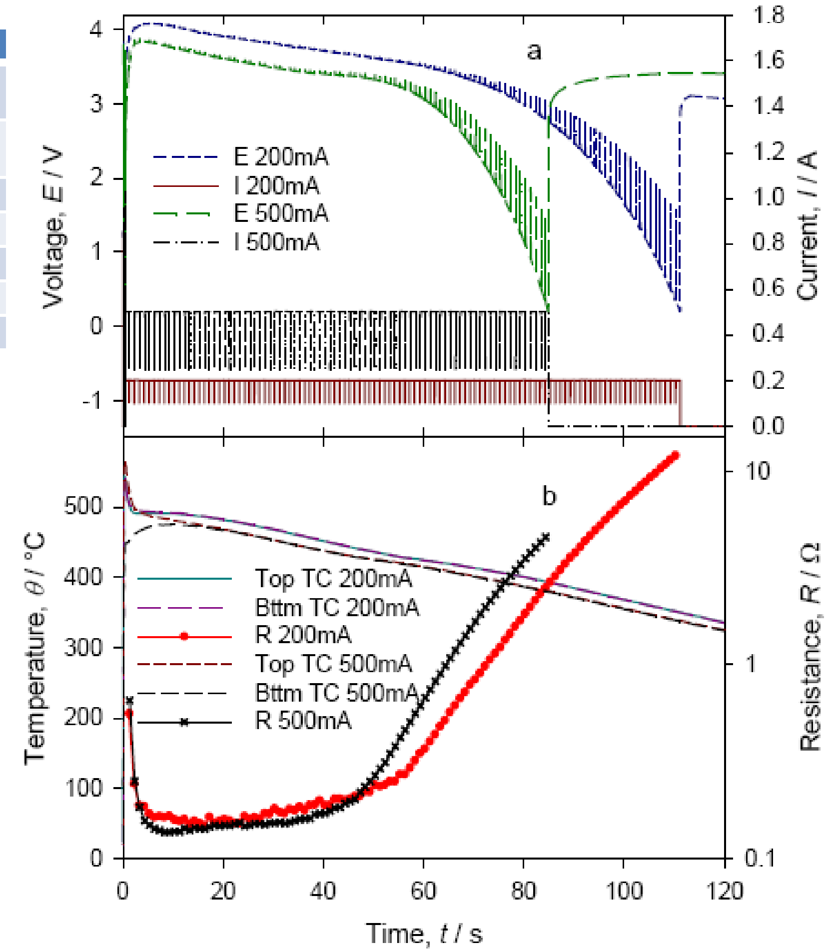
- Advantages: Higher heat of reaction than pyrotechnic heat pellets, Flame front velocity of 9 m/s is considerably faster than heat paper; The Ni-Al foils are electrically conductive both before and after initiation; NanoFoil generates a significantly steeper temperature rise than pyrotechnic pellets.
- Issues: Upon initiation, the foils tend to flow under pressure; Applied load drops upon initiation, which leads to an increase in the battery internal resistance.

Schematic of NanoFoil-heated
<u>2-cell thermal battery</u>



Name	Composition
Electrolyte	LiBr-LiCl-LiF eutectic (435ºC)
Electrolyte pellet	MgO/E: 47/53
Cathode	FeS_2
Cathode pellet	C/Fe/E:78/2/20
Anode	Li/Al: 20/80
Anode pellet	A/E: 90/10
Heat paper	$Zr/BaCrO_4$-fiber mix

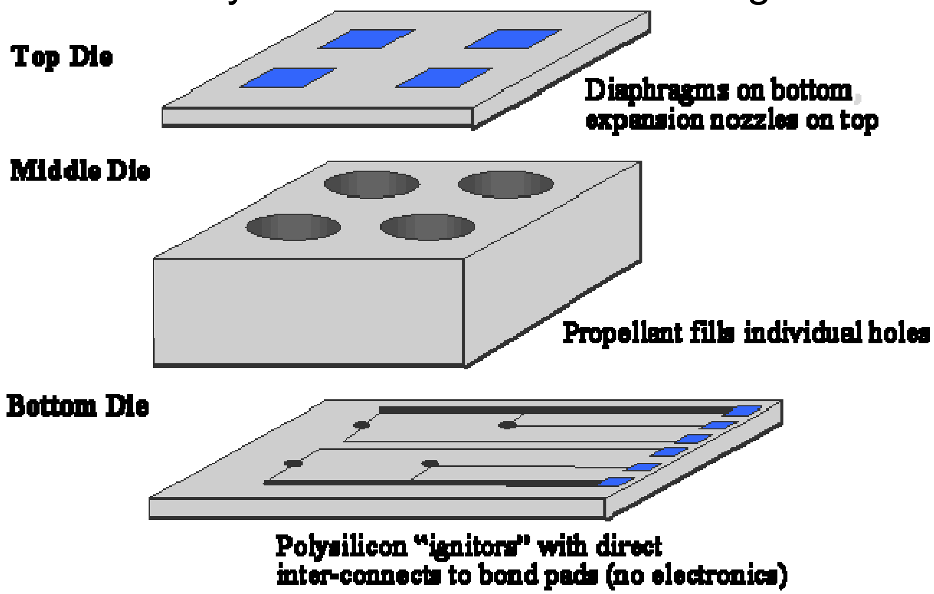
Photo of NanoFoil-heated
<u>2-cell thermal battery</u>



