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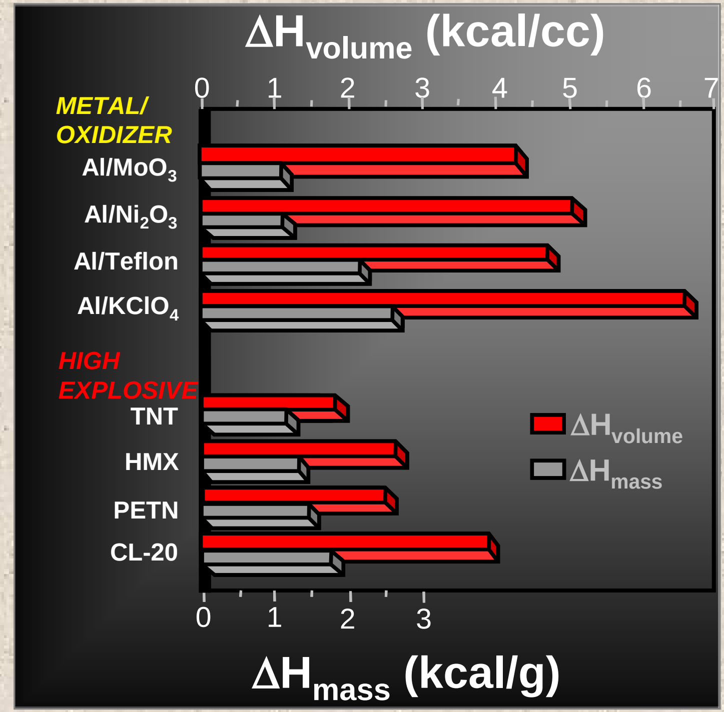
Probing the Reaction Dynamics of Nanoenergetic Materials

Department of Chemistry and Biochemistry

NanoEnergetic Materials

$$2Al + 3MO \rightarrow Al_2O_3 + 3M + \Delta H$$

↑ Fuel ↑ Oxidizer



Fischer and Grubelich, ***32nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference***, Lake Buena Vista, FL 1996.
Thomas N. Hall and James R. Holden, ***Navy Explosives Handbook, NSWCMP 88-116***, 1988.

Motivation

Thermodynamics

Energy release from Thermite > CHNO chemistry.

Kinetics

Thermites are much slower than CHNO Systems;

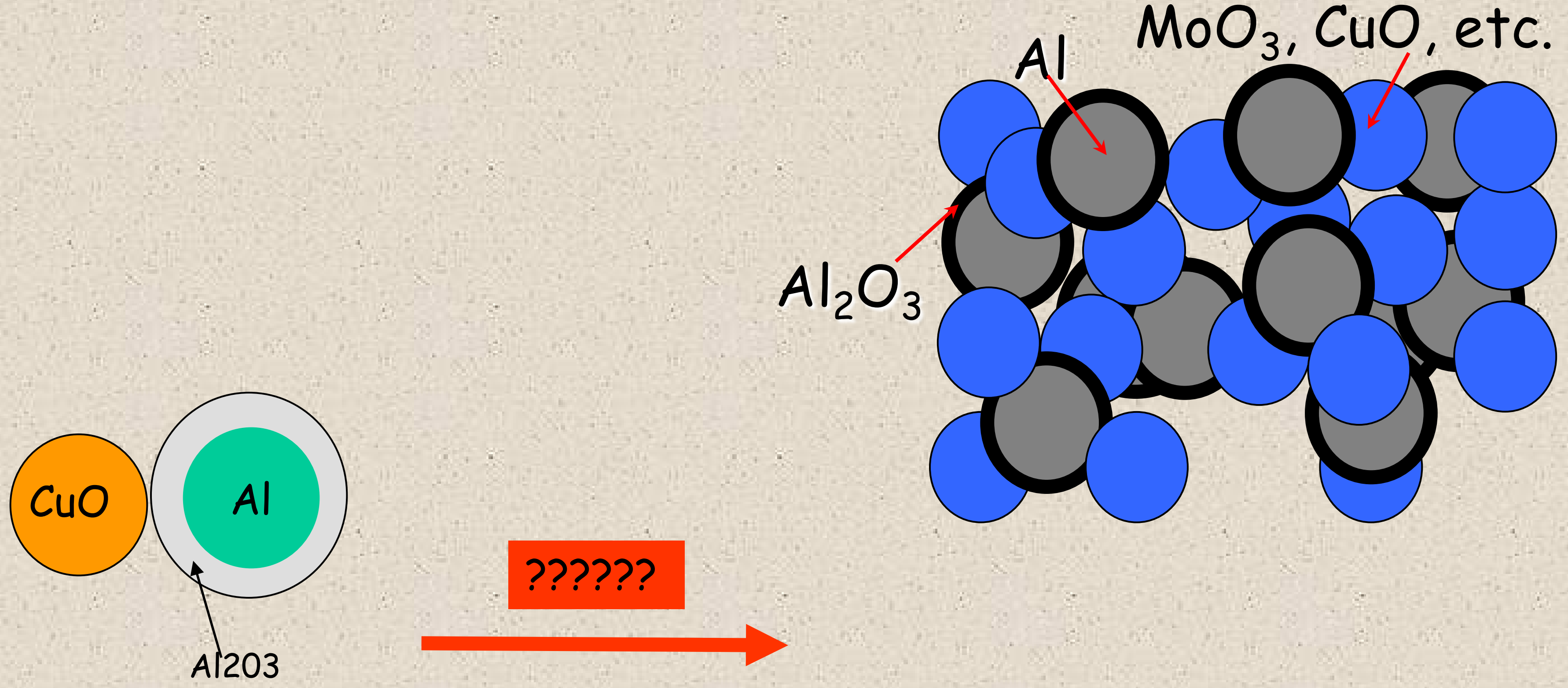
- Smaller thermites are faster => Nano

But, we know very little about mechanisms of ignition and propagation.

We are still groping to establish a conceptual mechanism, let alone advance to a mathematical model.

