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Reactive Multilayers that Exhibit Self-Propagating, High Temperature Formation Reactions

D.P. Adams
Sandia National Laboratories
Albuquerque, NM

University of Virginia
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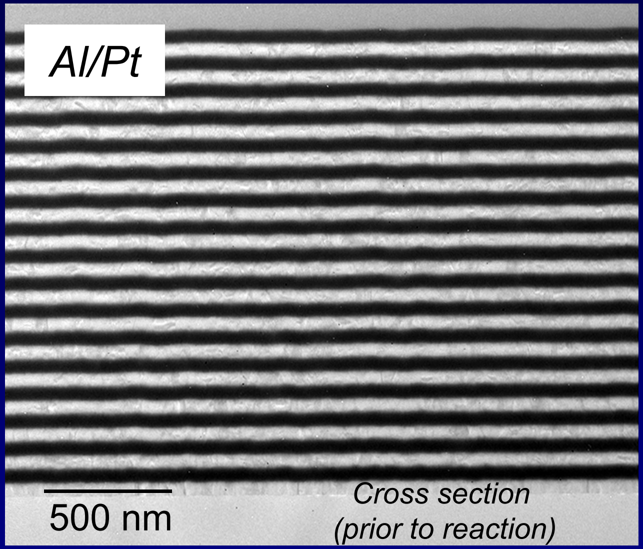
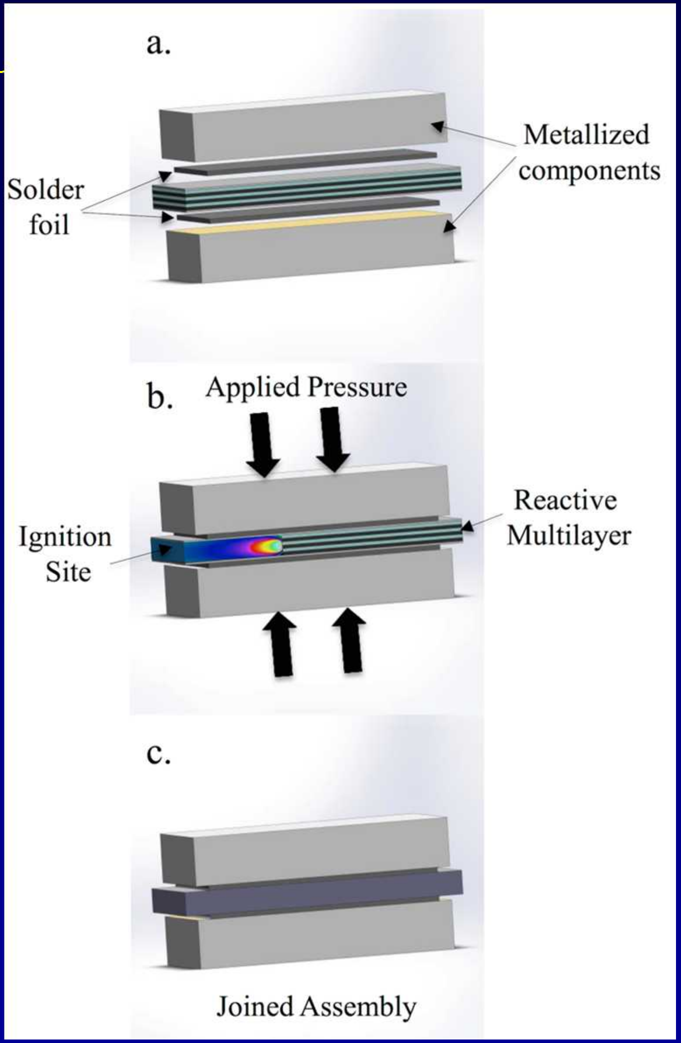
What is a reactive multilayer?

- Material containing two reactants that can be ignited at one or more points and undergo a self-propagating, gasless reaction wherein:
    - reactants are composed as alternating layers.
    - reaction is characterized by a wavefront speed, v_{rxn} with $v_{rxn} < v_{sound\ in\ solid}$ (deflagration, not detonation)



First report of reactive multilayer films: *Floro Rh/Si JVST 1986*

Reactive multilayers are used for local soldering, brazing and joining.



- Heterostructure that consists of two or more species that react.

$$M_1 + M_2 \rightarrow M_1M_2$$
$$M_1 + M_2O \rightarrow M_1O + M_2$$

- Commercial product (Nanofoil) is Ni(V)/Al 40-150 µm spearheaded by Weihs, Knio and others, now Indium Corp.

- Recent work with 1.6 µm thick sputtered Pd/Al films demonstrates Si bonding. (Jorg Braeuer, ECS Trans. 50, 2012).

- Our research demonstrate reactive transition metal / noble metal pairs that self-propagate. These form the intermetallic compounds that, in bulk form, are ductile (Gschneidner, Nat. Mater. 2003).

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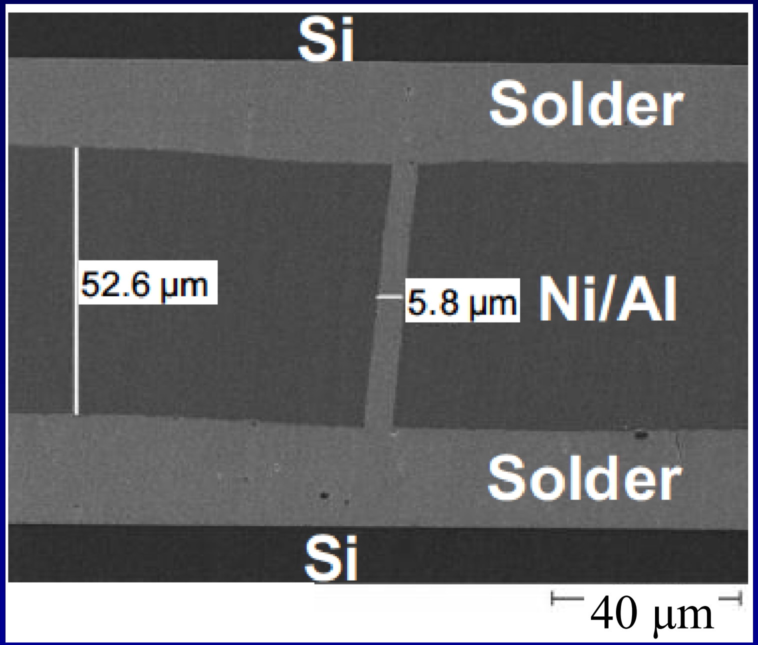

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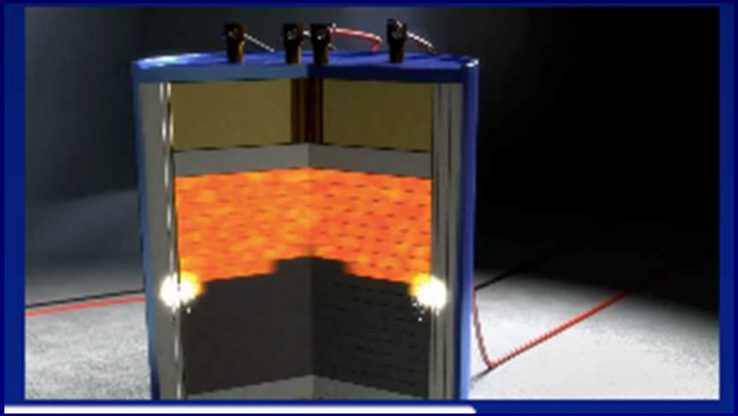
We are investigating alternative heat sources for reserve battery applications.

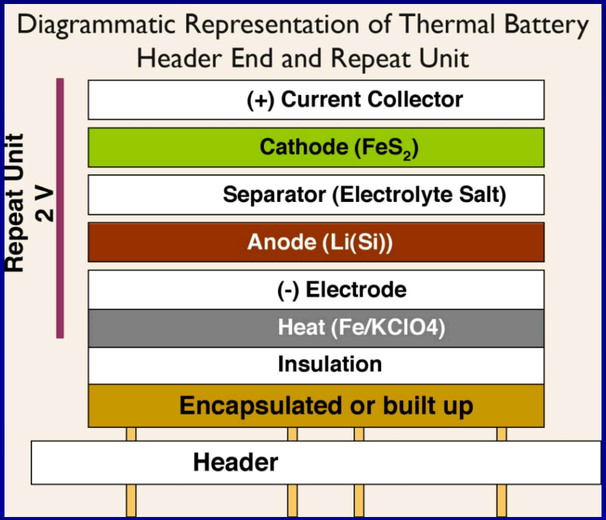
- Battery in which a key element (e.g electrolyte, cathode) is missing; it is somehow added in order to activate the battery.
  - Silver-zinc battery : electrolyte held in reservoir
  - A thermal battery : electrolyte is frozen



- Traditional heat source (thermal battery):

$$4Fe + KClO_4 \rightarrow 4FeO + KCl \quad (710\ cal/g)$$

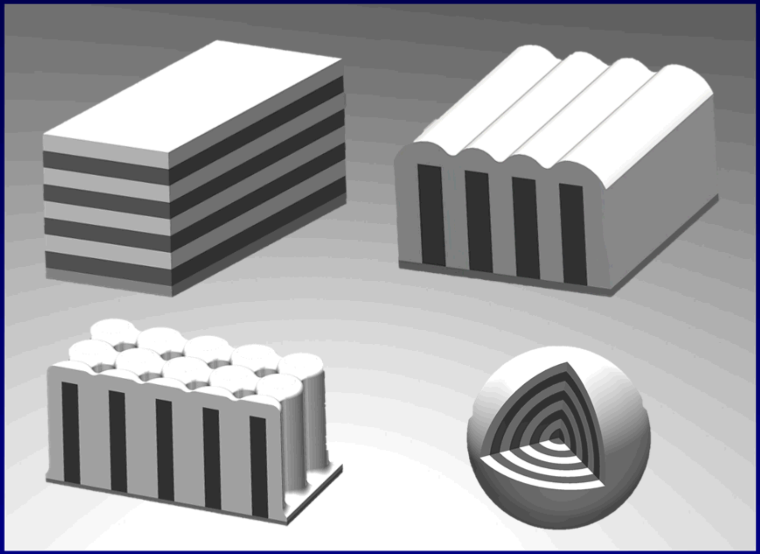
  - blends of $Fe/KClO_4$ are necessary
  - must be electronically conductive after burn so employ various compositions, e.g., 88/12 (w/w)



Reference: "Handbook of Batteries 3rd ed., D. Linden and T.B. Reddy, editors, McGraw Hill Inc., 2001.

Vapor deposition provides the desired level of control (thickness, composition, purity) for scientific study.

- Different fabrication methods
  - Lithography for patterning
  - Sputter deposition, Atomic layer deposition

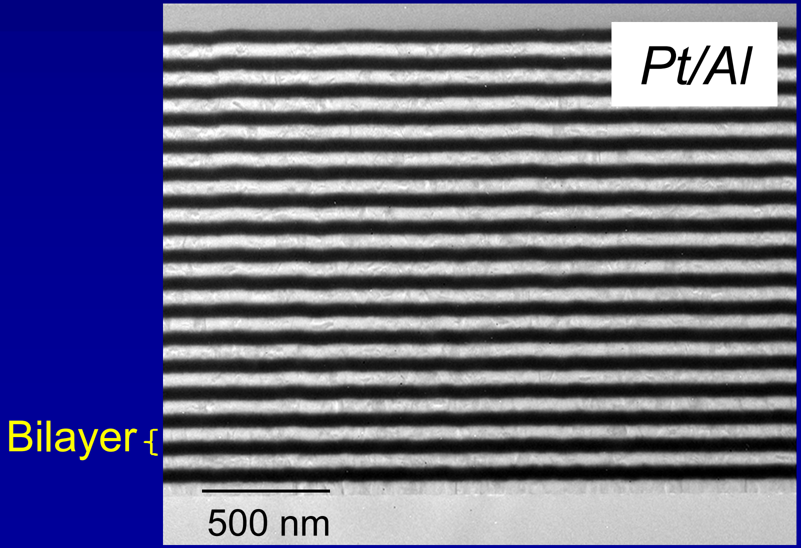


- Benefit from semiconductor industry tools
  - Ångström level precision
  - Uniform thickness over large areas

- Different materials (ΔH_o) include

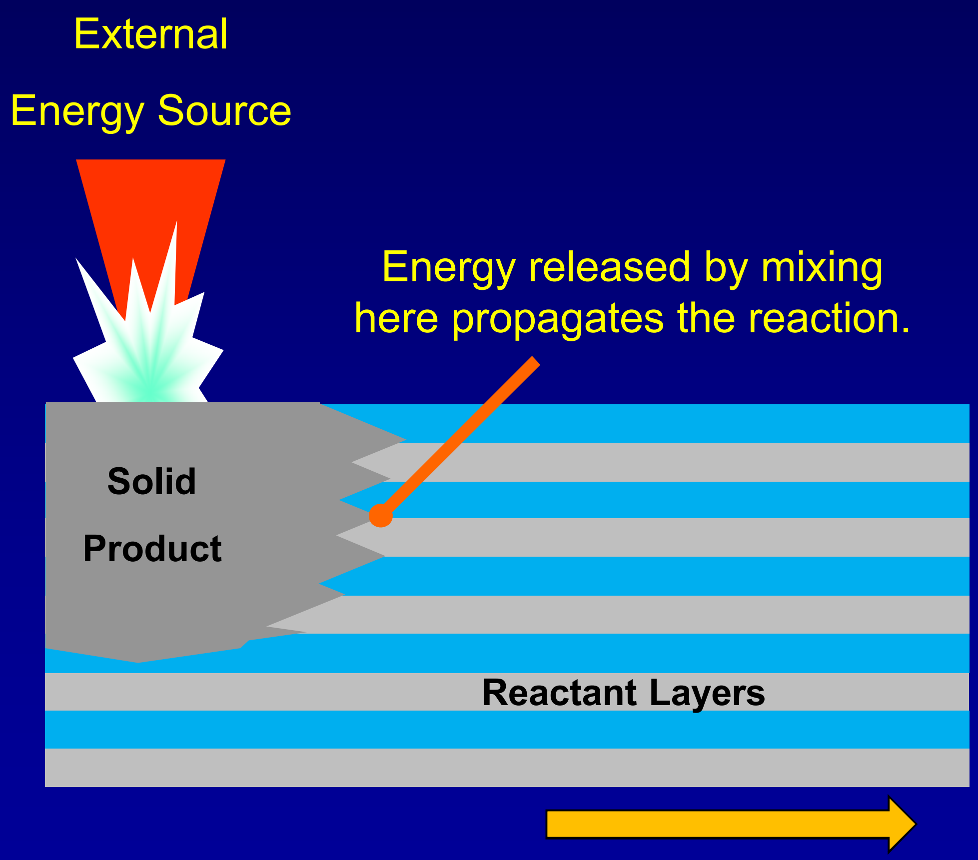
Ti/2B : - 4.8 kJ/g
Al/NiO: - 2.2 kJ/g
Co/Al : - 1.4 kJ/g
Pt/Al : - 0.9 kJ/g
Ni/Ti : - 0.6 kJ/g