Poret, J.C., Ding, M., Krieger, F., Swank, J., Chen, G., McMullan, C., NANOFOIL HEATING ELEMENTS FOR THERMAL BATTERIES, Proceedings of the Army Science Conference (26th), Orlando, Florida on 1-4, December 2008

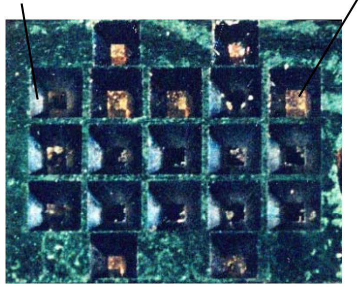
Digital Microthruster

Three-layer sandwich of silicon and glass

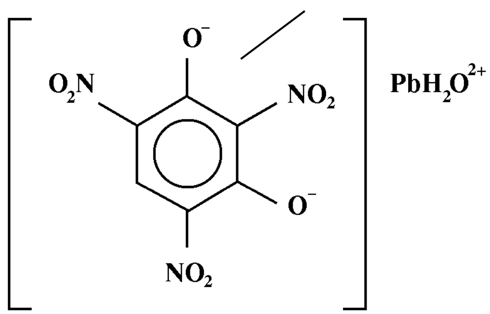


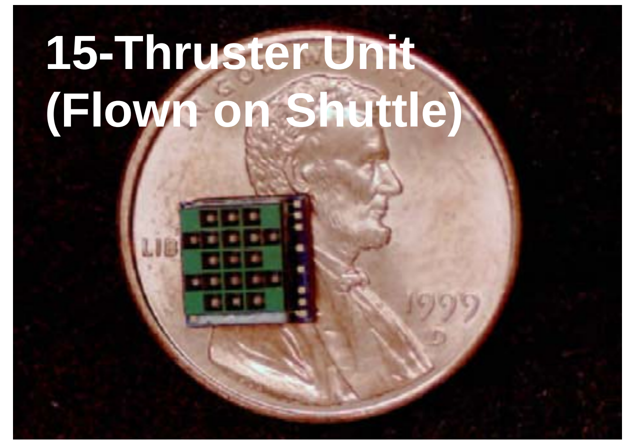
Diverging nozzles

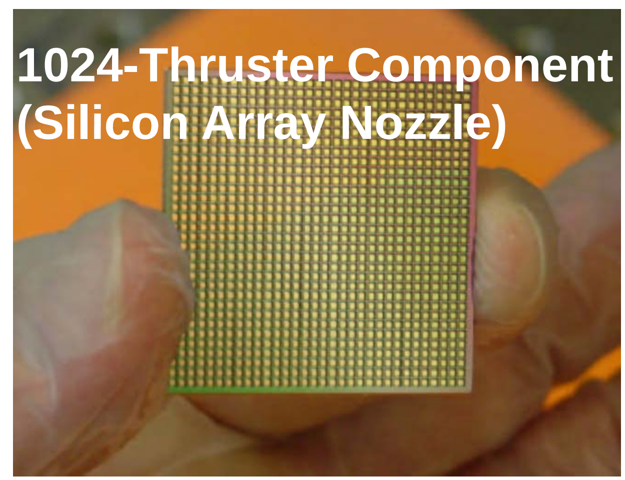
Silicon nitride rupture diaphragms

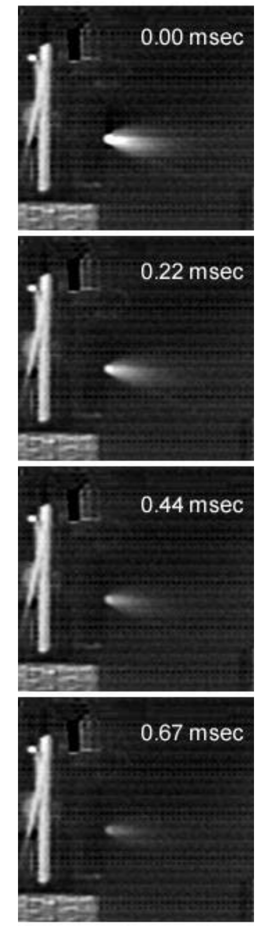


Lead Styphnate
$C_6H_3N_3O_8Pb$