Metastable Interstitial Composites

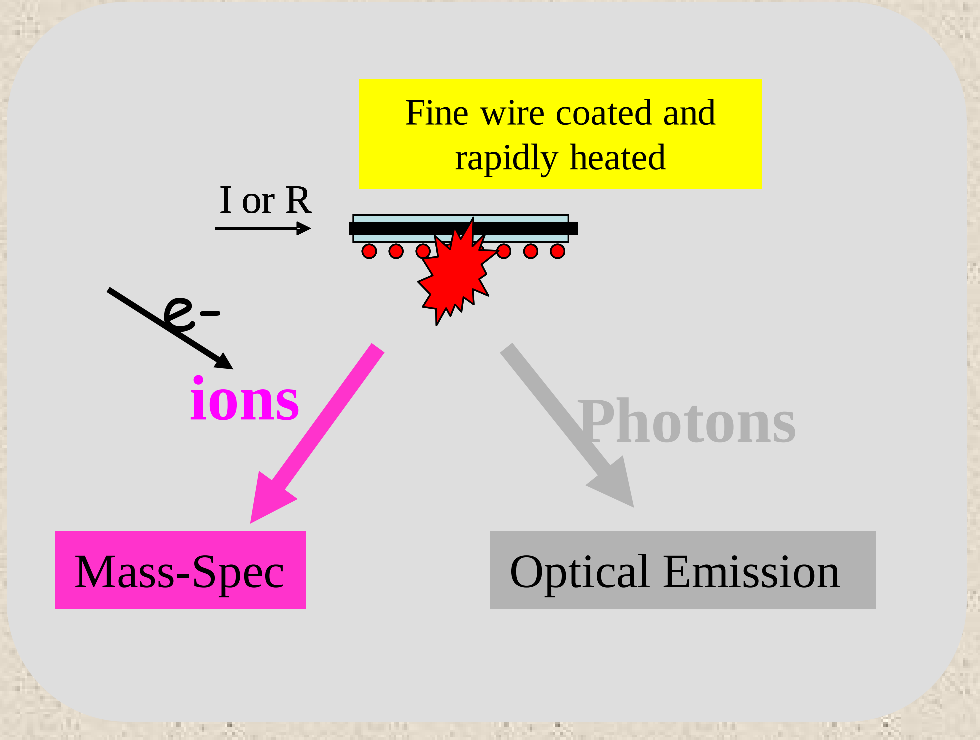
- How can we study the reactivity of nanocomposites ?



How to characterize the reactivity of powder of ultrafast nanocomposites ?

A New Approach: *T-Jump Mass Spectrometry/Optical Emission*

Basic Approach:



Coat wire with:

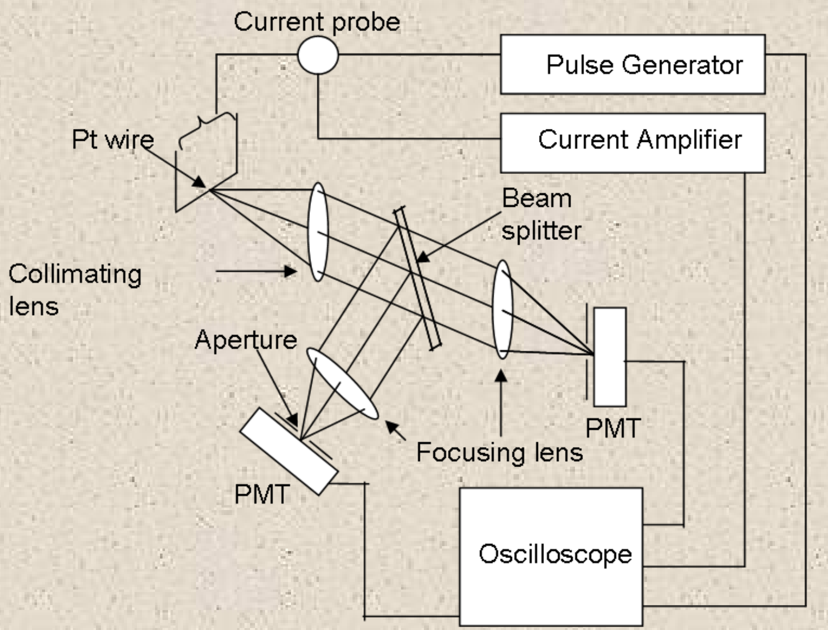
- Organics,
- Organics+ binder
- Thermites,
- Thermites + organics
- Sputtered thin films
- **Etc.**

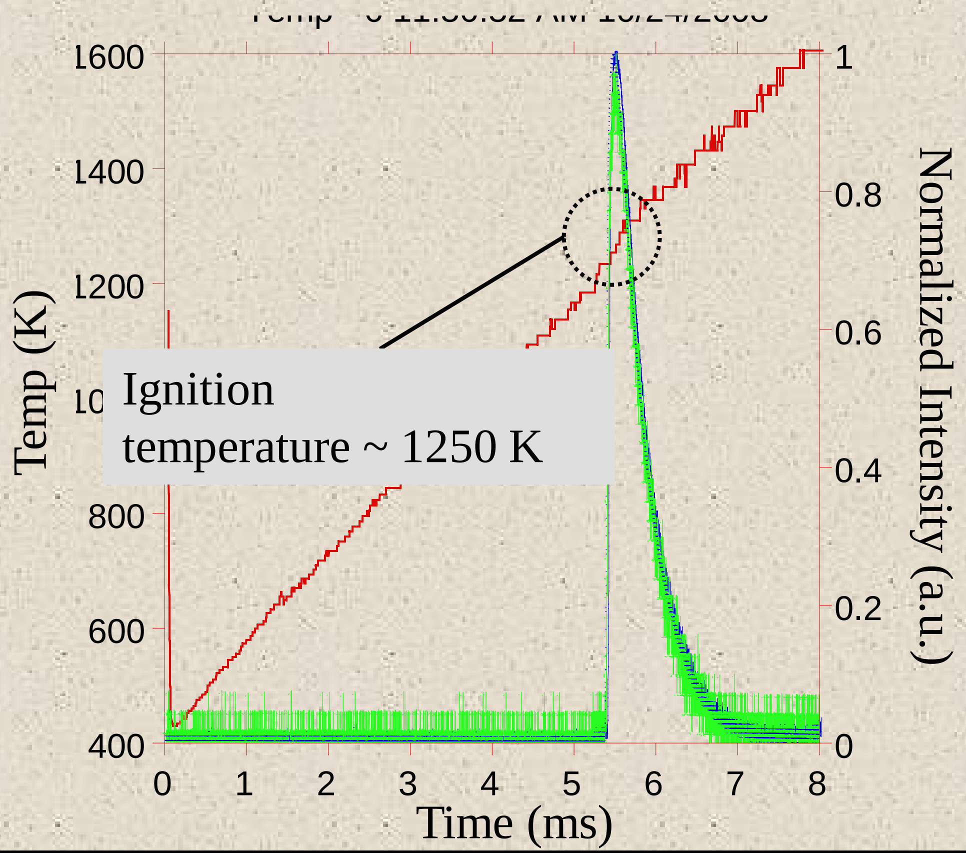
RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2009; **23**: 194–202

T-Jump Wire Ignition

Example of heating rate of 1.7 X 10^5 C/s

Wire temperature determined by resistance.