Compare to ΔH_o
TNT: -4.184 kJ/g

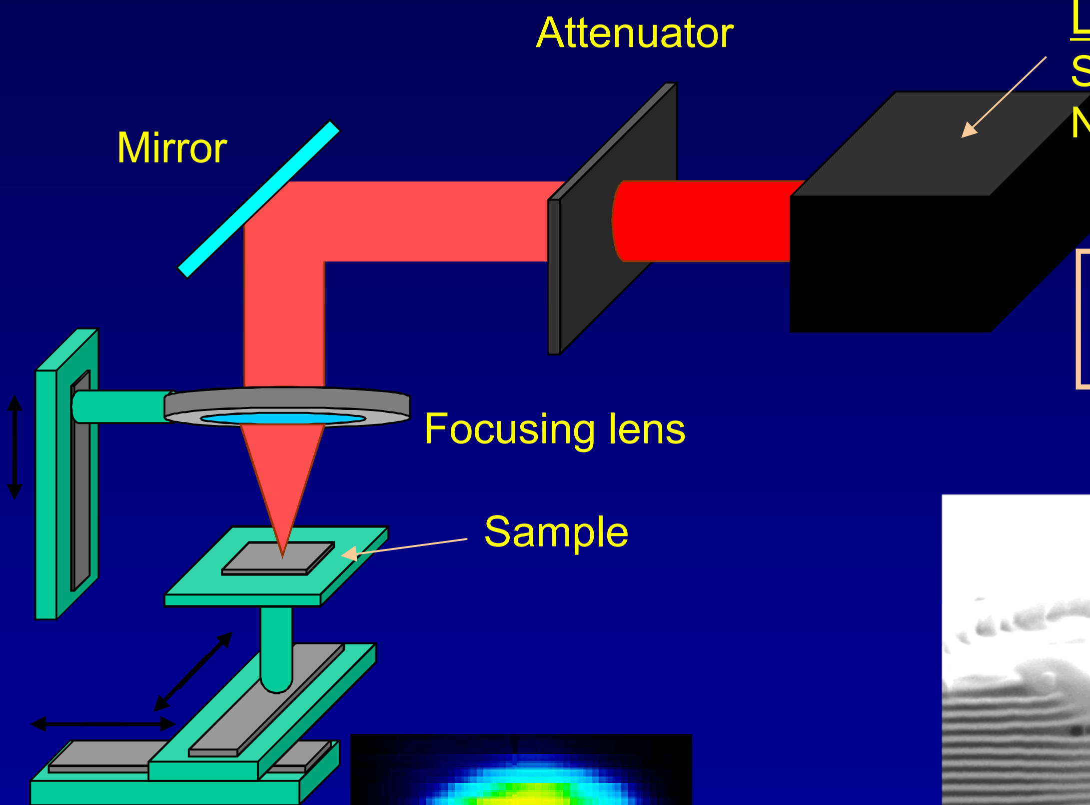


Reference: Cohesion in Metals: Transition Metal Alloys, F.R. deBoer (North Holland, 1988)

How does ignition occur at a point? How do the ignition requirements vary with multilayer design?

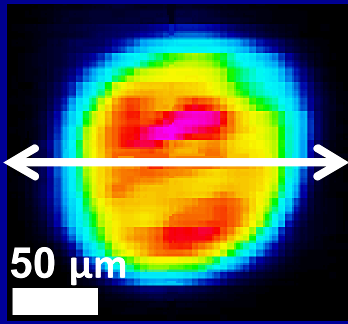


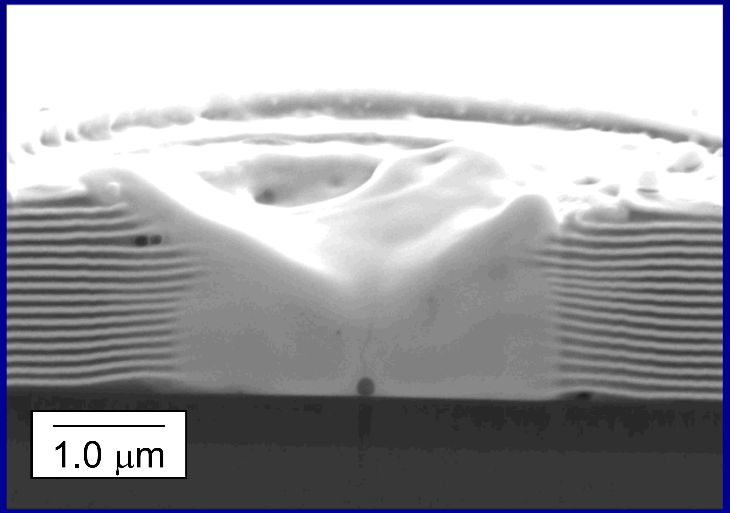
Single pulse irradiation is used to determine laser ignition thresholds



Laser systems:
Spectra-Physics Hurricane - Ti:sapphirer
Northrup Grumman – Diode fiber

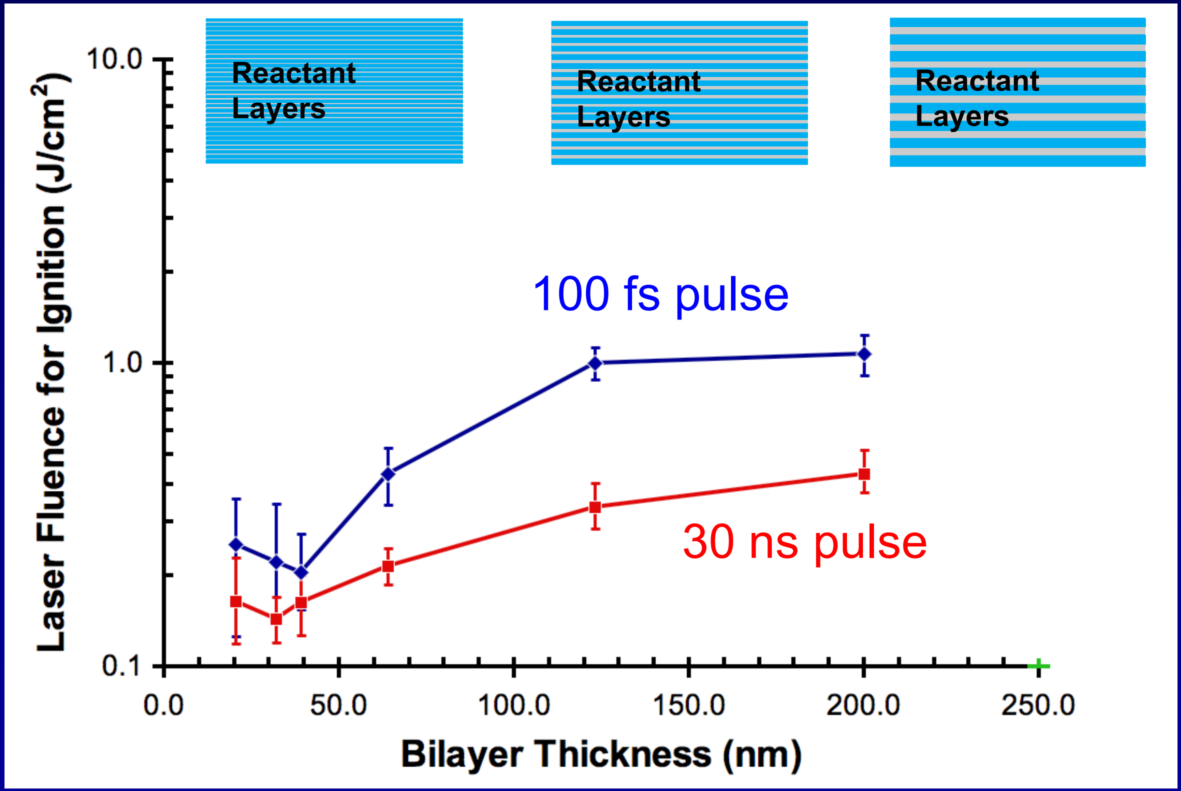
Single pulse output (800 nm)
150 fs, 1 ps, 30 ns, 10 μs to 1 s





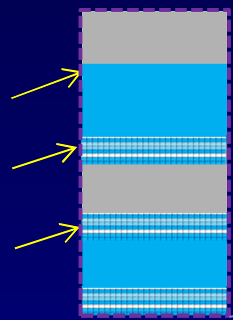
Al/Pt Irradiated with 80% threshold
(100 femtosecond pulse duration)

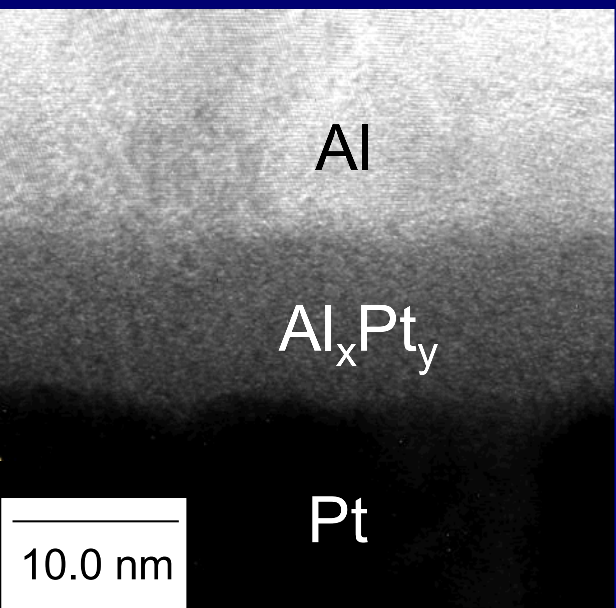
Laser ignition thresholds vary with multilayer design.

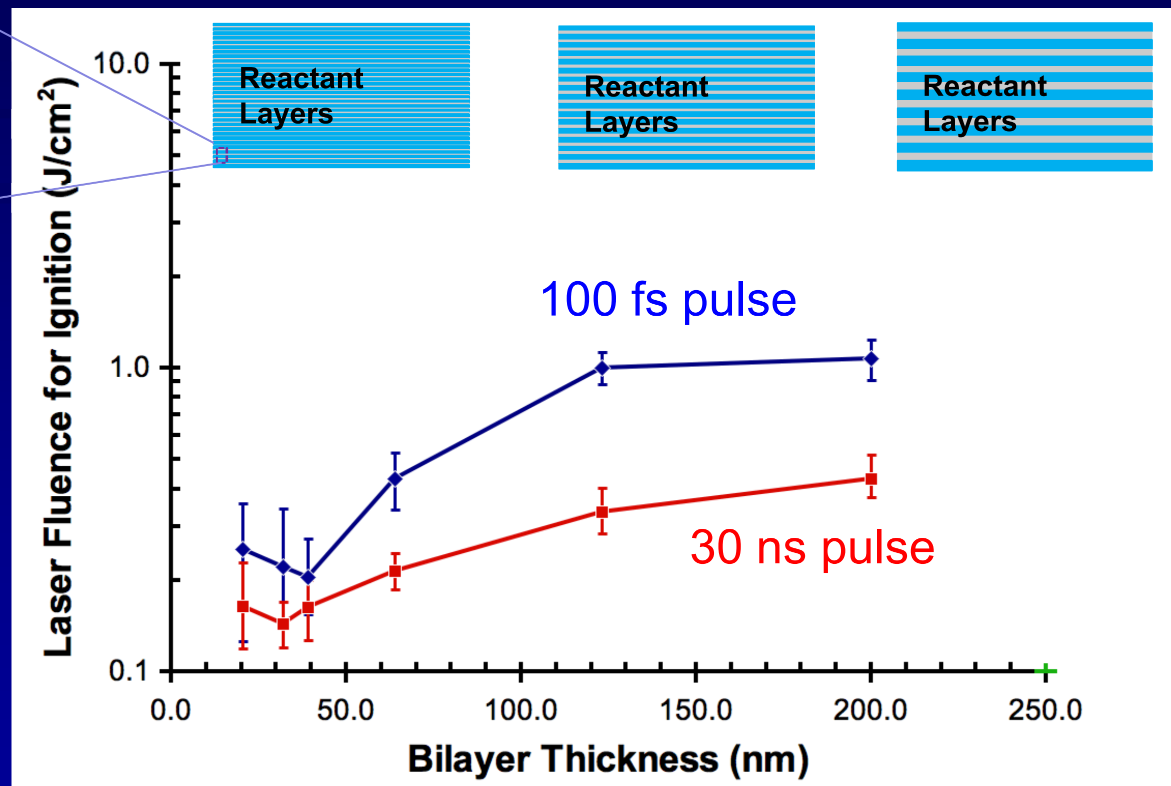


Results from testing 1.6 μm thick, freestanding Al/Pt multilayers
Incident Λ = 800 nm light

Laser ignition thresholds vary with multilayer design.







Available energy for reaction

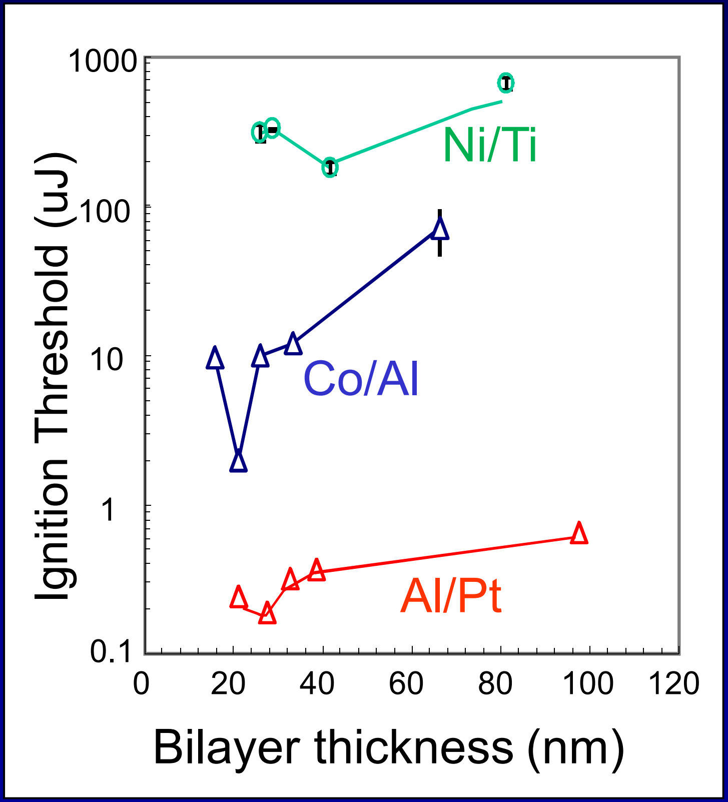
$\Delta H = \Delta H_o - E_{premix}$

Results from testing 1.6 μm thick, freestanding Al/Pt multilayers

Incident Λ = 800 nm light

Ignition thresholds vary with bilayer thickness and material system.

Single 30 nsec laser pulse ignition thresholds (in air). Identical spot size



Results compensate for reflectance loss

- Differences in speeds attributed to different ΔH_o , thermal properties mass diffusion rates.

