SAND2012-3398C

Reactive multilayers grown by sputter deposition

D.P. Adams
Sandia National Laboratories
Albuquerque, NM

<u>Sandia collaborators:</u>
R. Reeves, E.D. Jones Jr., J.P. McDonald†,
M. Rodriguez, M. Hobbs, V.C. Hodges

ICMCTF – AVS (San Diego)
April 26, 2012

† Currently at Dow Corning, Midland, MI

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

Sandia National Laboratories

Outline for presentation

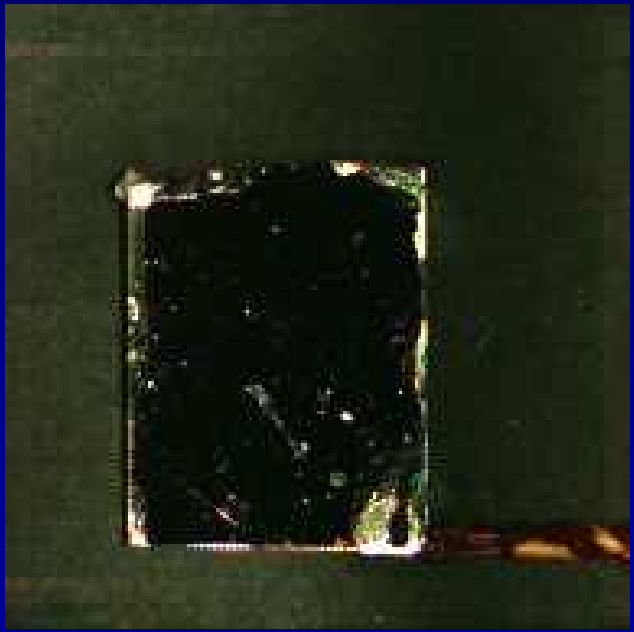
I. AVS-specific: advantages and challenges associated with sputter-deposition of reactive multilayers

II. Recent studies of

a. Ignition (our method: laser irradiation)

b. Reaction front instabilities

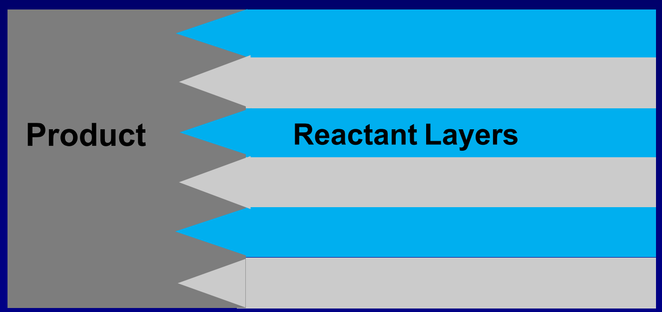
c. Effects of surrounding gaseous environment on speed, phase formation and more



1 cm

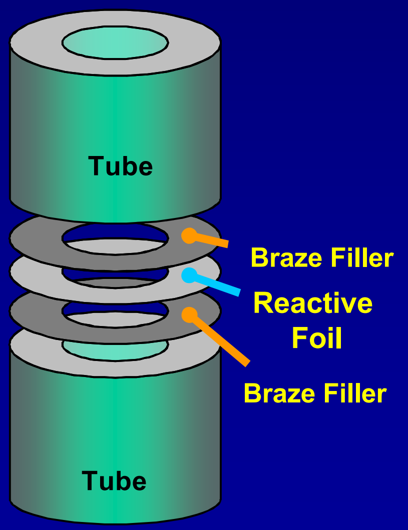
Reactive multilayers are useful for applications requiring confined heat (e.g., joining)

Depiction in cross section



__Applications:__

Joining, soldering,
Lid seal, MEMS.



__Key Properties:__

Stored chemical energy
Ignition at a point
Self-propagating Synthesis
Structure and Morphology **post**

__Early work on multilayers:__

Prentice US Patent 4,158,084 (1979).
Floro J. Vac. Sci. Tech. A (1986).
Makowiecki US Pat. 5,381,944 (1995).
Barbee, Weihs US Pat. 5,547,715 (1996).