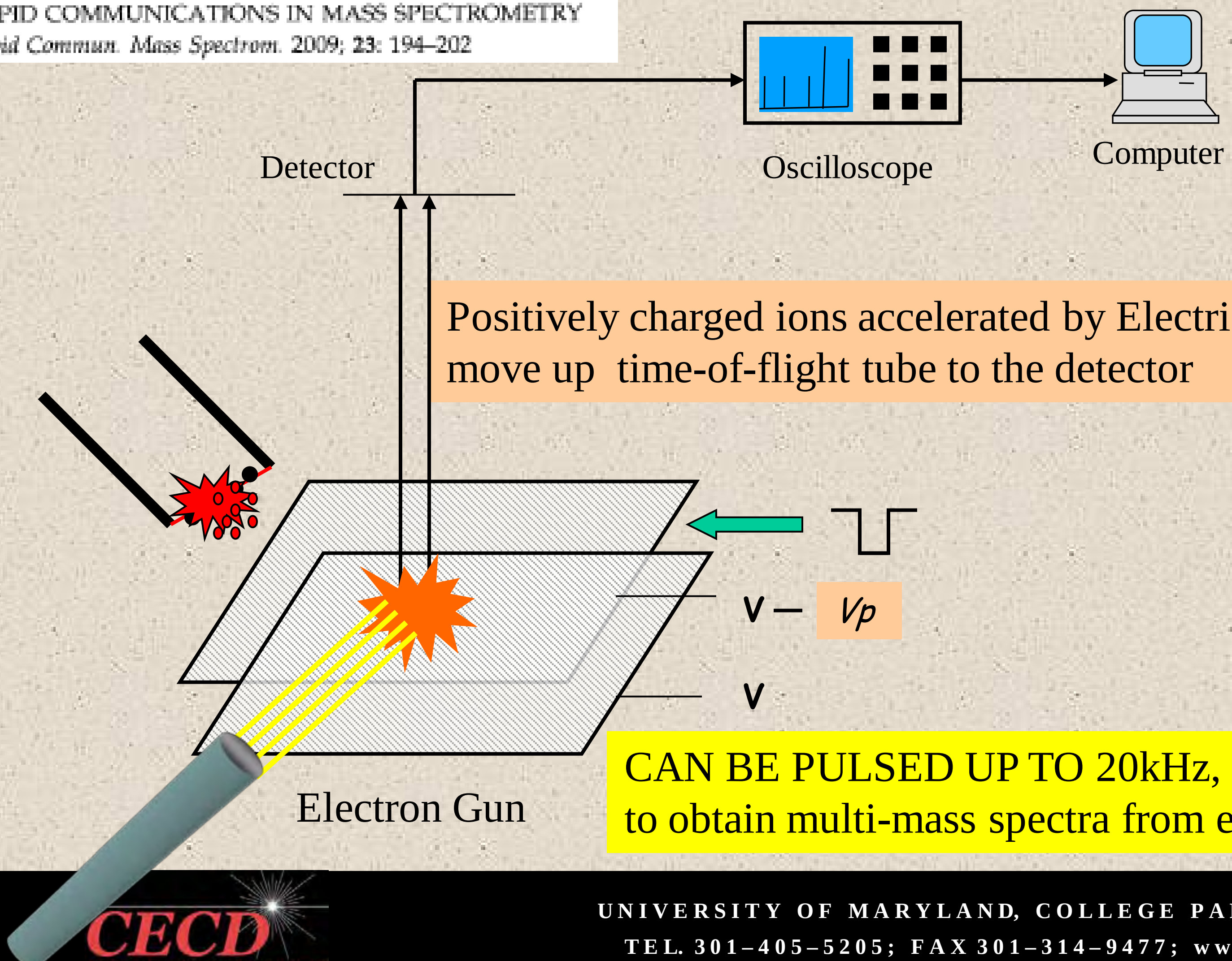




T-Jump Mass-Spectrometry

Possibility to study the ignition kinetics of Nanocomposites using mass spectrometry.

RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2009; **23**: 194–202

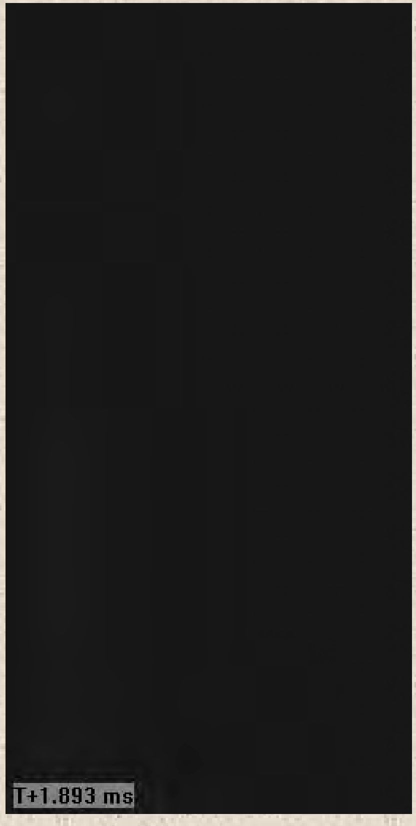


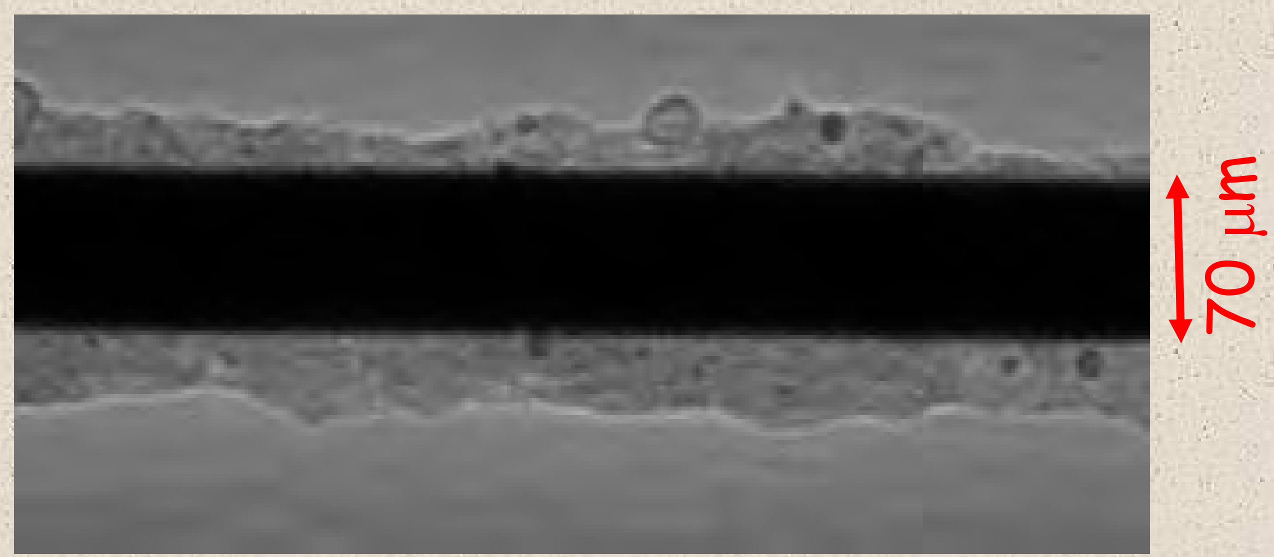
Positively charged ions accelerated by Electric field move up time-of-flight tube to the detector

CAN BE PULSED UP TO 20kHz,
to obtain multi-mass spectra from each combustion event.