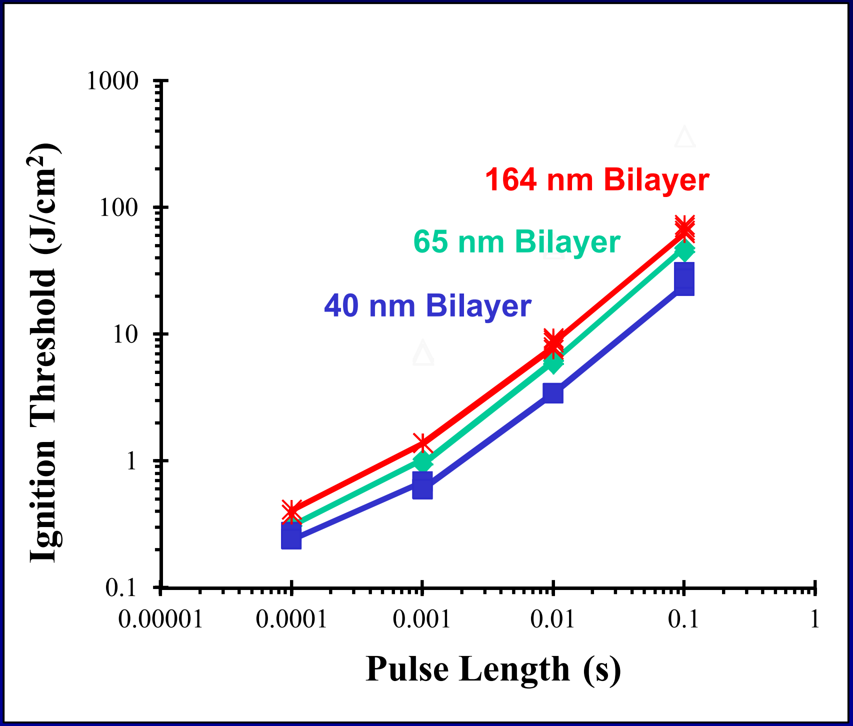
Heats of formation (molar)
Pt/Al : - 100 kJ/mol at.
Co/Al : - 60 kJ/mol at.
Ni/Ti : - 34 kJ/mol at.

Thermal diffusivity, κ_{avg}
Pt/Al : 0.49 cm^2/s
Co/Al : 0.47 cm^2/s
Ni/Ti : 0.086 cm^2/s

Y. Picard, J. P. McDonald, et al. Appl. Phys. Lett. 93 (2008).

Laser ignition thresholds vary with pulse length.

- Pulse lengths varied within from 0.0001 to 0.1 second.
- Thresholds increase with pulse length for full range explored.
- Results shown for three different bilayer designs (Al/Pt)



Results from testing 1.6 μm thick, freestanding Al/Pt multilayers
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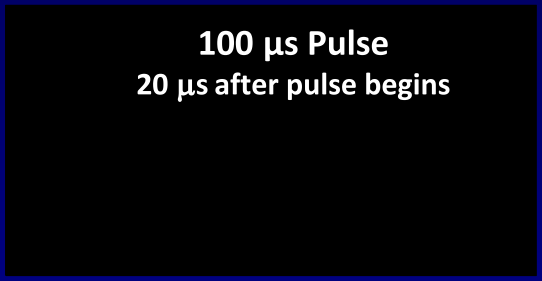
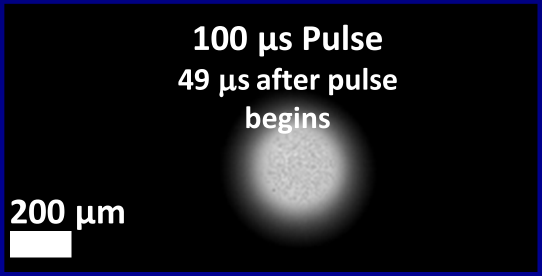
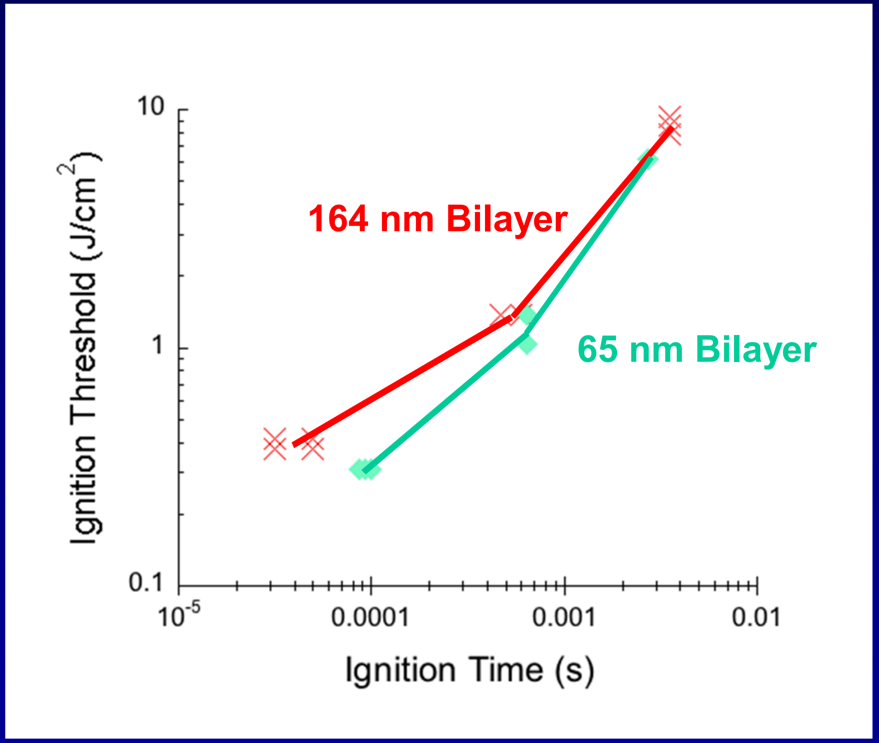
Laser ignition thresholds vary with pulse length.

High speed optical microscopy allows measurement of ignition times (which are < pulse length).



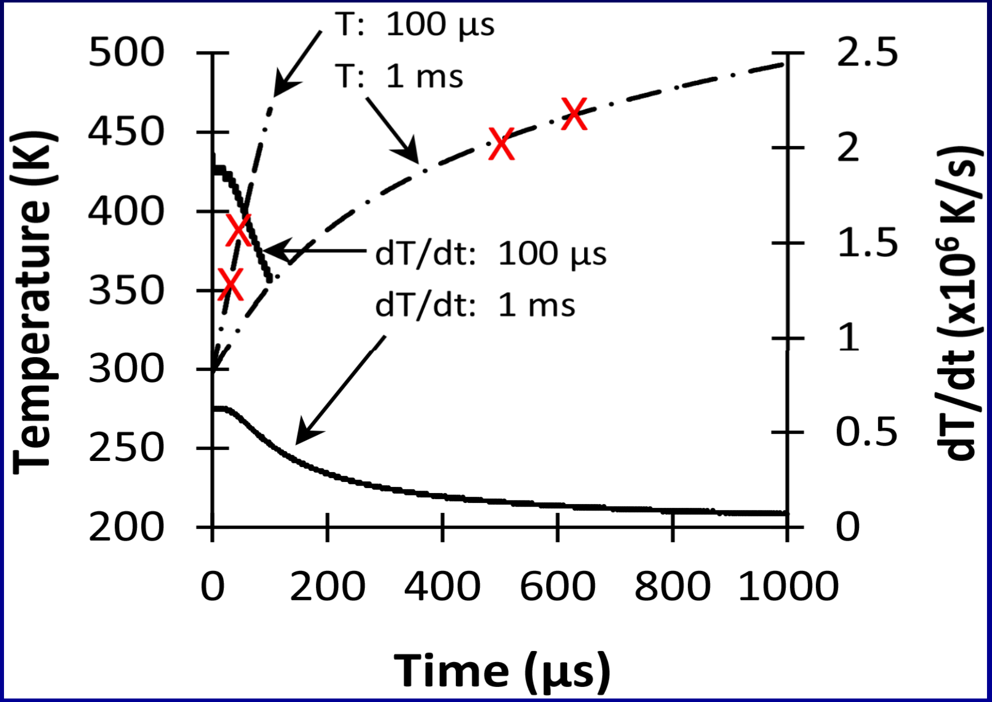




Results from testing 1.6 µm thick, freestanding Al/Pt multilayers
Incident Λ = 800 nm light

Finite element models account for heat losses and provide estimates of heating rates, temperatures.

- Models account for reflectance, rate of supplied energy, and thermal transport in multilayer.
- T and dT/dt are estimated at center of irradiated spot.
- Marks (X) denote measured ignition times.
- Can infer that ignition temperatures are well below T_{melt} (reactants).

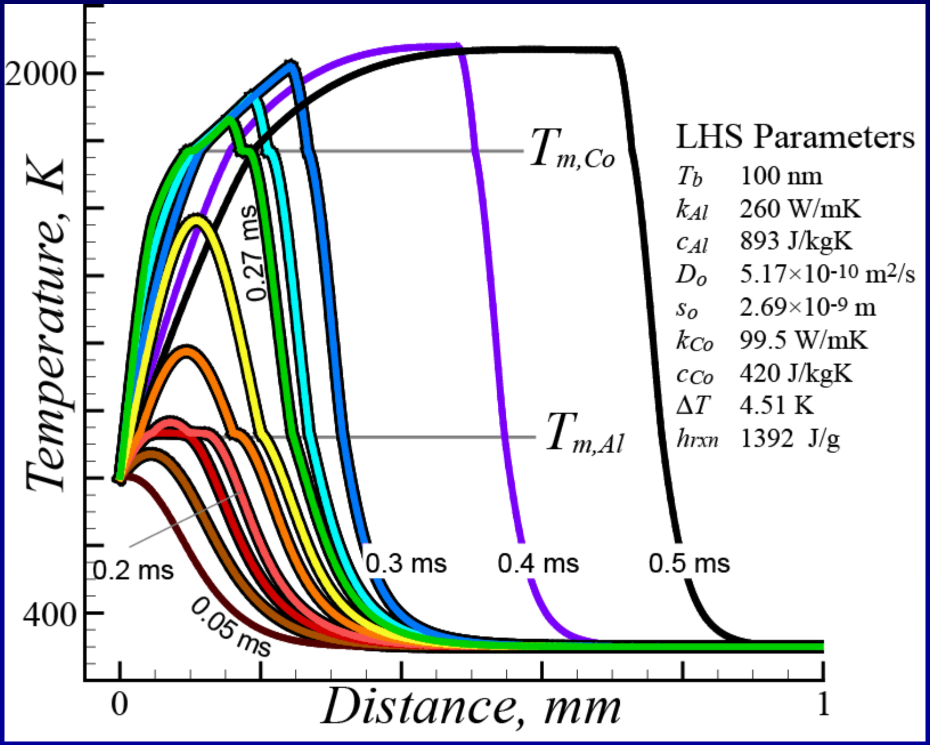


Results from testing 1.6 µm thick, freestanding Al/Pt multilayers
Incident Λ = 800 nm light

Point ignition involves the rapid excitation of a small volume and rapid heat release within the multilayer.

- Finite difference modeling of ignition and transition to self-propagating reaction.
- Temperature dependent material properties (e.g., latent heat of melting) are included.
- Different fixed temperatures were applied at an edge of modeled Co/Al and Pt/Al multilayers
- Consistent with single pulse ignition models suggest Al melting is not essential

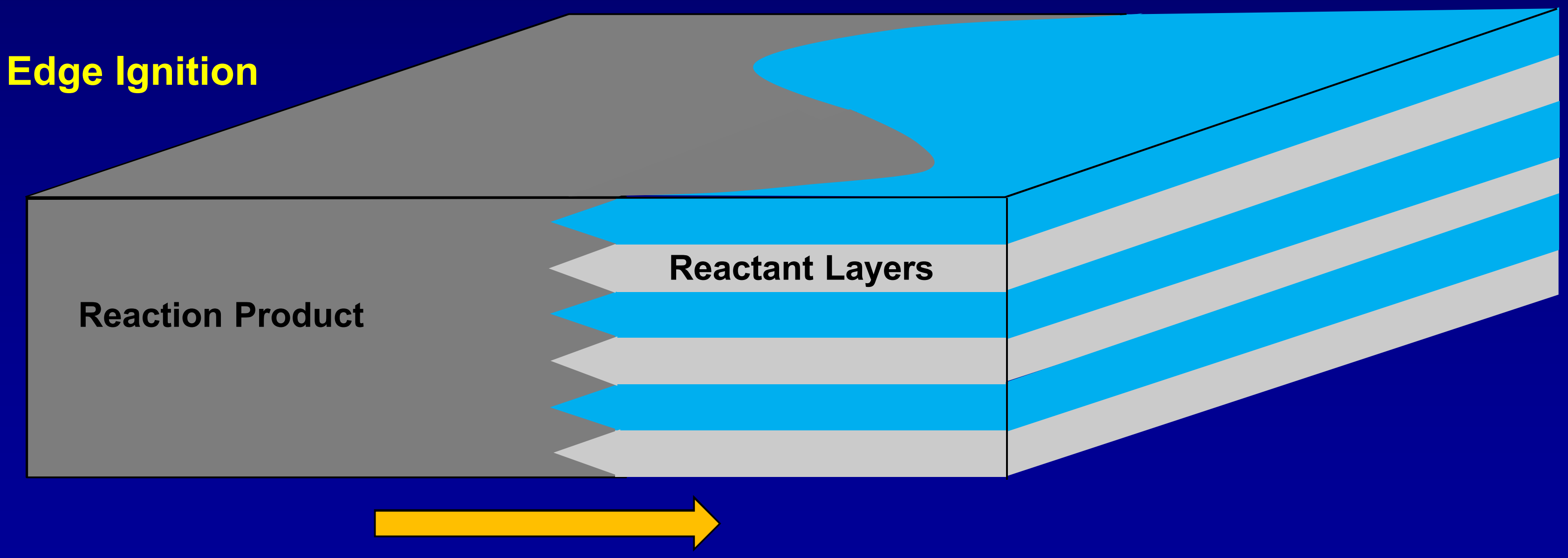
Results from finite difference modeling of Co/Al, edge ignition



Color lines are time steps.

M. Hobbs, D.P. Adams, et al.
Heat Transfer X. (2008).

How do reactions propagate at the microscale?



Propagating reaction front speeds vary with bilayer thickness.

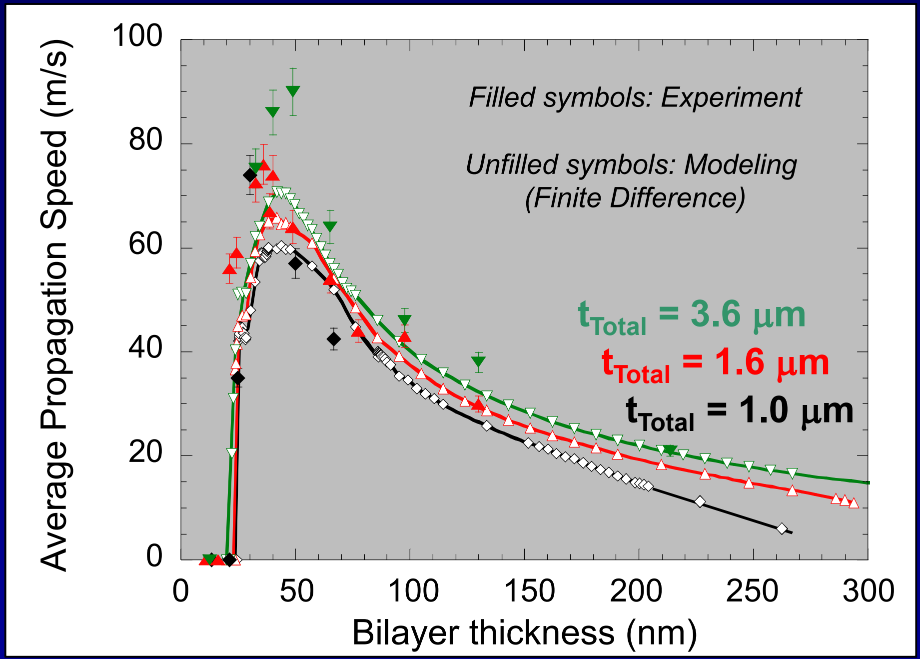
- Large range of bilayer thickness over which a decreased dimension gives rise to increased average speed.