__Even earlier work on monolithics:__

Wickersham, Greene, JVST A 1985.
Coffin, Proc. R. Soc. 1934.

Several vapor deposition techniques (evaporation, sputtering) have been used in the past to fabricate reactive multilayers.

- Typical design (not requirements):
  - Two reactant species
  - Single, out of plane periodicity
  - 2-1,000 reactant layers
  - Total thickness: 0.25-150 μm

- Reactant pairs generally have a large heat of reaction, ΔH_o:

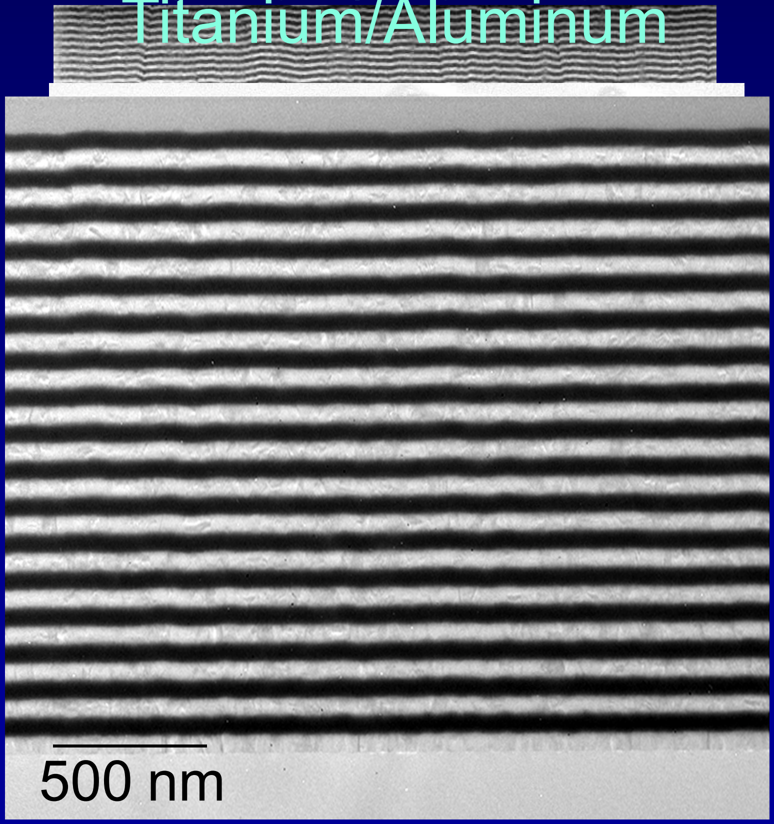
Ti/2B	:	- 4.8 kJ/g	compare: TNT ΔH_o = - 4.18 kJ/g
Al/NiO	:	- 2.2 kJ/g	
Ni/Al	:	- 1.4 kJ/g	
Al/Pt	:	- 0.9 kJ/g	
Ni/Ti	:	- 0.6 kJ/g	

- Reference previous work (multilayers)
  - Prentice US Patent (1979).
  - Floro J. Vac. Sci. Tech. A (1986).
  - Makowiecki US Pat. (1995).
  - Barbee, Weihs US Pat. (1996).