Ignition of NanoThermite in T-Jump Mass-Spec:

Al + CuO => Al2O3 + Cu





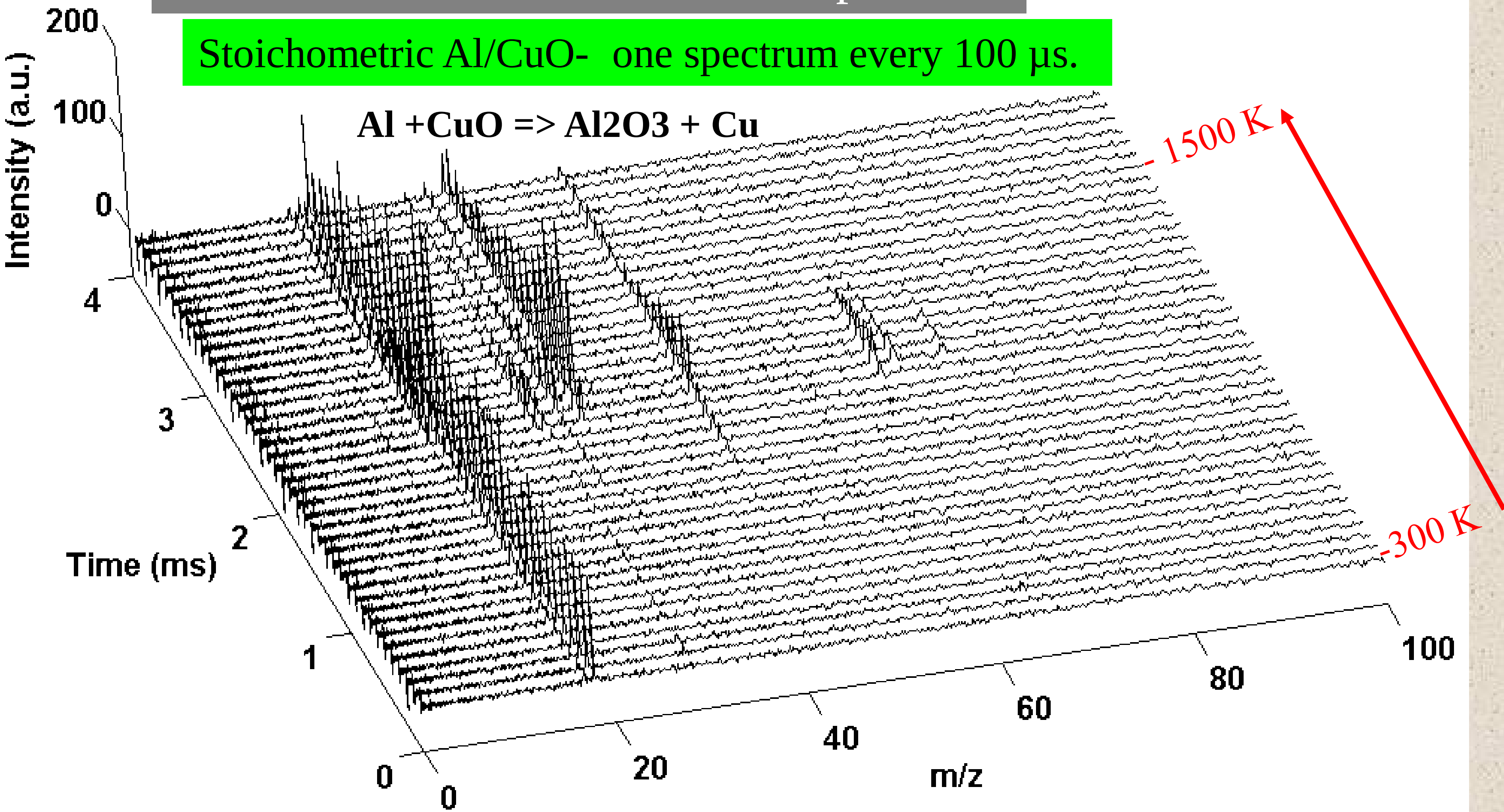
High Speed X-Ray Movie, **135,000 fps** (total time = 1.8 msec)

High speed video 33,000 fps

Obtained at Argonne National Lab
Collaboration with T. Hufnagel , JHU.

Time Resolved Thermite Mass-Spectrum

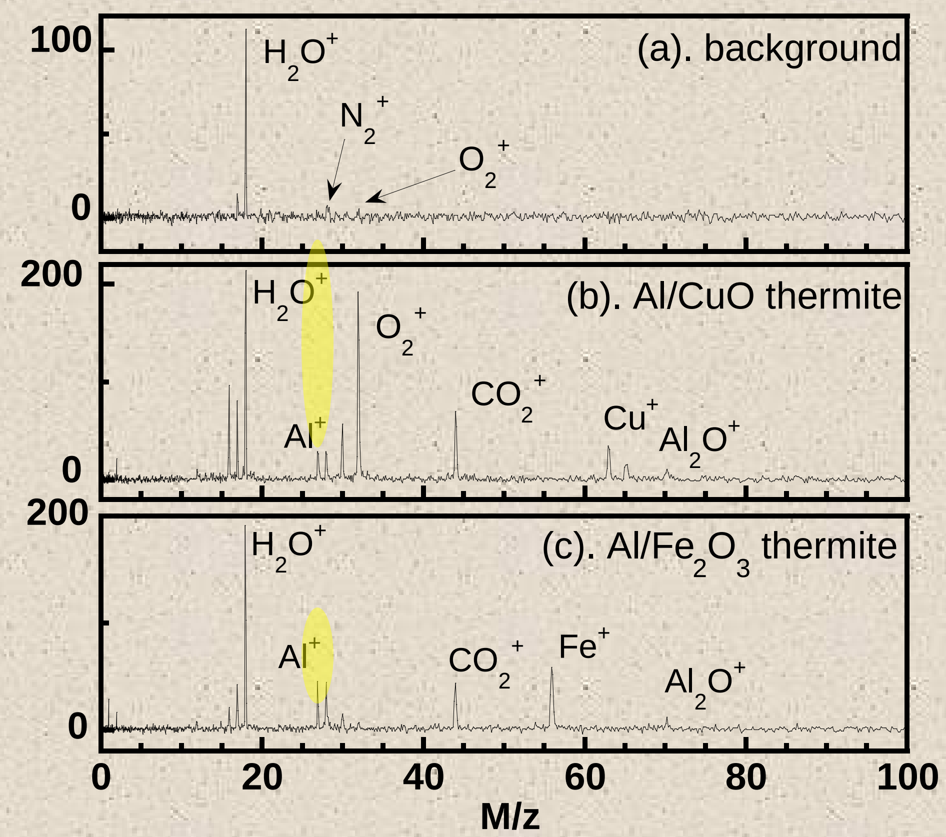
Stoichometric Al/CuO- one spectrum every 100 µs.