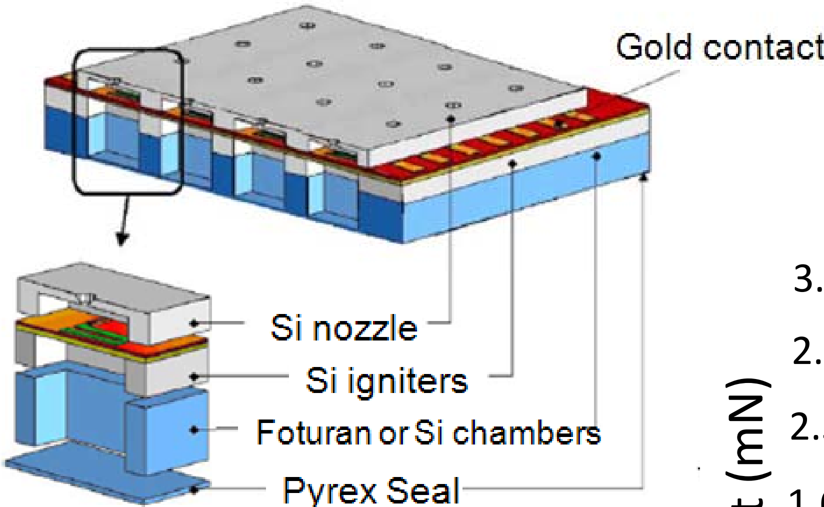


0.1 mNs of impulse bit
100W of power

5-100 mN of
thrust

Lewis et al., Sensors and Actuators 80, 143-154, 2000

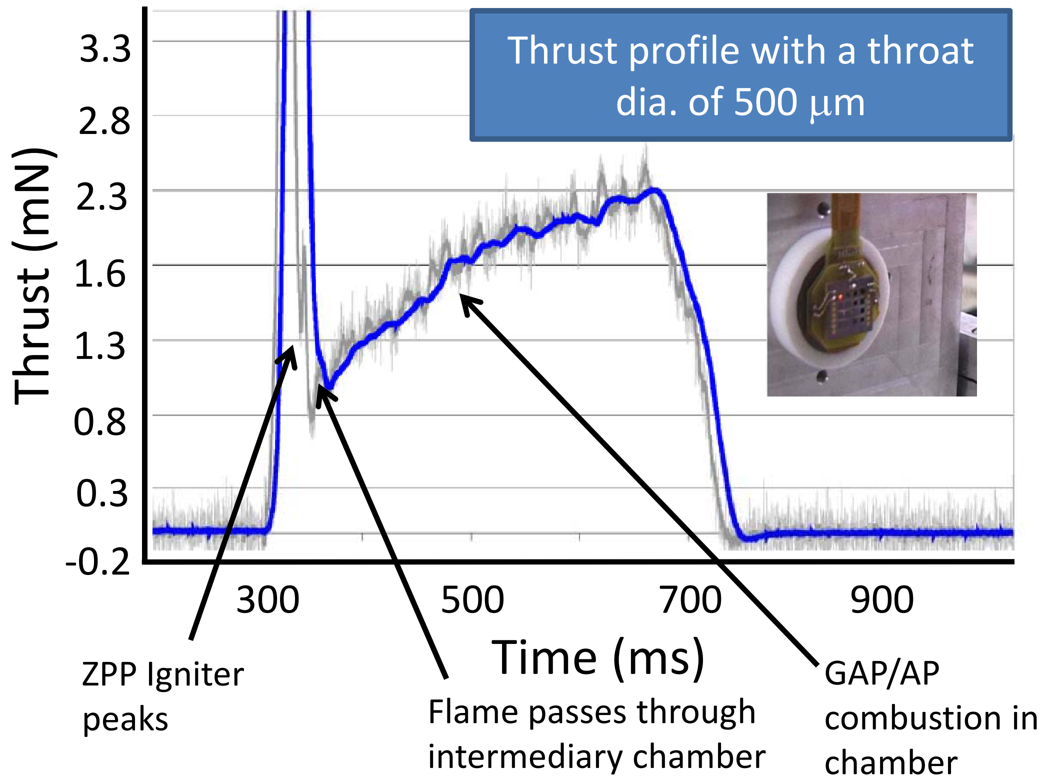
MEMS-based Pyrotechnical Microthrusters



- Polysilicon resistor igniter at nozzle
- Insulating groves to eliminate cross-talk
- Main grain was screen printed under vacuum
- 100% ignition success with 250 mW
- Thrusts ~0.3-2.3 mN

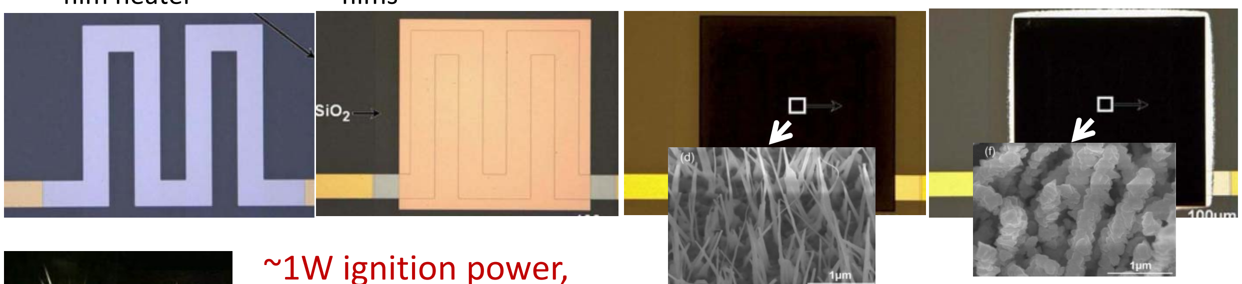
Rossi et al., Sensors and Actuators A, 121, 508-514, 2005, Sensors and Actuators A, 126, 241-252, 2006. Journal of MEMs, 15, 6, 1805-1815, 2006.