- Decreased speed for ultra-thin bilayers is due to the presence of relatively large amounts of premixed material.

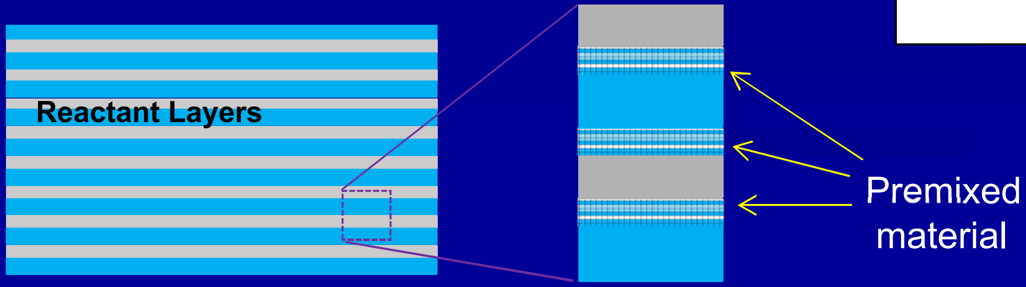
  first explanation: Wickersham, 1988

- Increased wavefront speed with total thickness.

Ex. Equiatomic Aluminum/Platinum on SiO_2



M. Hobbs, D.P. Adams et al. 8th World Congress Comp. Mech. 2008).

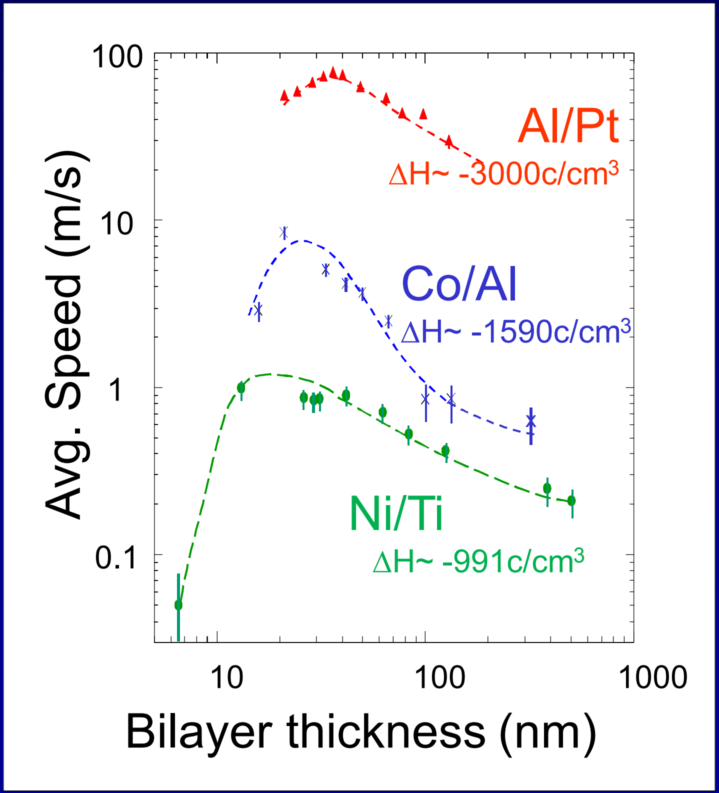


Propagation speeds can be tailored through multilayer design and composition.

Ignition in air

- General relationship between speed and bilayer thickness found for different metal pairs.
- Speeds vary across a large range from ~0.1 to ~90 m/s (deflagration).
- Differences (between materials) are explained by heat release rate and this is affected by:

  heat of formation (ΔH)
  mass transport
  thermal transport

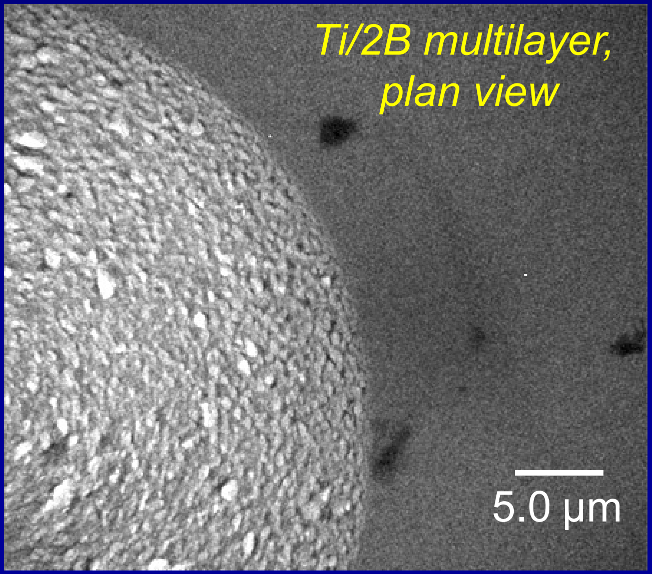


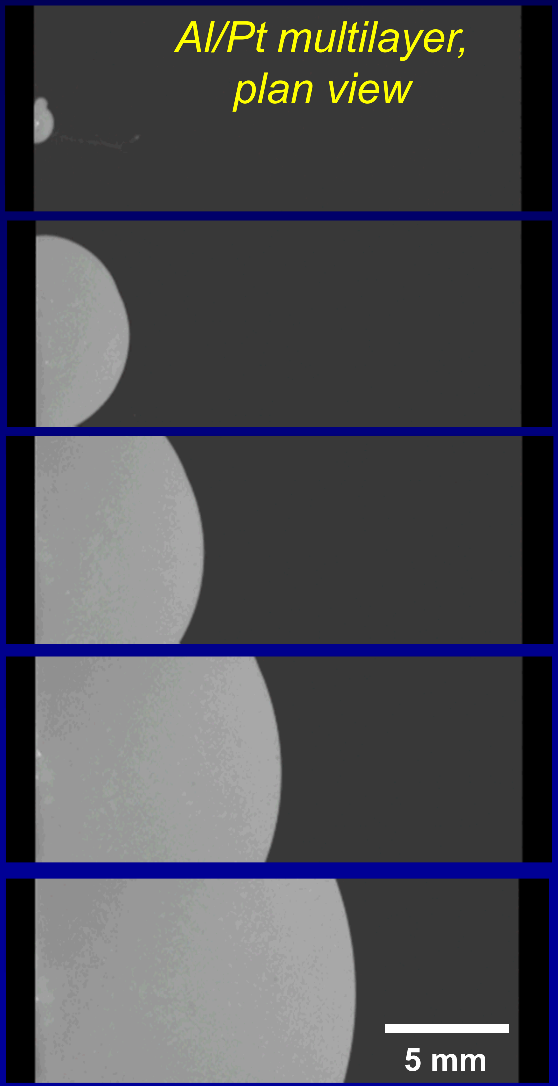
Y. Picard, J.P. McDonald, Appl. Phys. Lett. 93 (2008).

Many reactive multilayer systems (particularly those having large heats of formation) exhibit a stable reaction front.

- Reaction front is smooth / uniform.
- Characterized by a single radial velocity.

2 μs after ignition; viewed while reacting





80 μs

240 μs

400 μs

560 μs

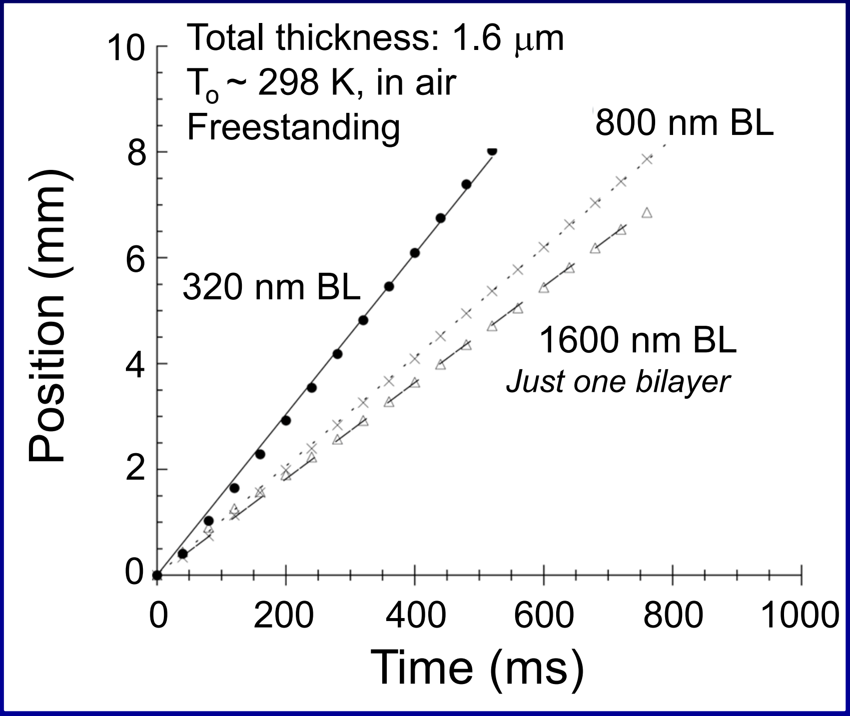
720 μs

T. LaGrange, G. Campbell, A. Gash, D.P. Adams et al. Microscopy & Microanalysis 93 (2012).

Evidence for stable propagation comes from plots of front position vs. time.

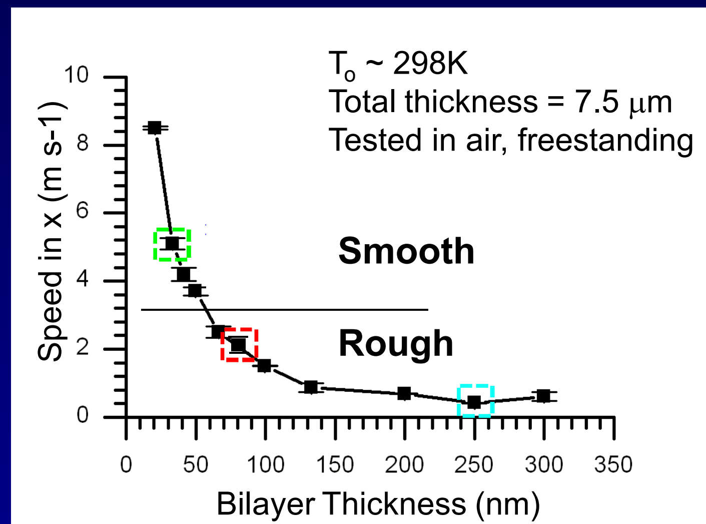
- Tests employ edge ignition.
- Position is characterized away from ignition zone (must be pre-determined).
- Measurements are made by high speed optical microscopy.
- Attribute the stable behavior to the high exothermicity, the enabled reaction kinetics, and the uniformity / purity of reactant layers.

Platinum/Aluminum

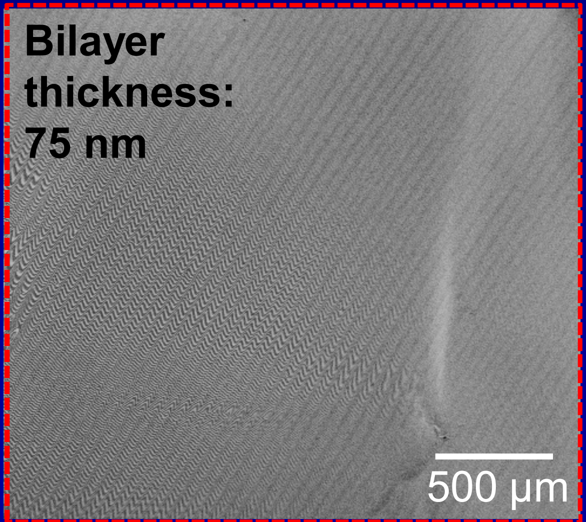


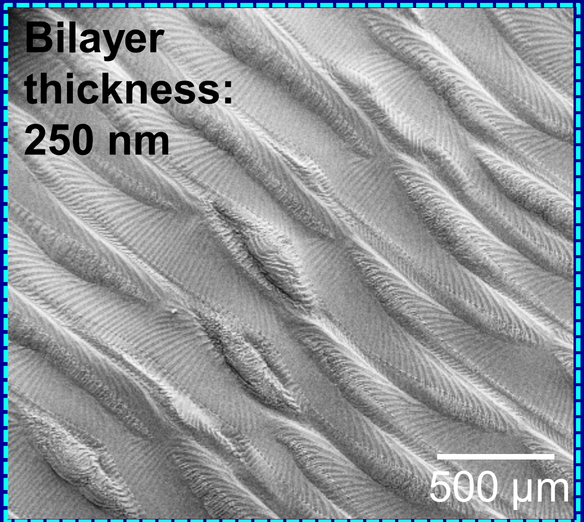
BL = bilayer

Co/Al multilayers exhibit stable and unstable propagating reactions depending on layer periodicity (which provides opportunity for study of stability criteria).