Al/CuO nanocomposite under heating rate 8.8 ×10^5 K/s

More Details in Thermite Spectra

Al +CuO => Al2O3 + Cu



Background:	
H2O	mass 18
N2	mass 28
O2	mass 32

Al/CuO thermite	
Oxygen species	mass 16, 32
Al	mass 27
Cu	mass 63,65
Al2O	mass 70

Al/Fe2O3 thermite	
Al	mass 27
Fe	mass 56
Al2O	mass 70

All have:	
CO	mass 28
CO2	mass 44

Difference between two systems: Oxygen species

Al2O is reaction product

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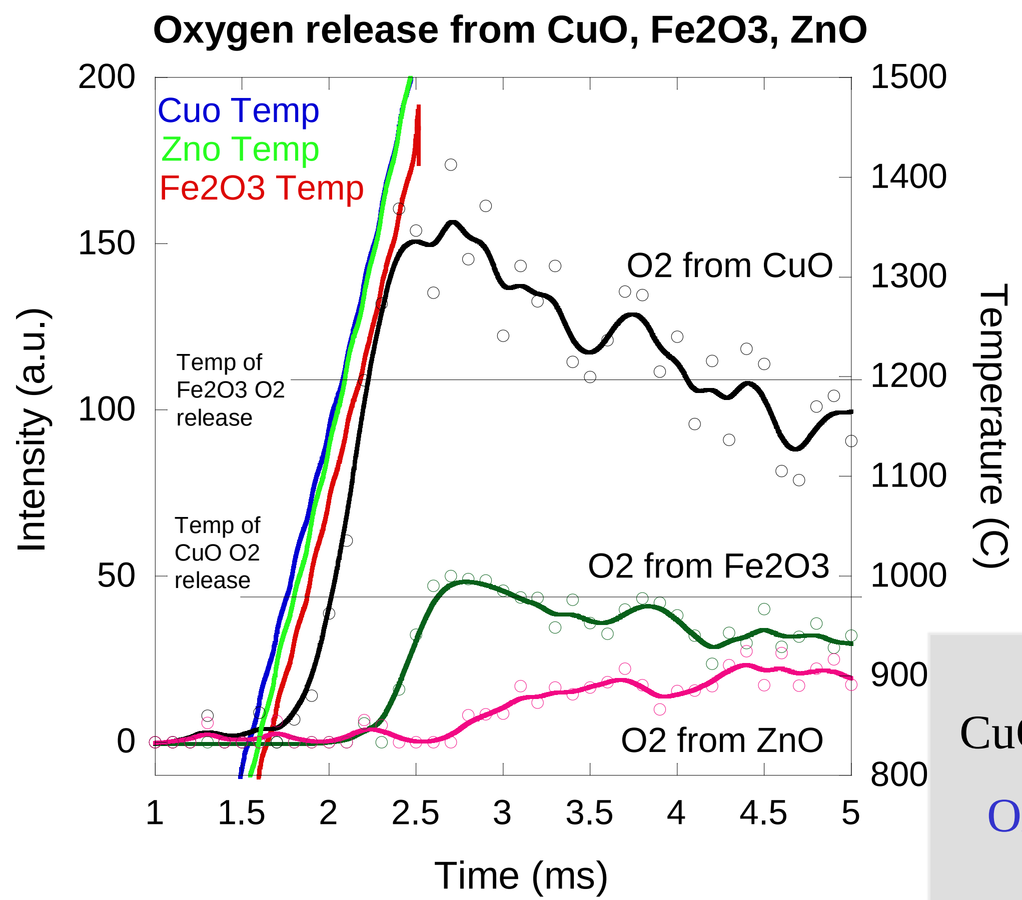
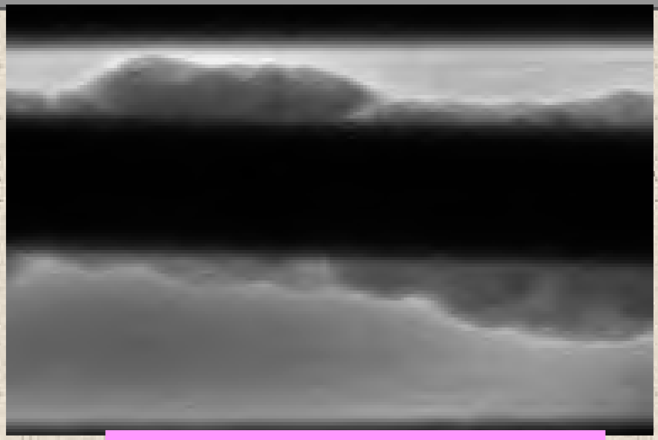
Comparison of O2 Release from CuO , Fe2O3, ZnO





Gas Release from CuO
X-Ray **135,000 fps**
Total time = 3 msec.

Reactivity From Pressure Cell:
CuO >> Fe2O3 >> ZnO (doesn't even burn)

Oxidizer Decomposition (Melting) Point:
CuO < Fe2O3 < ZnO

Results suggest that oxidizer decomposition to release O2 is important for ignition and that the amount of O2 release correlates with the reactivity.

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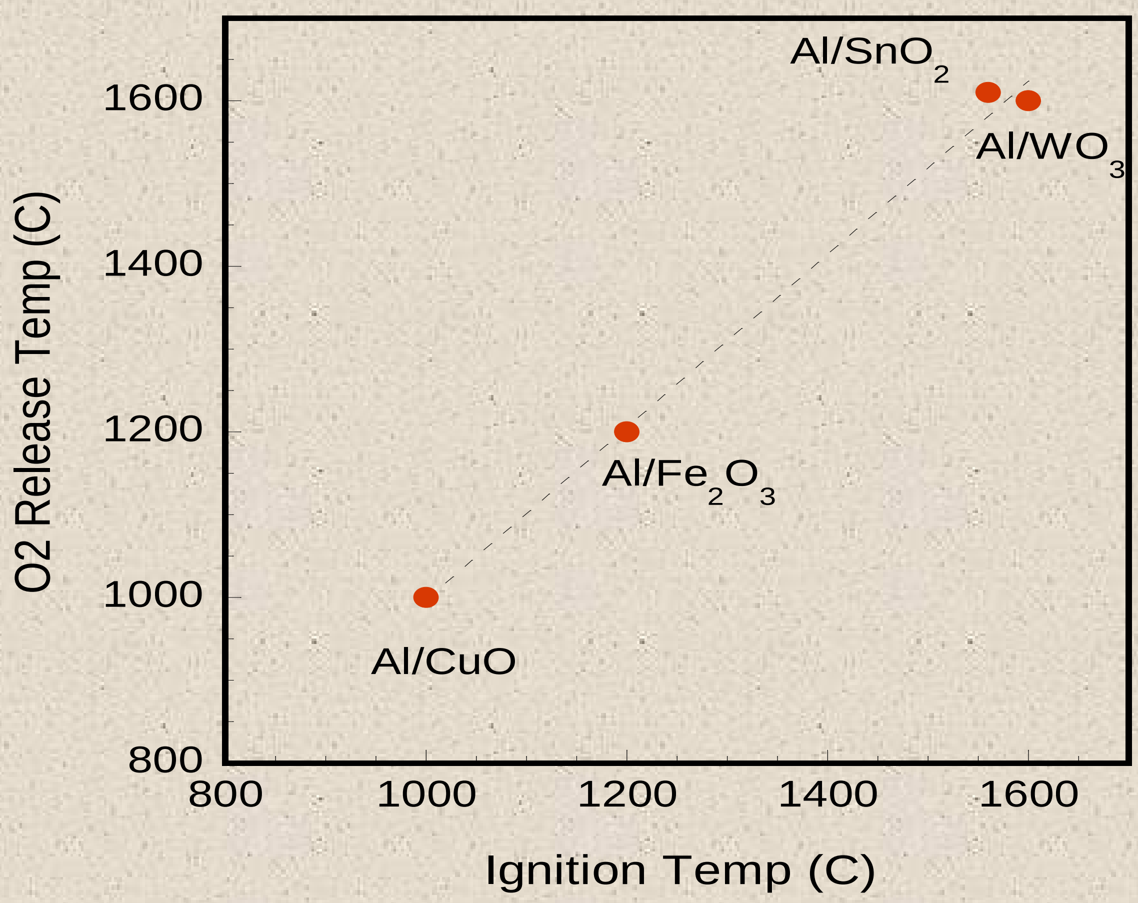
O2 Release Temperature vs. Ignition Temperature

Comparing thermite ignition with O2 release from the neat oxide powders:



There is a strong correlation between O2 release and the ignition temperature.