- 100 addressable microthrusters with 3 main micromachined layers
- Combustion chamber 1.5 x 1.5 x 1 mm
- glycidyle azide polymer (GAP) mixed with AP and Zr particles propellant
- zirconium perchlorate potassium primer



MEMS Device Integrating Nanothermite Al/CuO

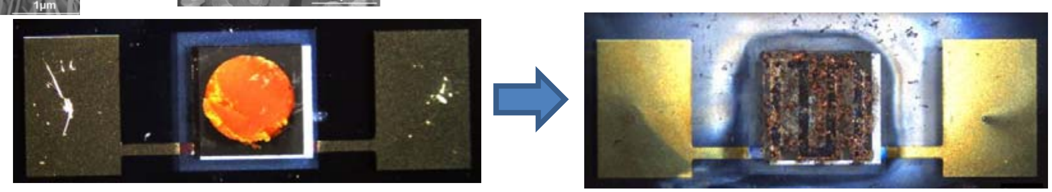
Micro initiator/ Micodetonator → CuO/Al nanothermite on igniter chip ($1mm^2$)



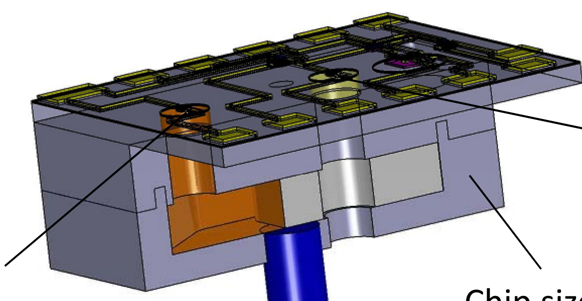
Ignition of a propellant has been demonstrated

Zhang, et al, *Nanotechnology 18 (2007)*
Zhang, et al, *J. of Micro ElectroMechanical Systems, 2008*

~1W ignition power,
0.1 ms ignition delay,
0.12 mJ ignition energy
60 mJ output energy

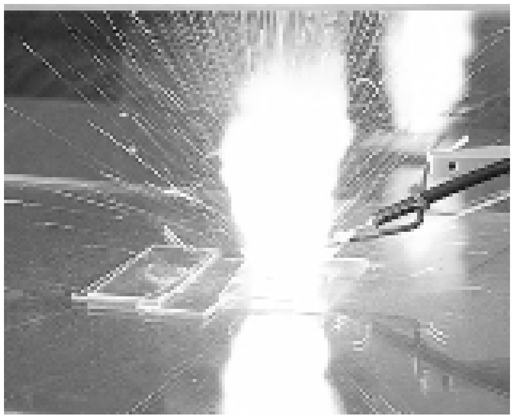


1 cm^3 MEMS Safe Arm Fire → MEMS integrate sensors, circuitry, actuator, electrical protections (pyrotechnical switches), highly energetic material ($[Co(NH_3)_6]_2[Mn(NO_3)_4]_3$, Al/CuO nanothermite), moving barrier….

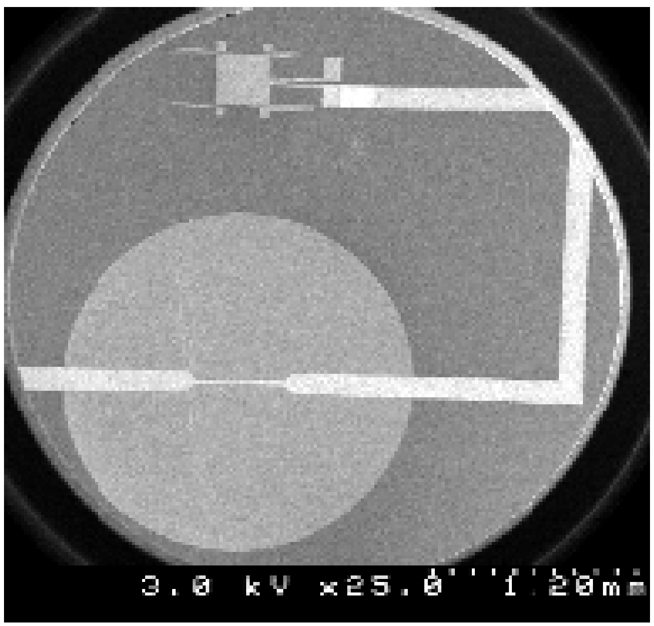


Pezous et al*J. Phys & Chem. Solids 71, (2010)*
Pezouset al*, Sensors and Actuators A159, 2010*