Final morphology





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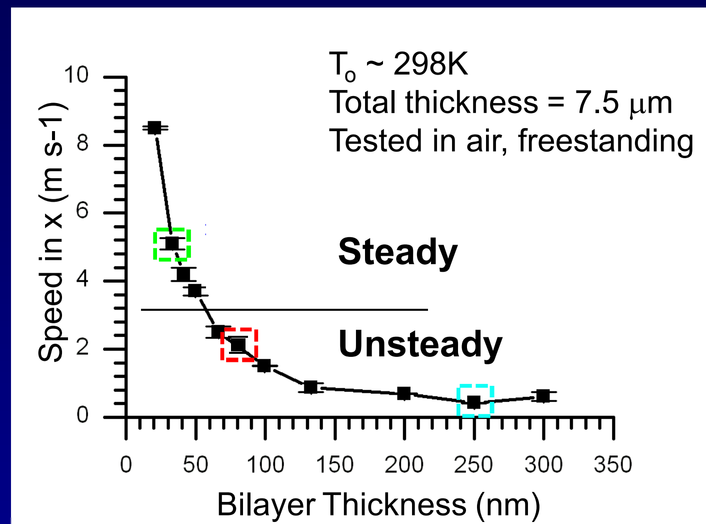
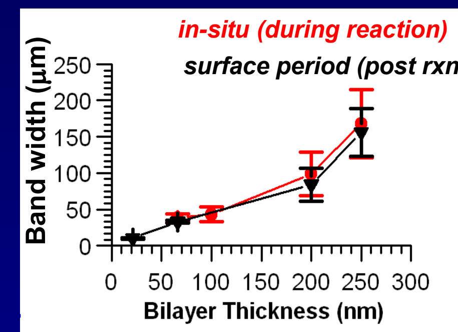
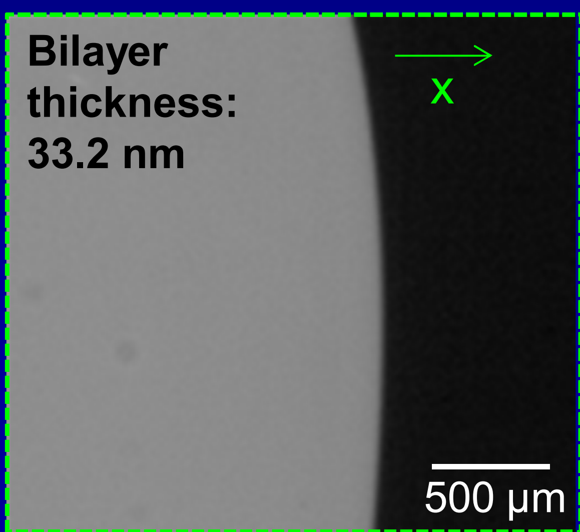
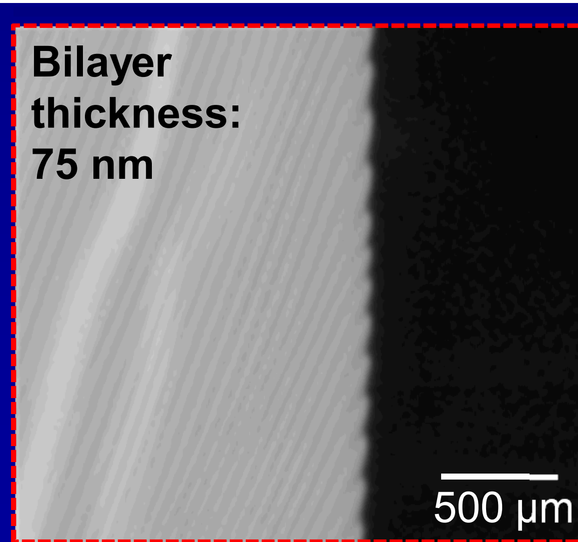
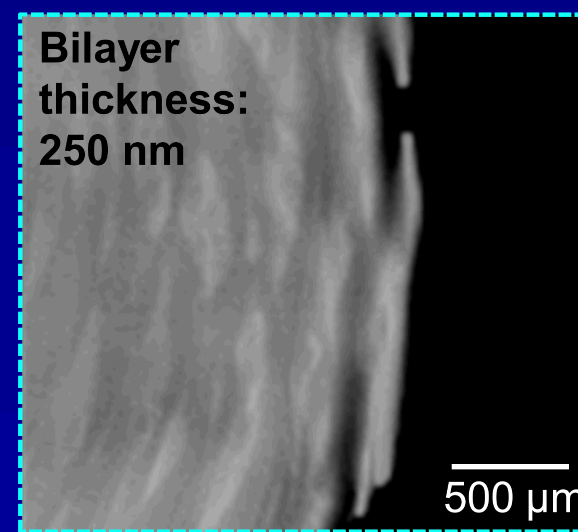




Wavefront morphology



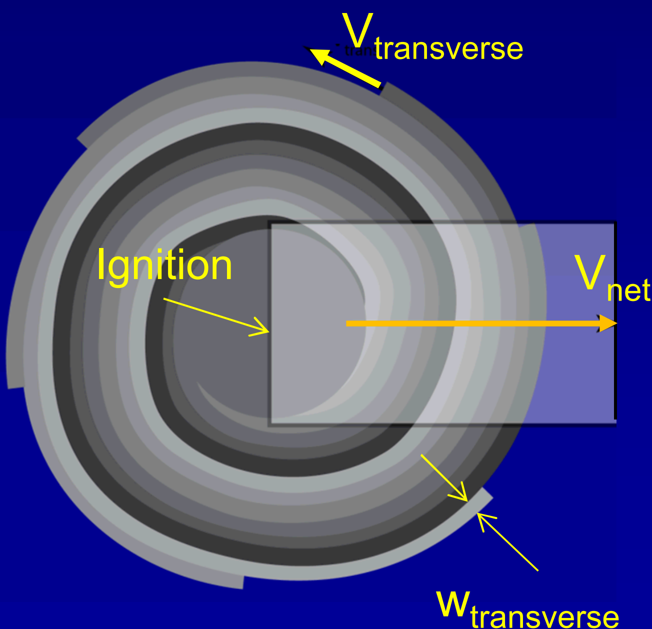




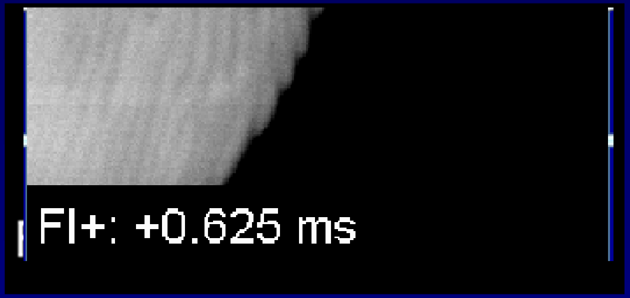
Large bilayer thickness Co/Al multilayers are characterized by 2-D (spin-like) instabilities.

- Stalled fronts in net forward direction.
- Propagation of narrow, transverse bands.

  - single direction (akin to classical spin combustion*)
  - opposing directions (akin to chain combustion*)

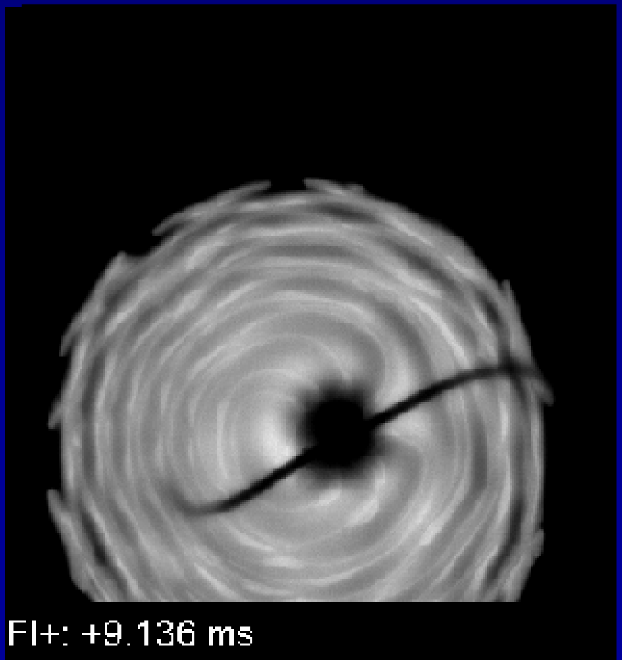


Cobalt/Aluminum (in plan view)



Bilayer: 66 nm

200 μm



Bilayer: 132 nm

1 mm

- A.S. Mukasyan, S.G. Vadchenko, I.O. Khomenko, Combustion Modes in the Ti-N System at Low Pressures. Combust. And Flame (1997).

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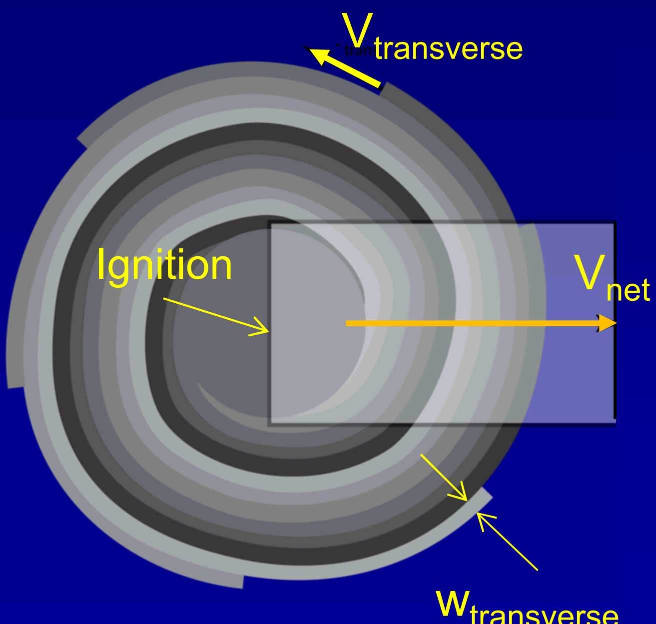
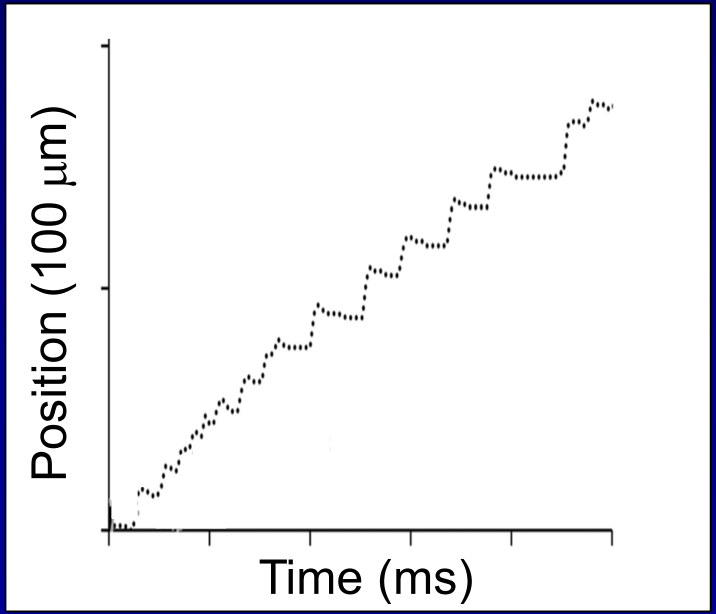


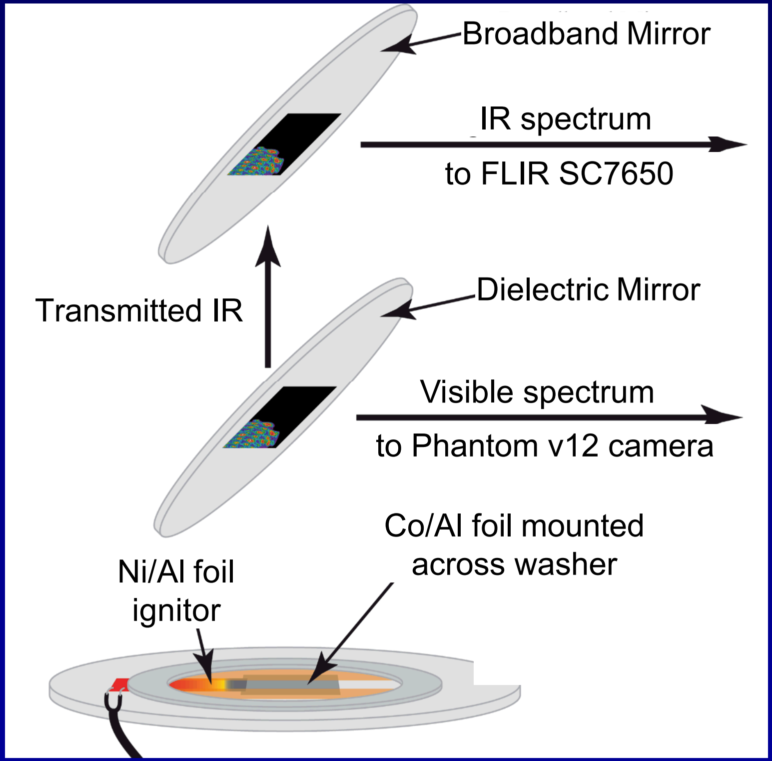


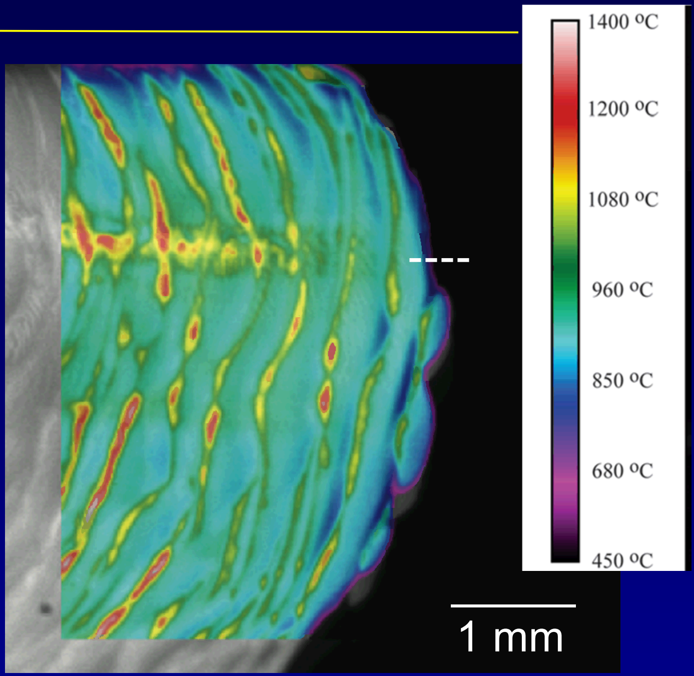
General position – time plot for unstable fronts

- A.S. Mukasyan, S.G. Vadchenko, I.O. Khomenko, Combustion Modes in the Ti-N System at Low Pressures. Combust. And Flame (1997).

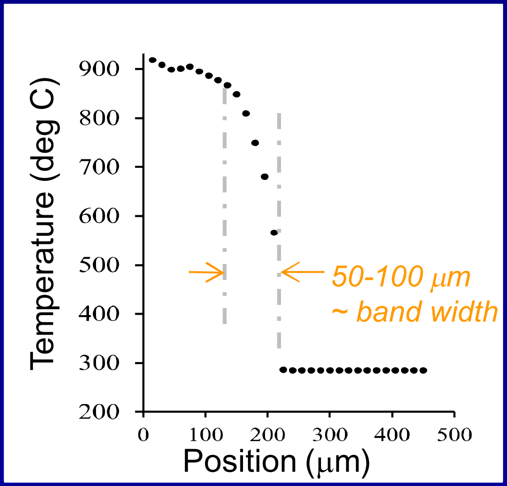
2-D instability is characterized by large temperature variations and chemical kinetics that vary over μm scale.