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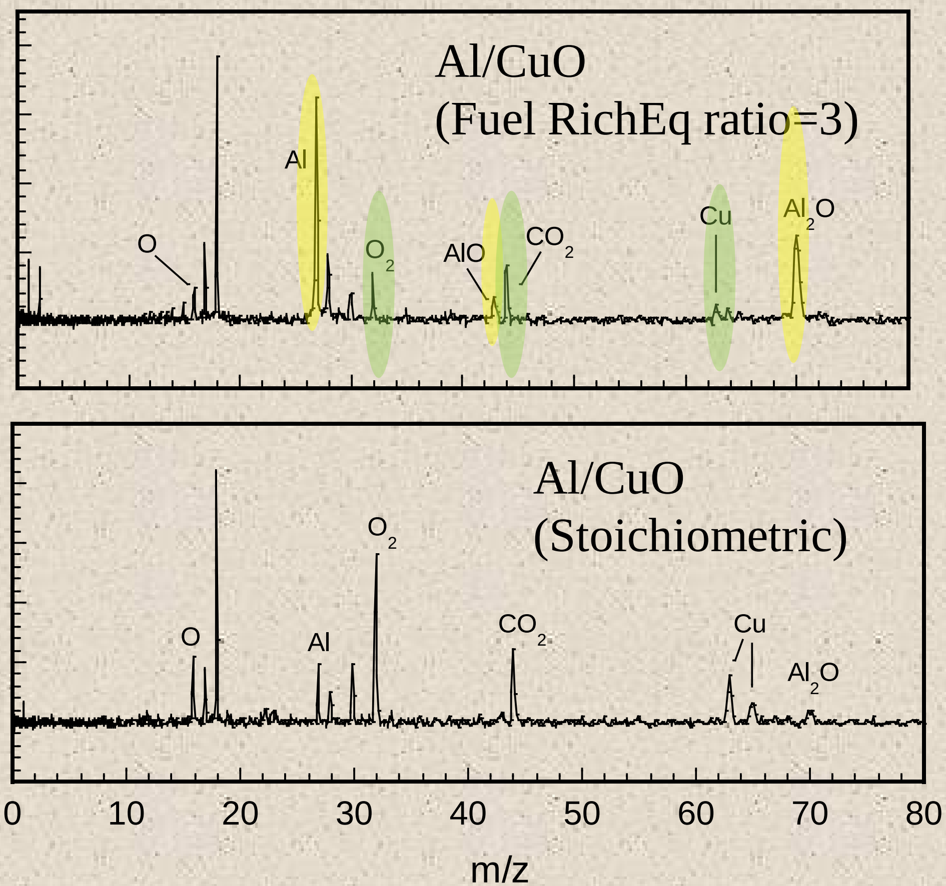
Fuel Rich VS Stoichiometric



-Shift from excess oxidizer (high O2 peak) to excess fuel (high Al peak)

Enhanced Peaks

Al

AlO (new peak)

Al_2O

Diminished Peaks

O, O_2

CO_2

Cu

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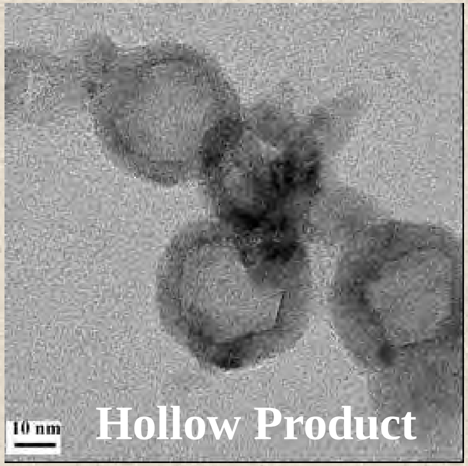
How does the Al get out, since it has an oxide shell ?

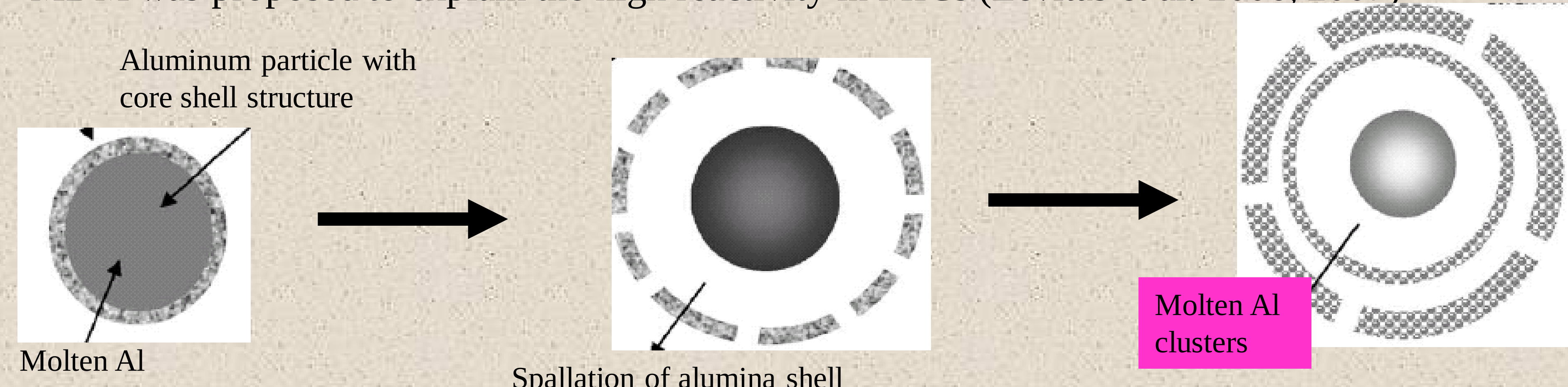
Diffusion mechanism for nano-aluminum
•Molten aluminum diffuses outward.
•Aluminum reacts with oxygen.