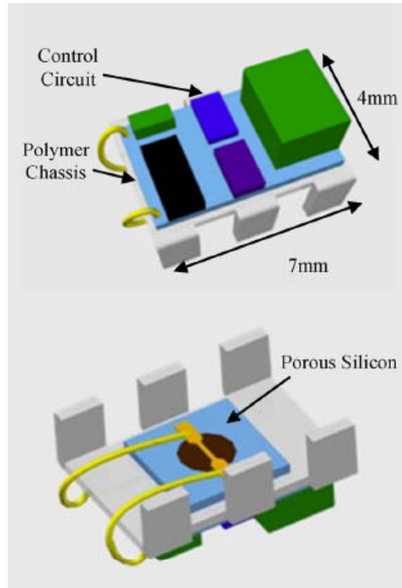
Jumping Sensor based on MEMs Fabrication and Nanonergetic Porous Silicon

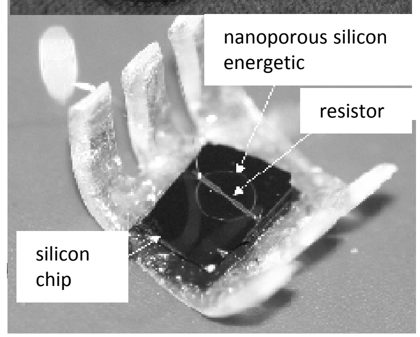


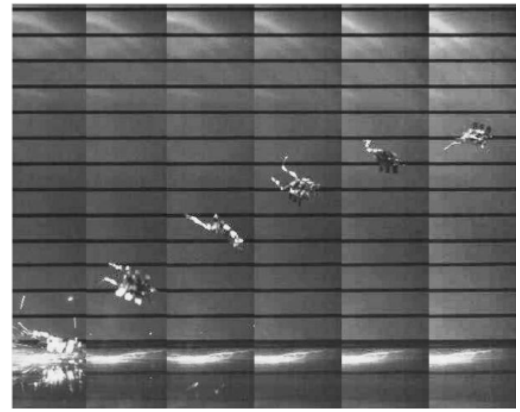
Ignition of nanoporous energetic silicon via spark