Coincident optical and thermal imaging of flame fronts (emissivity assumed = 0.04)



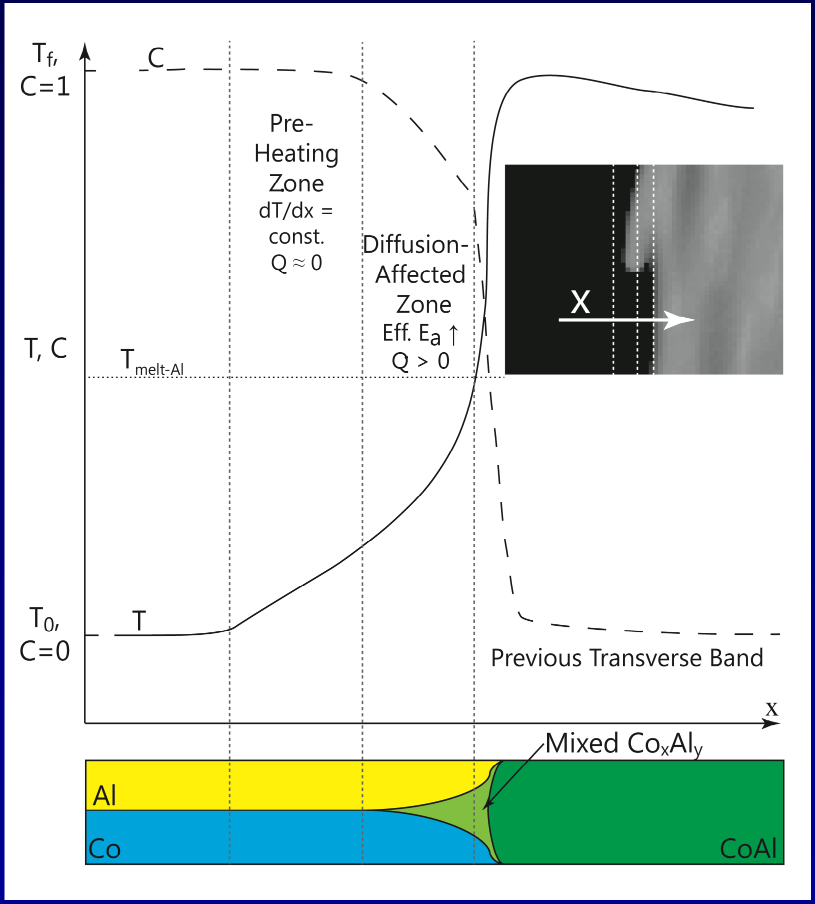


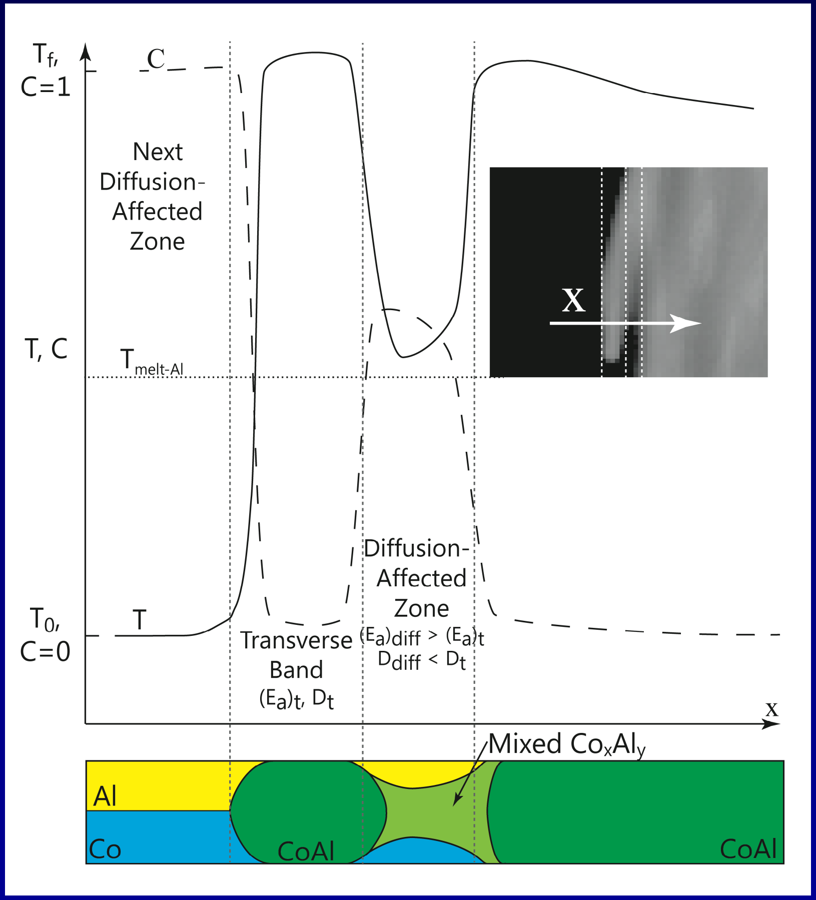
Temperature profile across dotted line drawn above



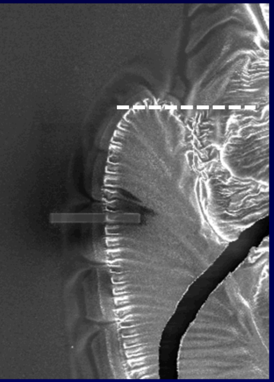
R.V. Reeves et al.,
J. Appl. Phys. 115 (2013).

Proposed mechanism for unstable propagation

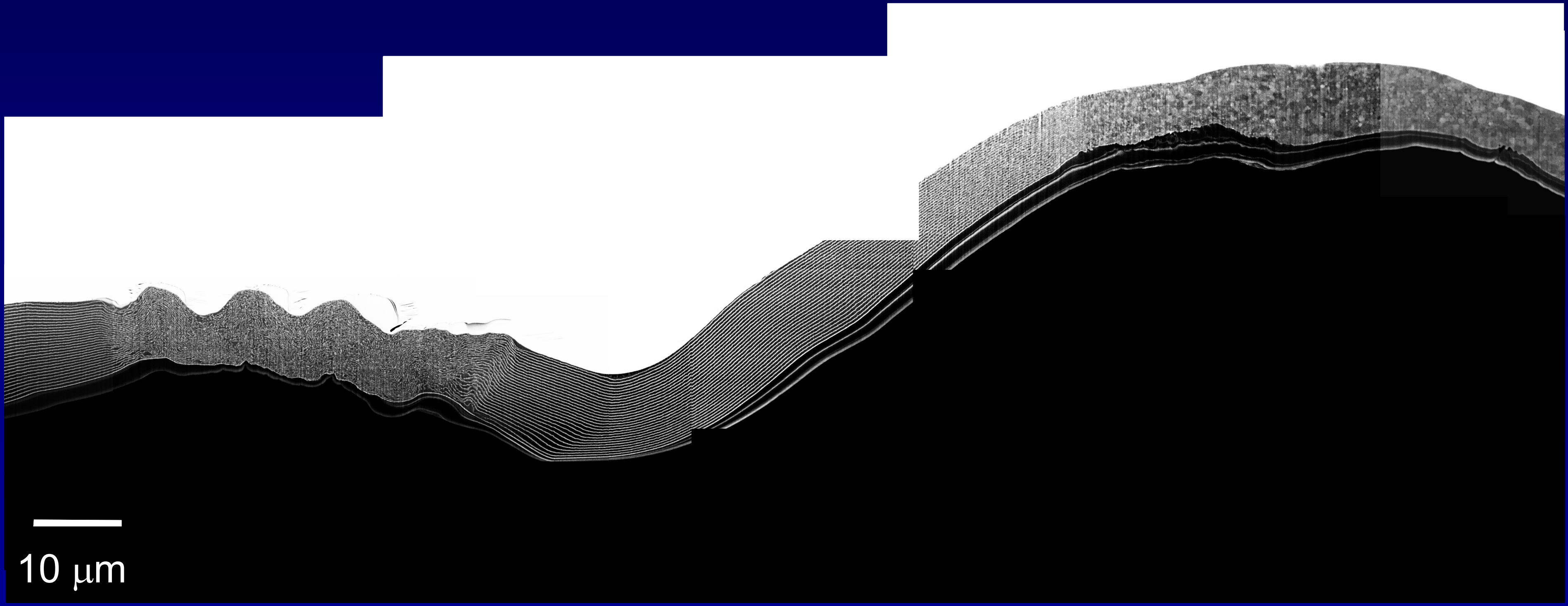




- Preheated, unreacted region hosts next transverse band
- Diffusion affected zone reacts more slowly, after transverse band passage
- Reaction behavior dependent on system kinetics and temperature history