We have observed hollow particles observed in Oxidation of Nanoaluminum



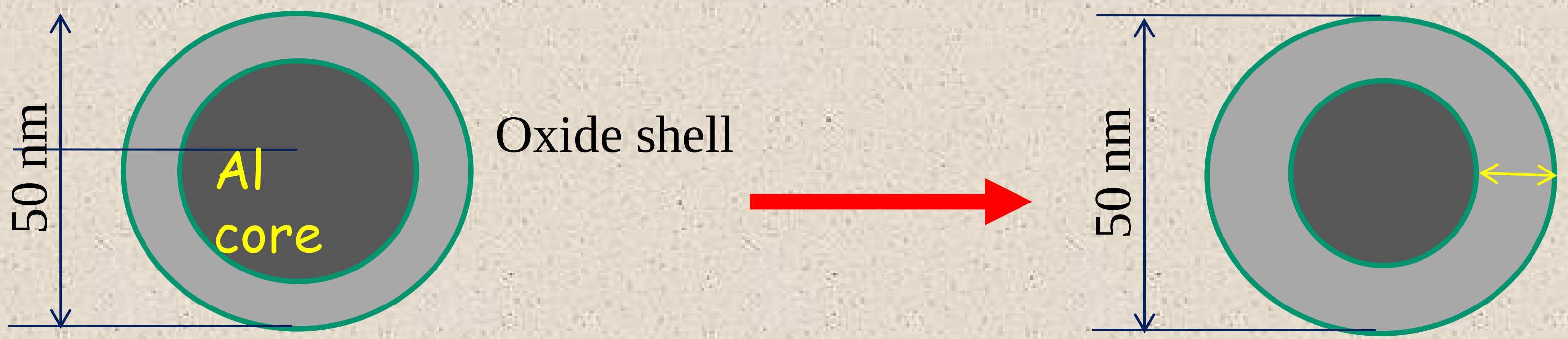
Melt Dispersion

MDM was proposed to explain the high reactivity in MICs (Levitas et al. 2006, 2007)



What is Role of Oxide Thickness on Reaction Time

Al nanoparticles (~50 nm dia) usually have an oxide shell of **~ 2nm**.



Prepare Al with different Oxide Shell thickness

Al particles are oxidized @ 400 C for different lengths of time :

a) 6 mins - **3 nm shell** (based on wt. gain)

b) 12 mins - **4 nm shell**

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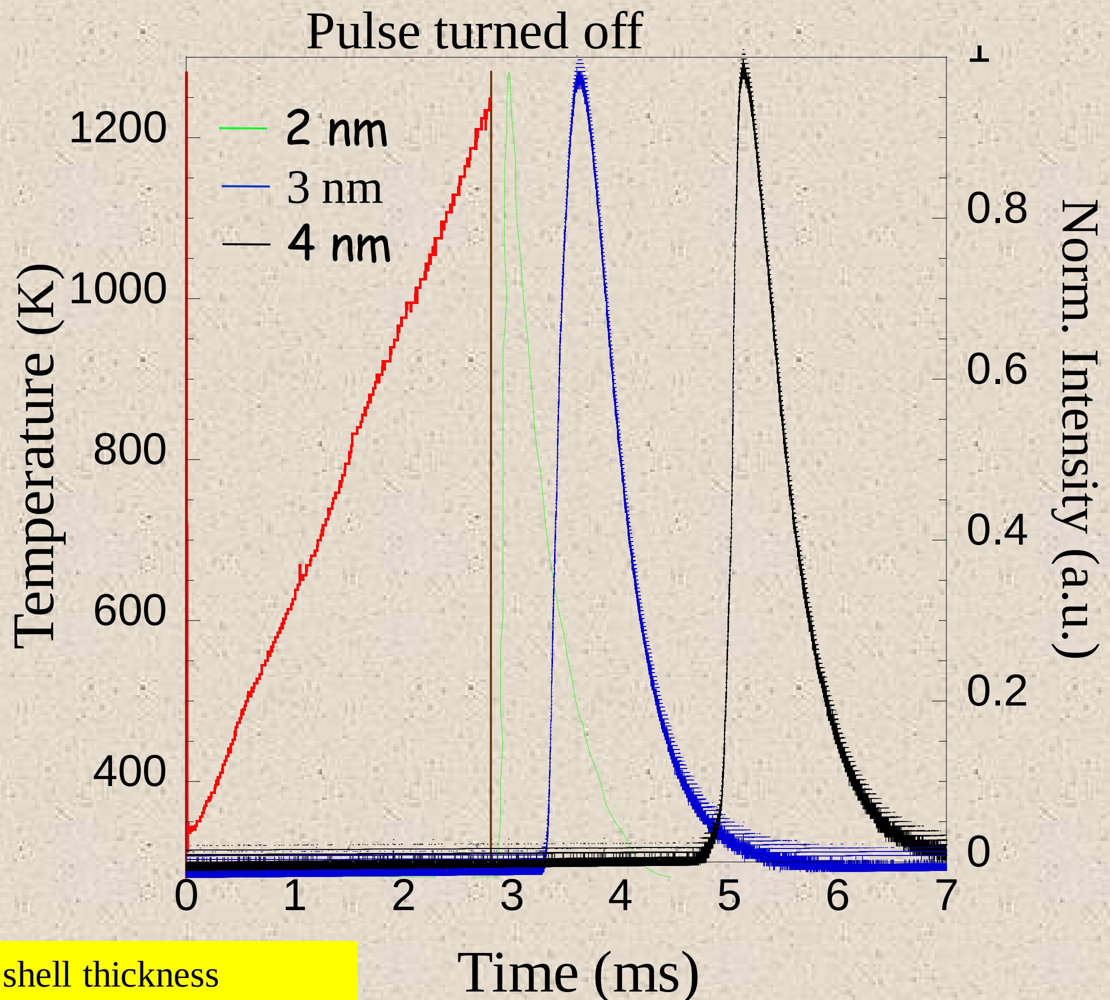
Ignition Delay vs Oxide Shell Thickness