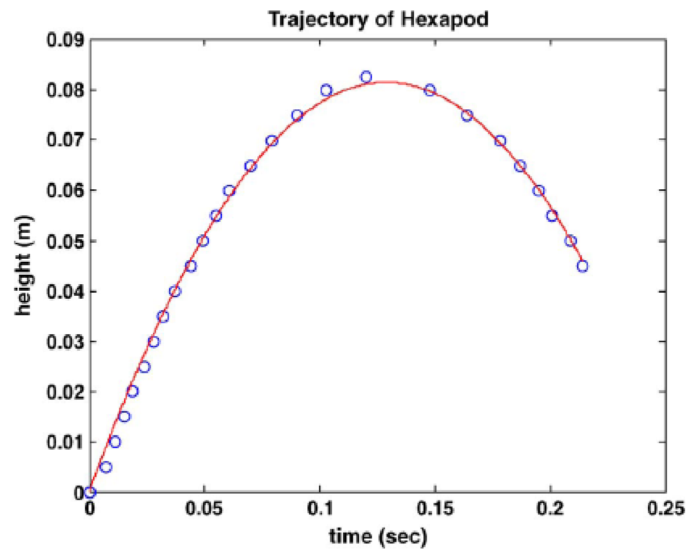


Integrated nanoenergetic silicon and MEMs sensor





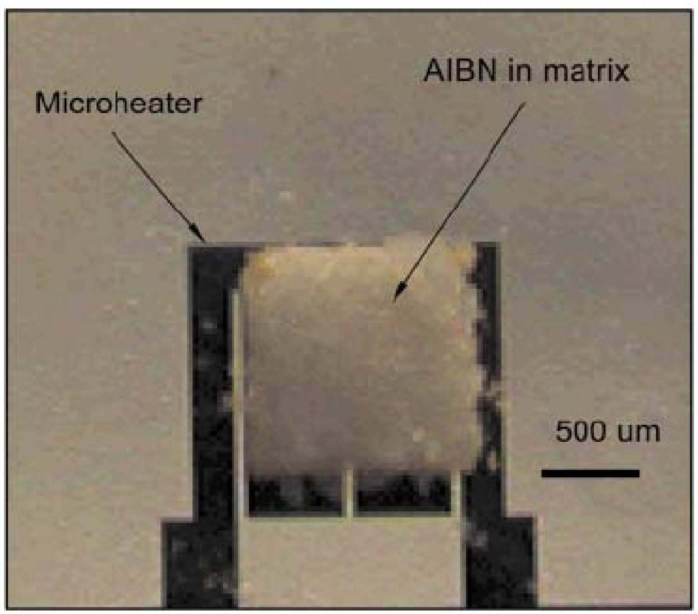


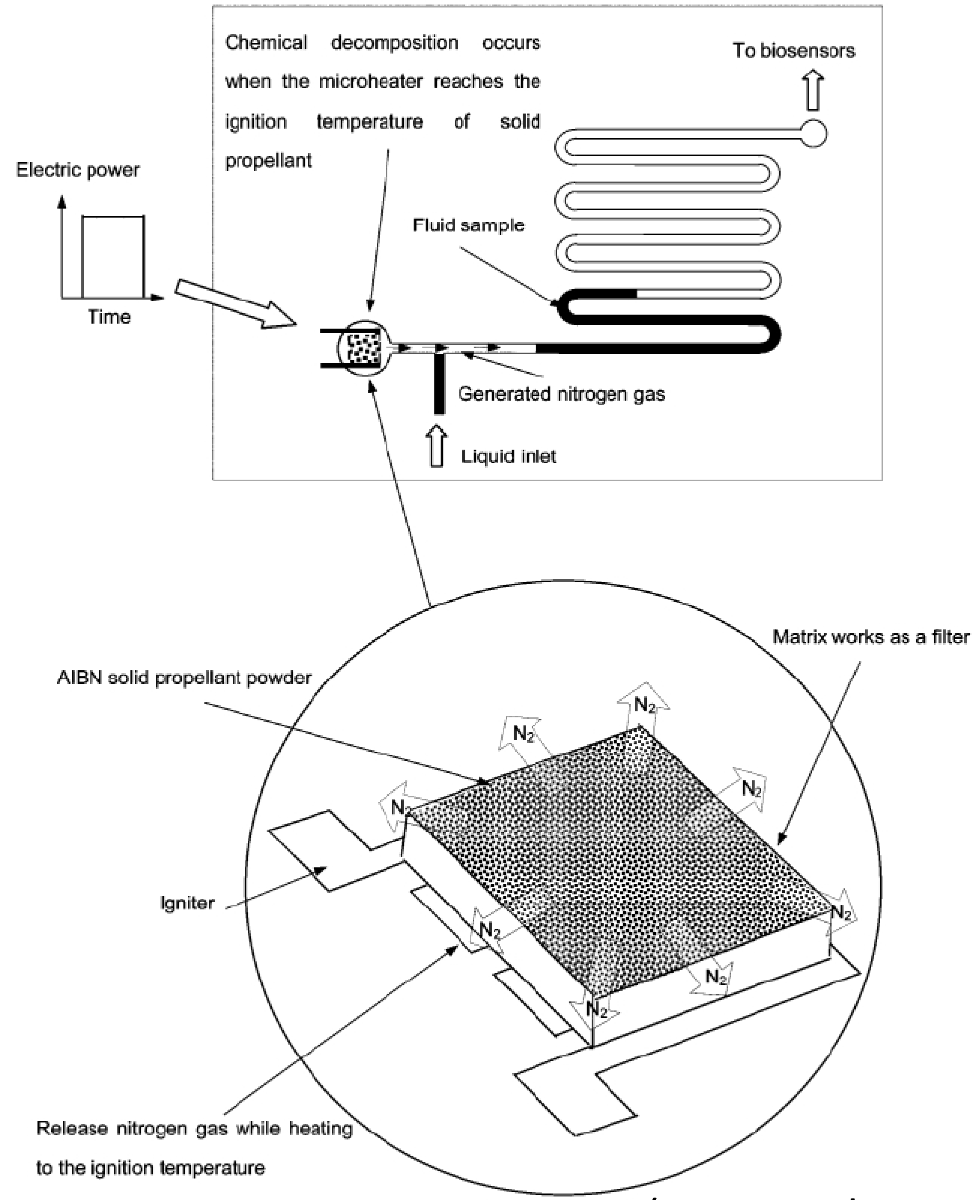


Churaman et al., J. MEMs, 21, 1, 198, 2012.