Sectioned area of quenched specimen that exhibited 2-D instability



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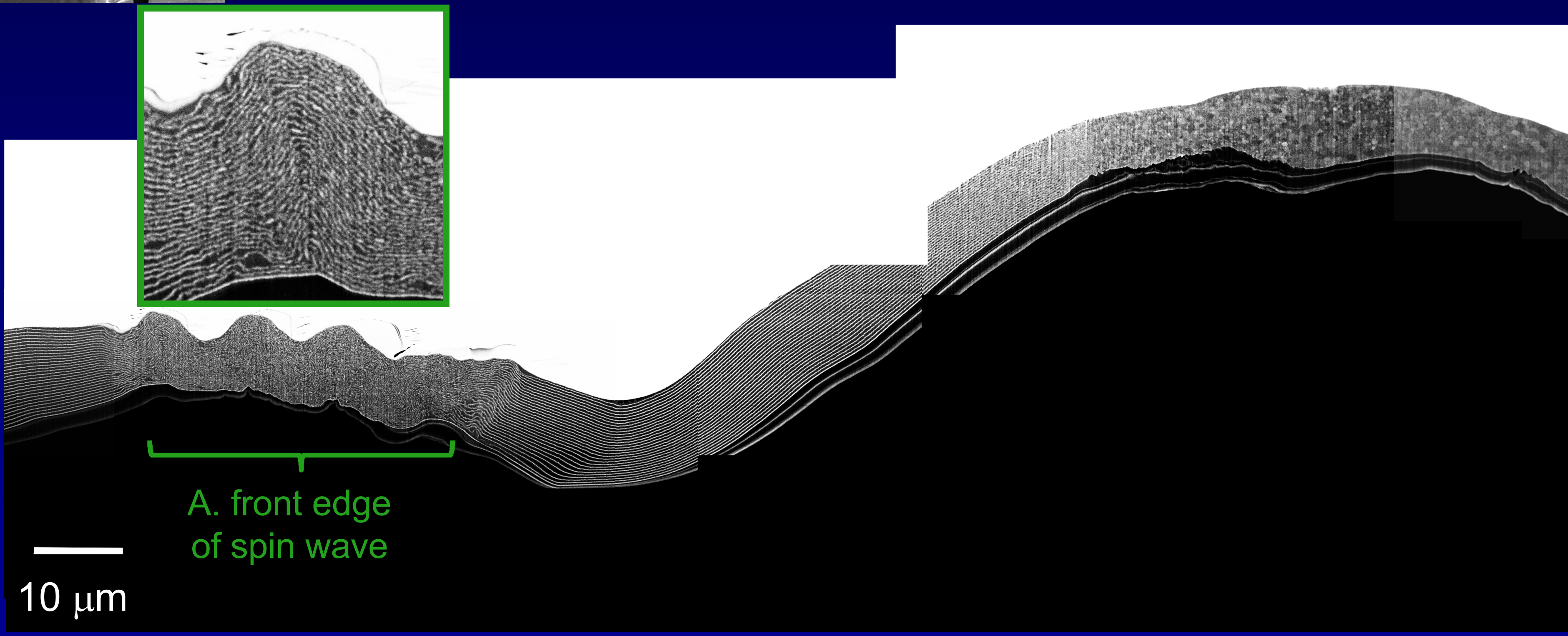
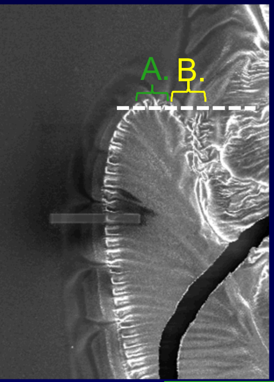
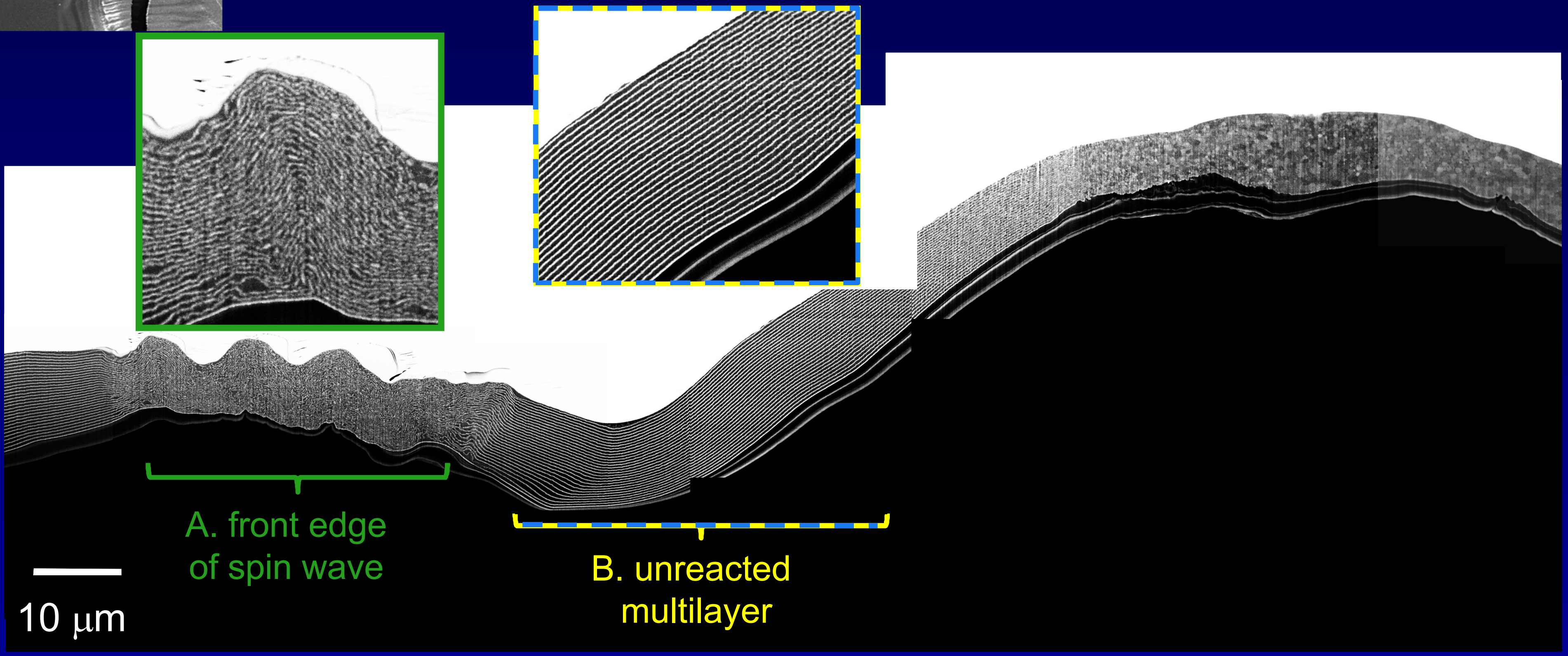
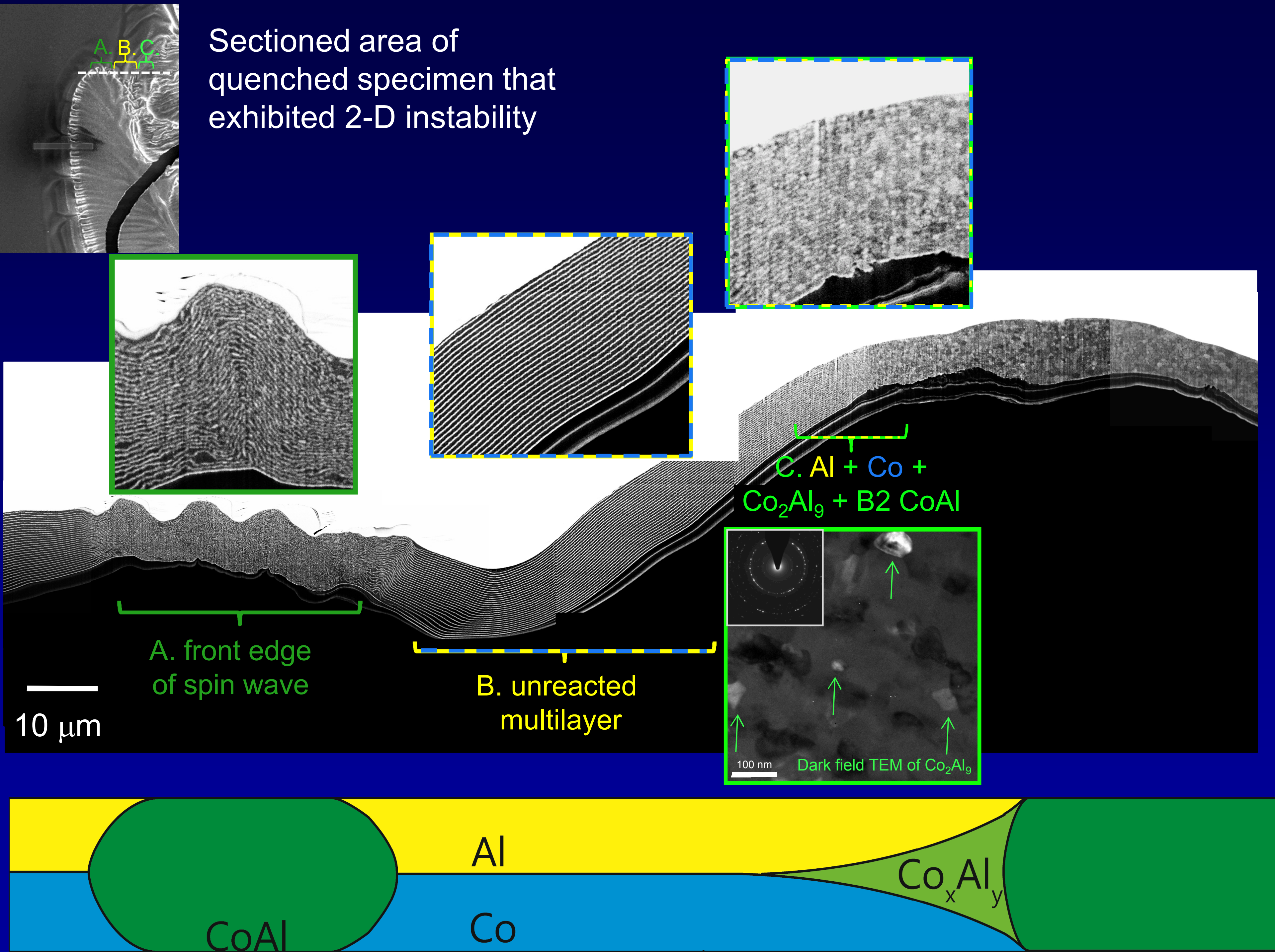
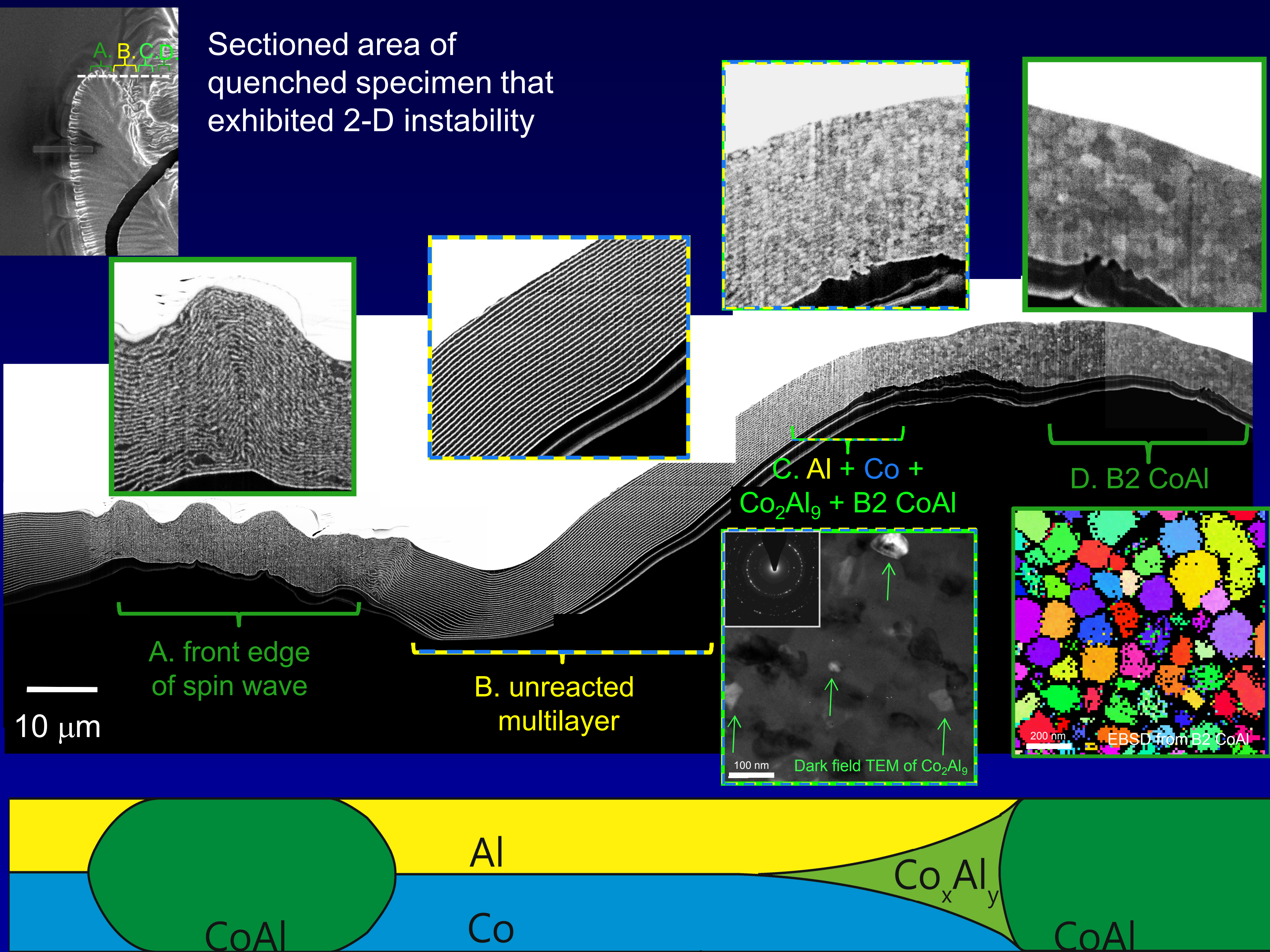




Sectioned area of quenched specimen that exhibited 2-D instability



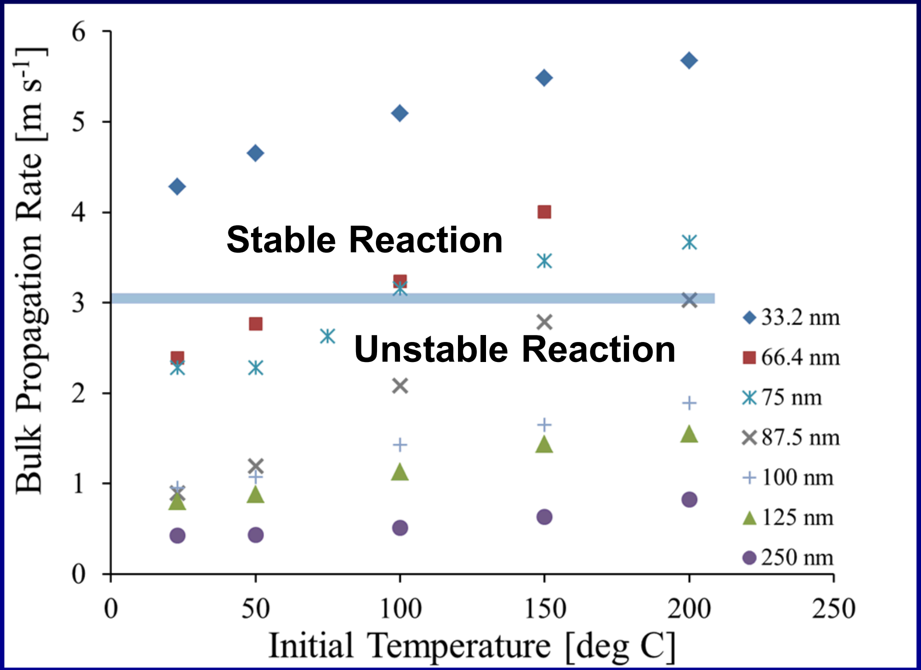

Sectioned area of quenched specimen that exhibited 2-D instability
A. B. C.
C. Al + Co + Co_2Al_9 + B2 CoAl
A. front edge of spin wave
B. unreacted multilayer
10 μm
100 nm
Dark field TEM of Co_2Al_9
Al
Co
CoAl
Co_xAl_y



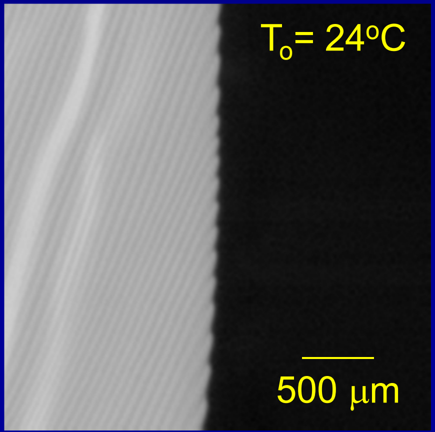
Sectioned area of quenched specimen that exhibited 2-D instability
A. B. C. D
A. front edge of spin wave
B. unreacted multilayer
C. Al + Co + Co_2Al_9 + B2 CoAl
D. B2 CoAl
10 µm
100 nm
Dark field TEM of Co_2Al_9
200 nm
EBSD from B2 CoAl
Al
Co
CoAl
Co_xAl_y
CoAl

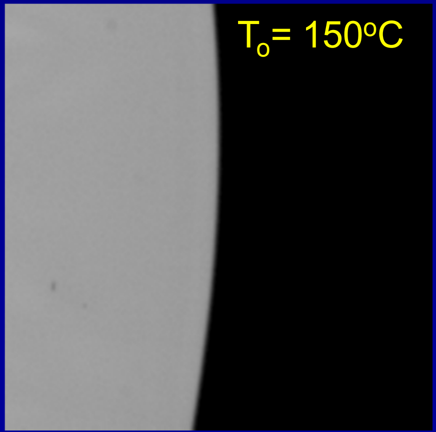
Preheat experiments demonstrate stability with increasing ambient temperature, T_o.

- Stable reaction fronts when bulk propagation speed is raised to > 3 m/s.
- At onset of stability, heat losses will be similar across designs.
- Suggests that a critical forward heat transfer rate defines the stability bndry.



R.V. Reeves, D.P. Adams
J. Appl. Phys. 115 (2013).

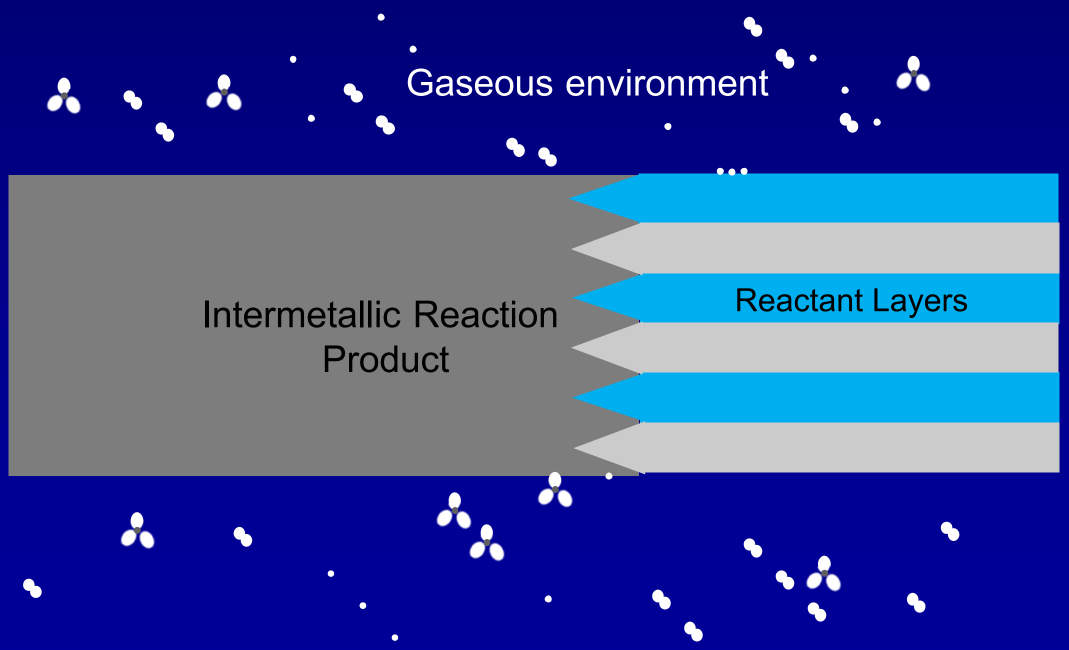




75 nm bilayer
Co/Al
Total thickness: 7.5 µm

Are self-propagating reactions in reactive multilayers affected by the surrounding gaseous environment?

If so, how?