- Ignition delay increases with shell thickness
- Suggests a transport limit

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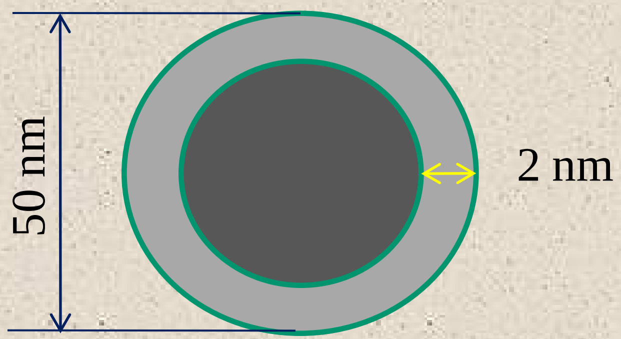
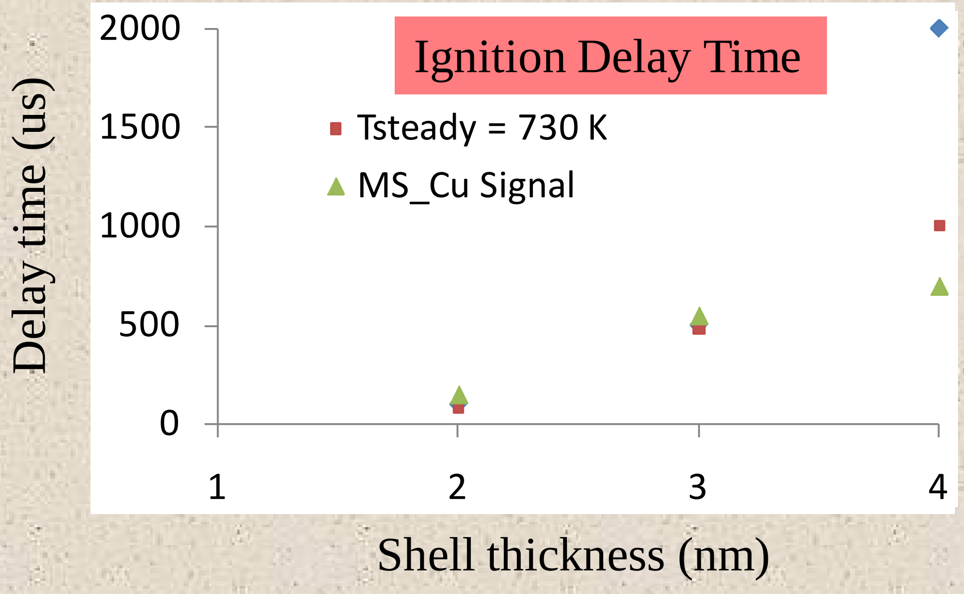
Effective Diffusion Coefficient in Oxide Shell from Ignition Delay





Effective diffusion coeff., $D_{eff} = L^2/t$

Steady State Temperature = 730 K

L (nm)	t (us)	D_{eff} (cm^2/s)
2	80	5e-10
3	480	1.9e-10
4	1000	1.6e-10

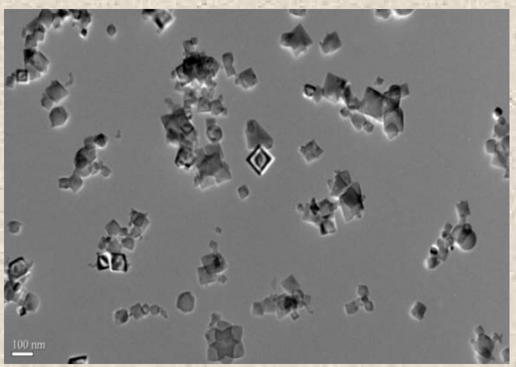
Effective Diff. Coeff. are consistent.

Park et al., J. Phys. Chem. B, 2005
D= 10E-8 – 10E-9 cm2/sec

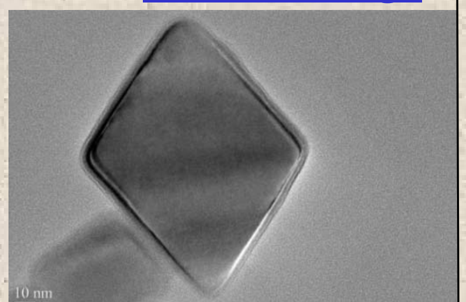
Vashista and co-workers 10E-6 cm2/sec

Mass spectrometric data shows same trend in ignition delay

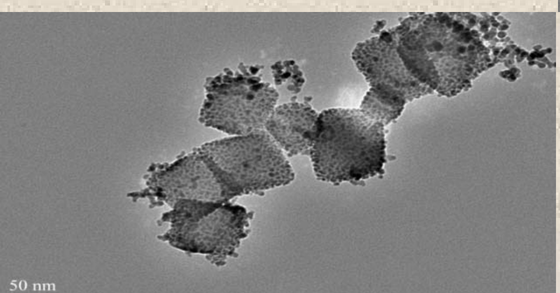
NanoCrystals of Al

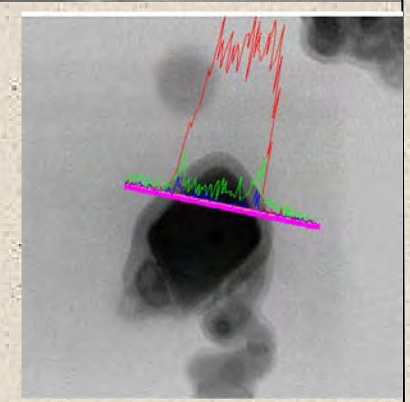


Hi-Res Image



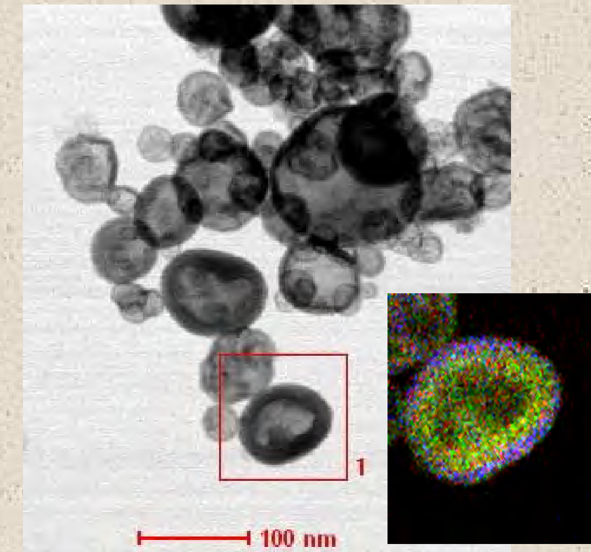
Coating Al with Ni





Al coated with Perfluorohexadecanoic Acid

Core-Shell Reactive Oxidizers



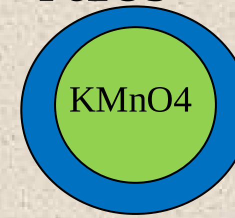
Elemental Map

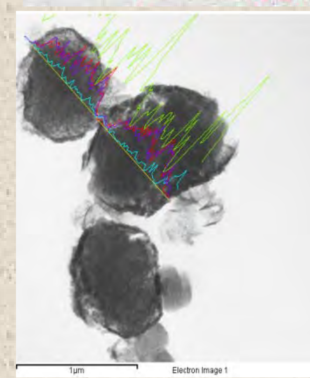
Fe

O

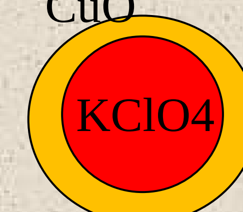
Mn

Fe2O3





CuO



Conclusions

- Development of new mass spectrometry tool enables us to probe reaction dynamics of ultra-fast condensed state systems at high heating rates.

- Metal oxides appear to release O2 and the ignition temperature would appear to correlate with O2 release. However, some other systems not discussed today show indications of heterogeneous reactions.

- Al from oxide coated particles seem to leak out by a diffusion mechanism.

- A very short transient ion generation pulse (20 us) occurs just at the ignition point (not discussed today)

- New classes of nanocomposites offer opportunities to tune reaction profiles.

Publications may be downloaded from **www.enme.umd.edu/~mrz**