Combustion-based Actuators

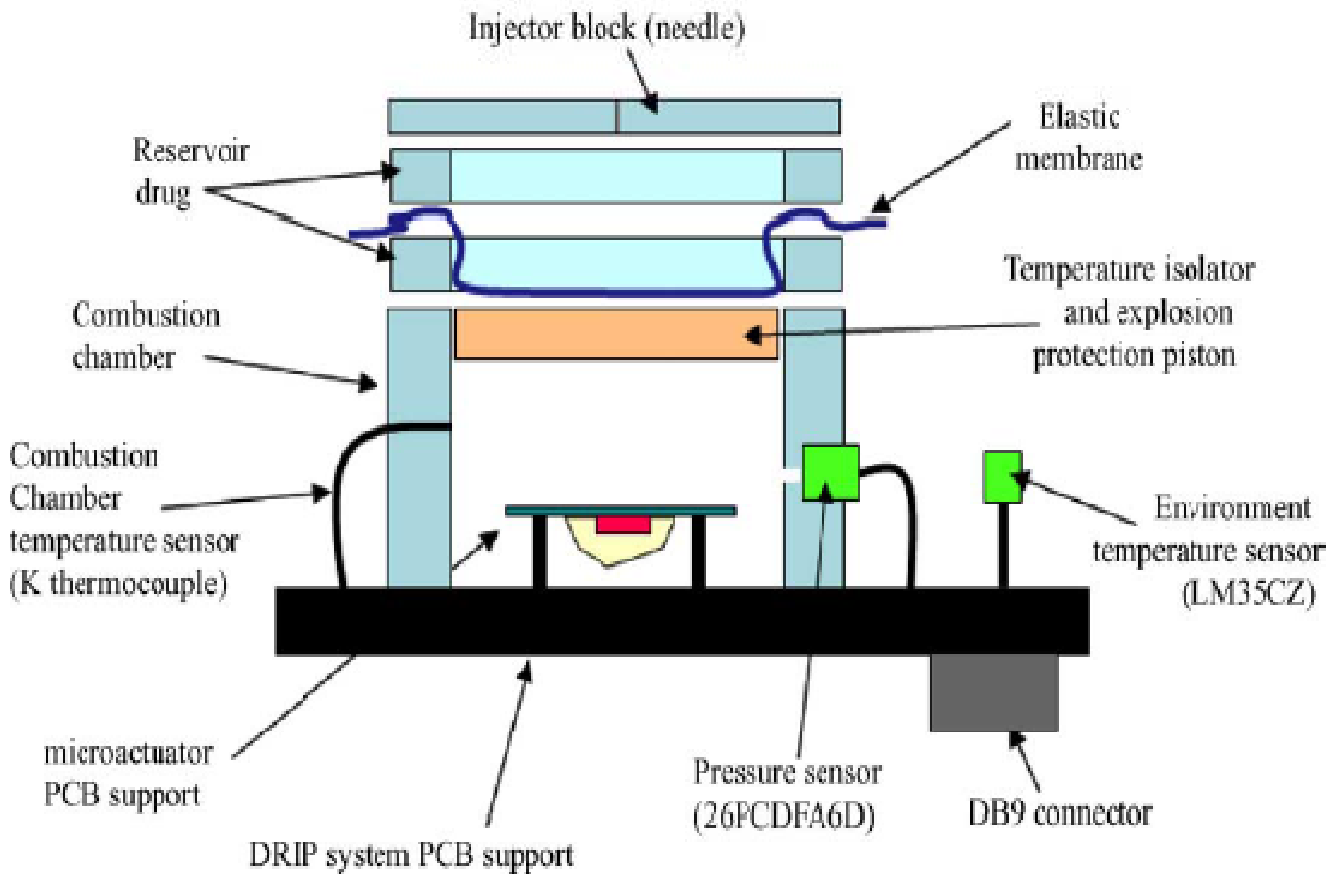
- Azobisiobutyronitrile (AIBN) decomposition as the solid chemical propellant
- Successfully pumped de-ionized water through a 70mm long channel with a cross section of 100μm*50μm at a flow rate of 17 ml/min while consuming only 189mJ of electric power decomposed



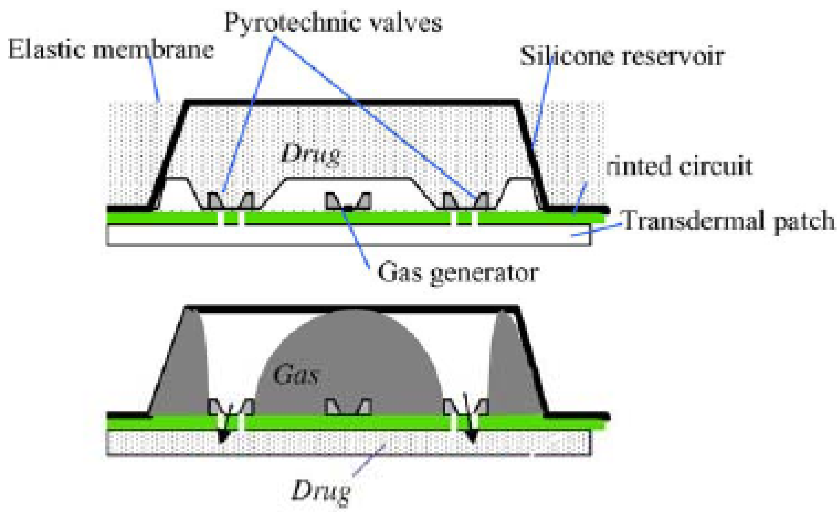


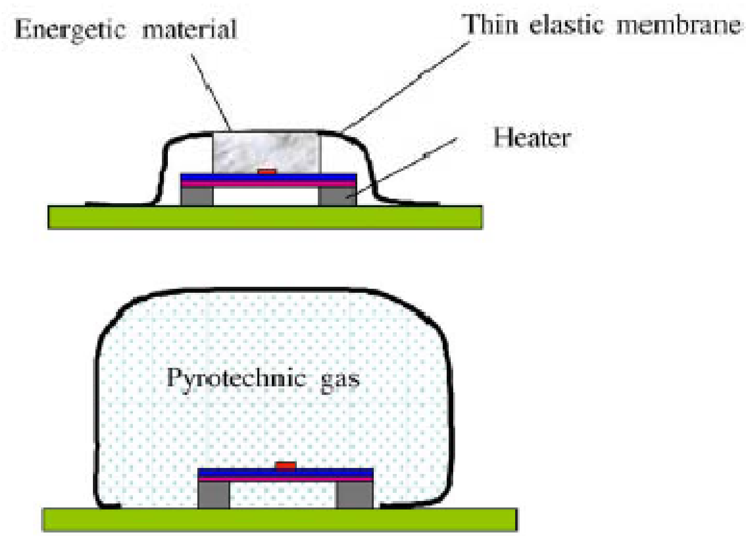
(Hong et al., 2003)