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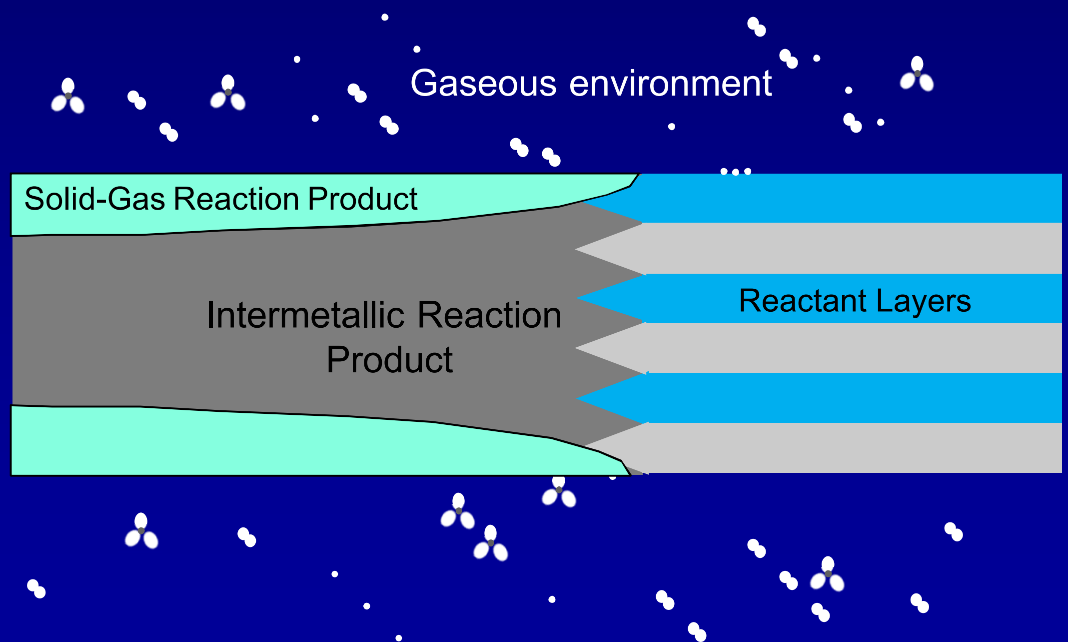
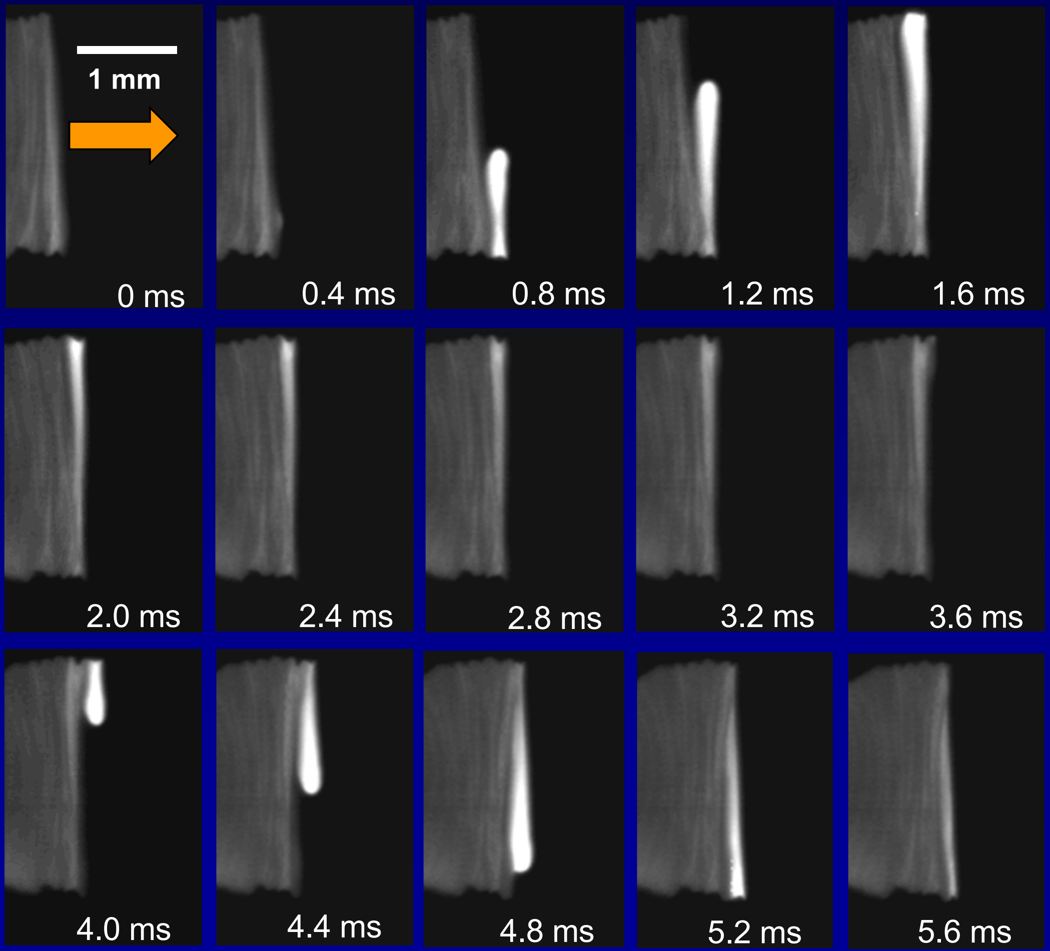


Ni/Ti exhibits a 2-D reaction front instability when reacted in vacuum.

- Transverse reaction bands nucleate at foil edges and, on occasion, at the point of intersection of colliding bands.
- Transverse band speed exceeds average propagation speed.
- Band widths are similar to those exhibited by Co/Al and other systems.

Nickel / Titanium



Plan view images

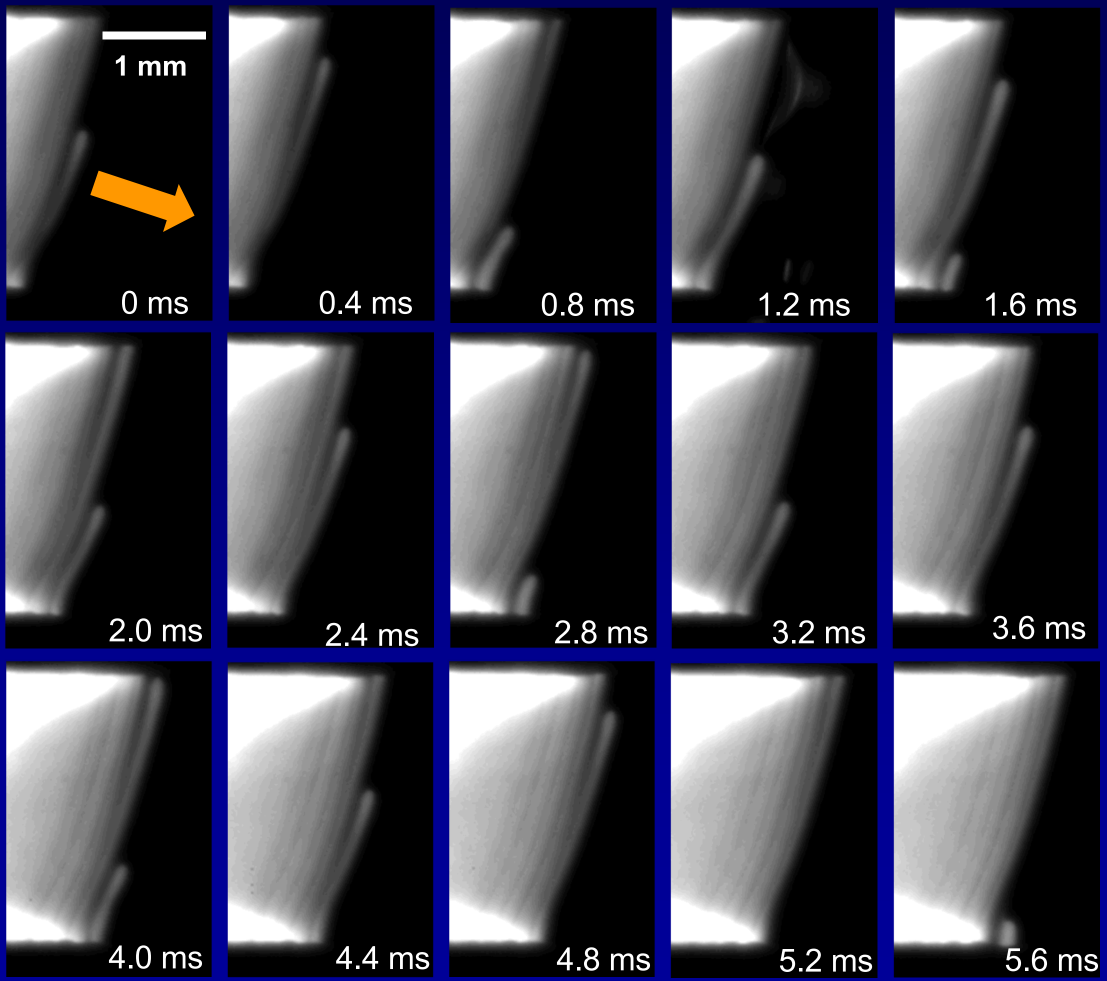
Bilayer thickness = 473 nm; Total thickness = ~ 5.0 μm
Ti capped (two sides); P = 300 mTorr

Ni/Ti exhibits a 2-D reaction front instability and undergoes secondary combustion when reacted in air.

- Similar to reactions in vacuum, reaction bands propagate transversely.
- A second reaction ‘wave appears behind the intermetallic reaction front.
- Second reaction front is faster along the edges of foils.

Plan view images

Nickel / Titanium

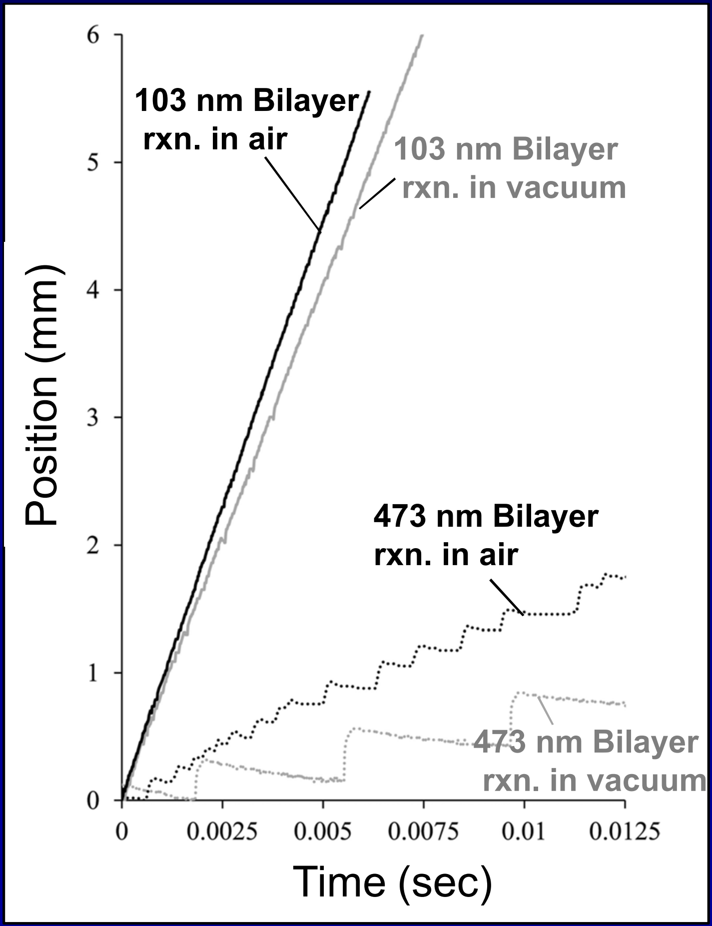


Bilayer thickness = 473 nm; Total thickness = ~ 5.0 μm
Ti capped (two sides); P = 670 mTorr air

Experiments reveal how air increases the average propagation speed of Ni/Ti multilayers.

- Frequency of transverse bands is increased when air is present.
- Air does not change the transverse band speed in Ni/Ti.
- The nucleation rate of transverse reaction bands at foil edges is increased when oxygen is present and is responsible for increased net speed (in forward direction).

Nickel/Titanium



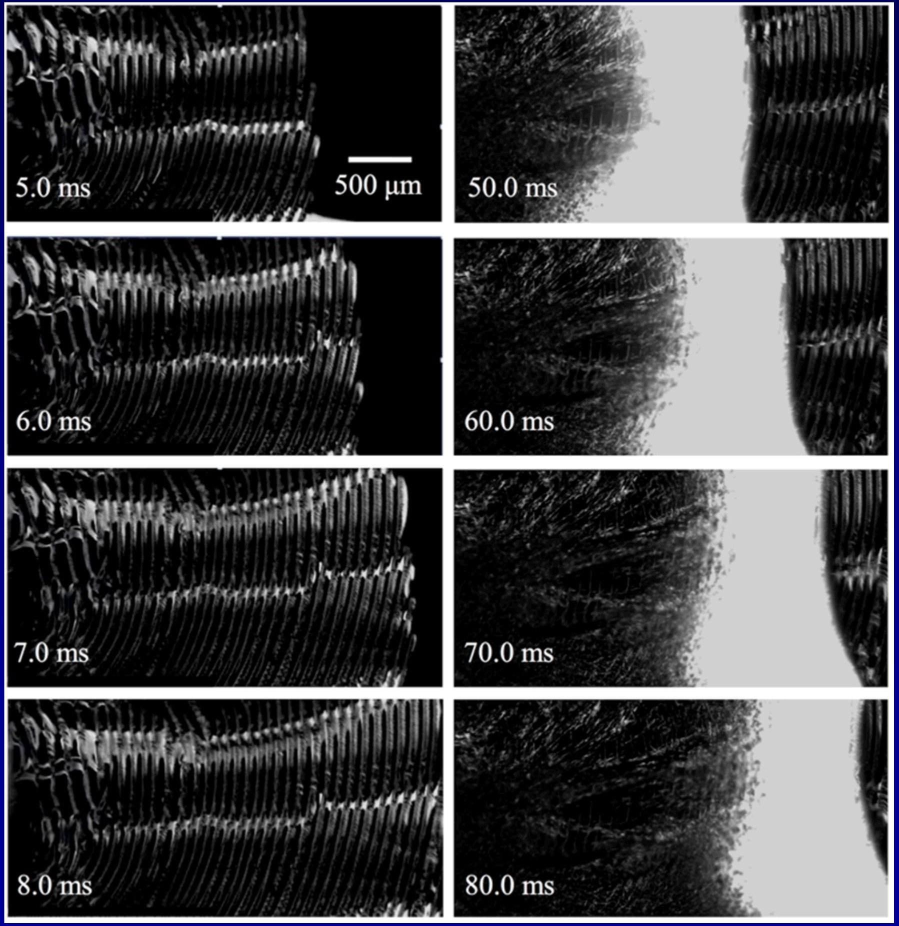
Total thickness = 5.0 μm
Ti capped both sides

D.P. Adams, 6/14

Some systems exhibit a fast intermetallic wave and a slow, subsequent self-propagating oxidation wave.

- Intermetallic formation reaction moves at v_{net} ~ 0.9 m/s and exhibits a 2-D instability.
- Oxidation wave trails intermetallic with v = 0.036 ± 0.012 m/s.
- Oxidation wave disturbs the initial periodic morphology produced by propagating intermetallic bands.
- Oxidation wave is stable.

Scandium/Copper



Bilayer thickness: 41 nm
Total thickness = 2.5 μm.

Summary

- Sputter-deposition provides the required level of control (purity, density, composition, interfacial area) for scientific study and applications.

- Ignition sensitivity and wavefront speed can be tailored via multilayer design.

- Highly exothermic reactive multilayers exhibit stable reactions, but multilayers having low or moderate ΔH_o exhibit unstable modes.

- 2-D instabilities are prevalent in low exothermicity bimetallic multilayers (includes Ni/Al, Co/Al, Ni/Ti, Sc/Ag.

- We suggest that a critical forward heat transfer rate defines the stability boundary for 2-D (spin) behaviors in reactive multilayers.

- Many bimetallic multilayers exhibit secondary combustion reactions when reacted in air and this leads to a mixture of intermetallic and oxide products.