Nickel/Titanium

Platinum/Aluminum

Titanium/Aluminum

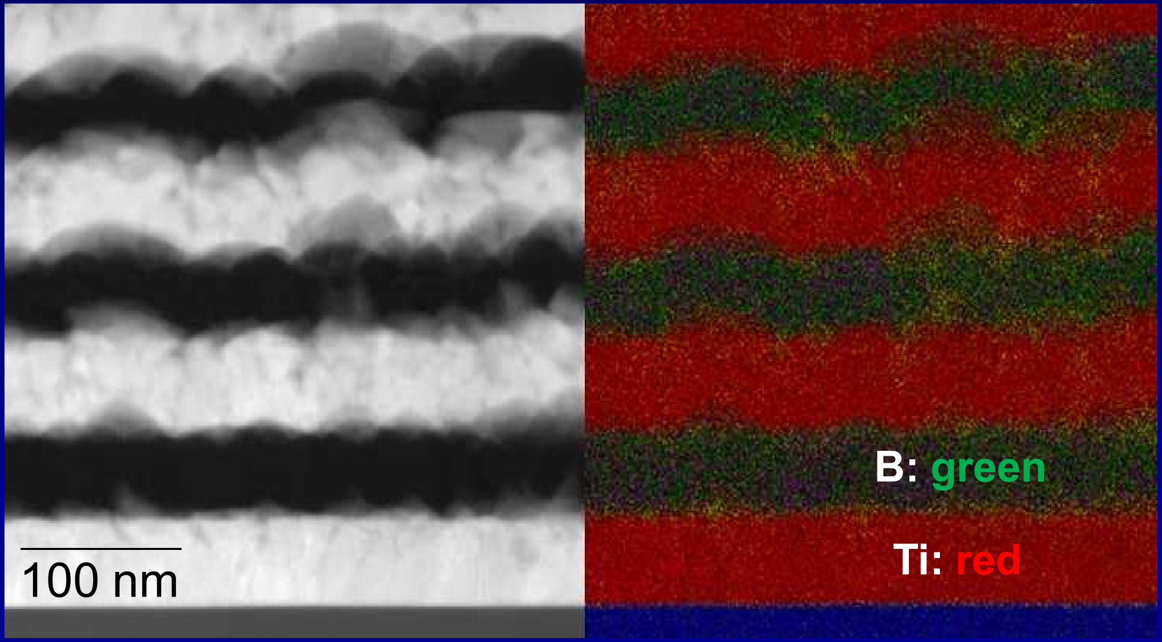


Multilayers in XS by TEM

We use sputter deposition to control thickness, number of layers and composition.

- Accuracy: Individual layer thickness control ~10 Å.
- Composition tailored by design (layer thicknesses) once reactant densities known.
- Must ensure that changes in calibration during a lengthy deposition are negligible.
- Surface roughness evolves.
- Composition is generally improved compared with compacted powders but not as good as MBE-grown films.