Drug Injection



Microenergetic Valve





- Applied on ARIAN 5 Launch Vehicle.
- Designed to isolate, prior to actuation, the gaseous fluid present in the upstream high pressure tank (400 bar) or passivation of the downstream pressure tank.
- React time < 5 ms

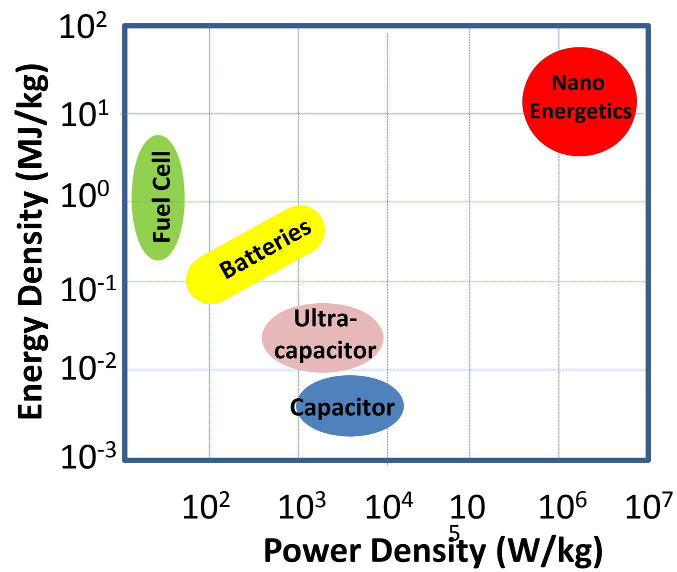
What are new directions for nanotechnology and combustion?

Directions Forward

- Towards "atomically" precise and functionalized nanoenergetic material.
- Develop smart nanoenergetic materials to perform a desired function instead of simply reacting in an uncontrolled fashion.
  - Activated by T, P, the presence of a particular chemical compound, or external stimuli, such as an electrical field or light, e.g., initiate a reaction at a particular T, release a particular compound at a particular T, transition from a deflagration to a detonation at a particular instant in time, turn on or turn off a reaction, or accelerate or slow a reaction with time or location.
- Develop multifunctional nanoenergetic <u>systems.</u>

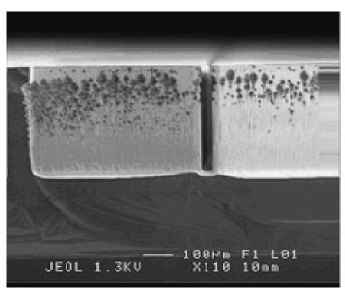
Nanoengineered Energetic Materials

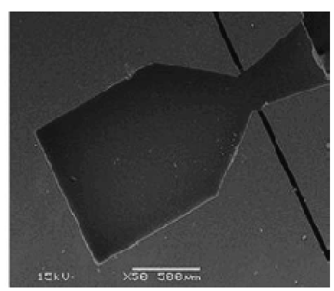
- *At the microscale: engineer the nanoenergetic directly on a MEMS chip*
  - Heat (200 - 3000°C), pressure (kPa-Gpa), specific gases (neutral gas, ionized gas) on demand => propulsion, power, actuation, instrument calibration, pumping, switches, initiators
  - MEMs fabrication methodology: soft lithography, screen and inkjet printing, PVD, etc.
  - New fuels and oxidizers: porous silicon, nanothermites, and intermetallics
- *Scale-up to the macroscale*



Challenges and Issues

- Scientific oriented
  - Thermal quenching
  - New EM formulation
  - Structural material development
- Engineering oriented
  - Selection of EM and structural material
  - Fabrication and integration of the device
  - Ignition
  - Pressure control
  - Filling
  - Sealing (Superglue so far!)
- Public perception, safety, and regulations affect things also





Summary

- Nanoenergetics have numerous characteristics that make them attractive for use in fuels and energetic materials.
- From an ignition and combustion perspective, heterogeneous and condensed phase processes become significantly more important.
- Fabrication and assembly of energetic composite materials (by various techniques, self assembly, cold spraying, ball milling, sol gel, gas-phase processes, etc) are research directions.
- Current research is emphasizing manipulation of individual atoms and molecules to produce organized MEMs embedded multifunctional nano energetic materials for generation of gas – pressure (kPa-Gpa), heat (200 - 3000°C), and chemical species (Neutral gas, Ionized gas) with highly controllable performances (rate of heat release, …) and properties (sensitivity, stability…).

Thank you

Questions?