Example Ti/2B multilayer grown by sputter deposition

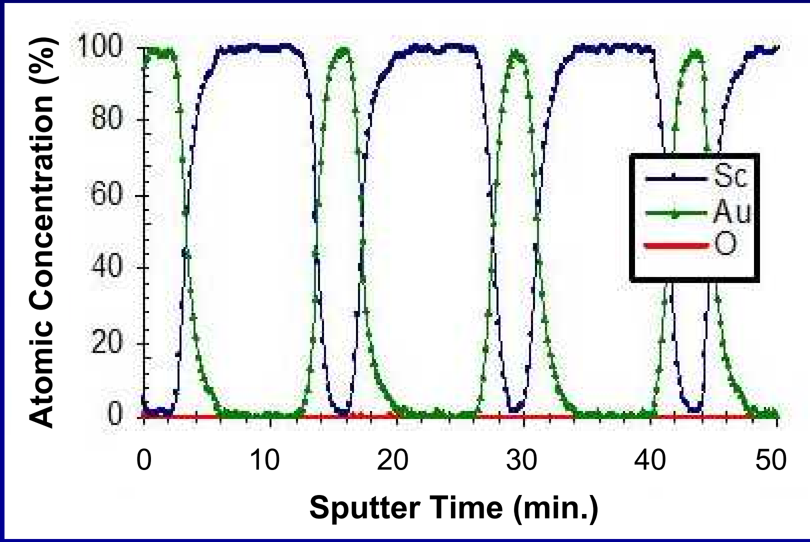


Trace O: yellow

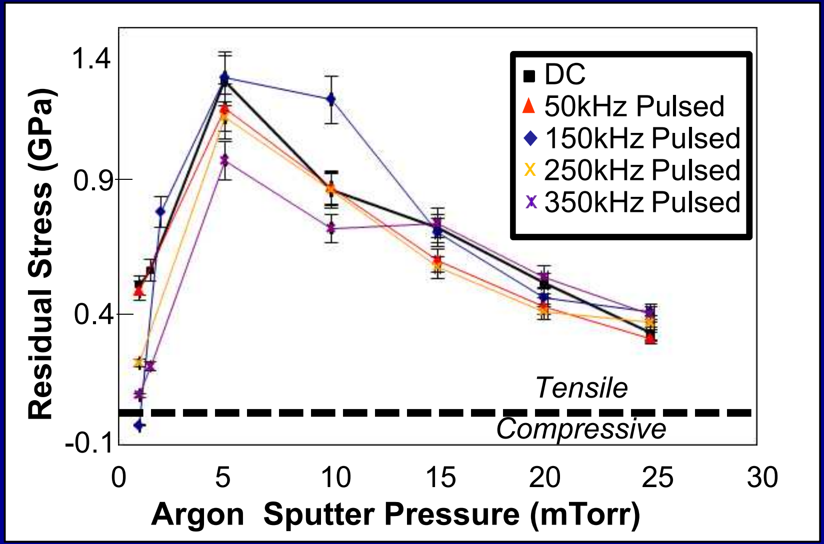
Images generated using an aberration-corrected STEM (Titan G2 80-200) having a windowless Si drift detector array.

With effort, sputter deposition can achieve the desired purity and residual stress.

Purity evaluated by Auger electron spectroscopy



Residual Stress evaluated by wafer curvature techniques

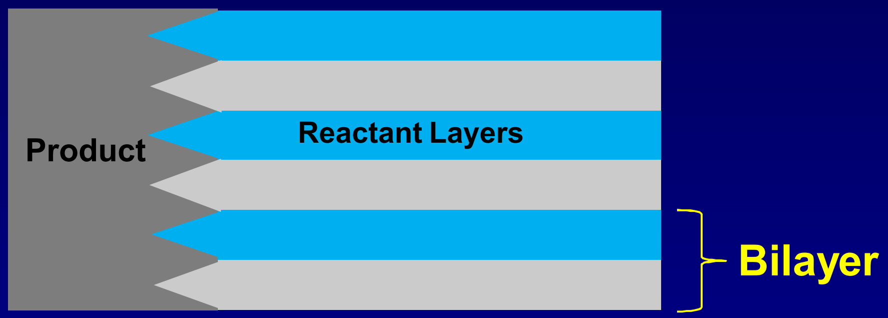


Challenges come with depositing reactant layers that have a propensity to oxidize and to develop large residual stress.

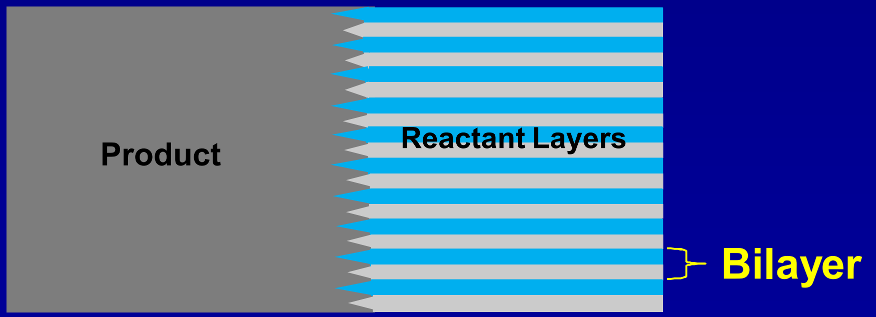
The bilayer thickness is often varied (from film-to-film) to study ignition sensitivity and reaction kinetics.

- Bilayer thickness is the combined thickness of 1 reactant layer A and 1 reactant layer B.
- This dimension is generally considered to be 2X the effective diffusion length for mixing.
- Bilayer thickness affects heat release rate.
- There is a limiting factor for ultra-thin layers …..

Slow release rate

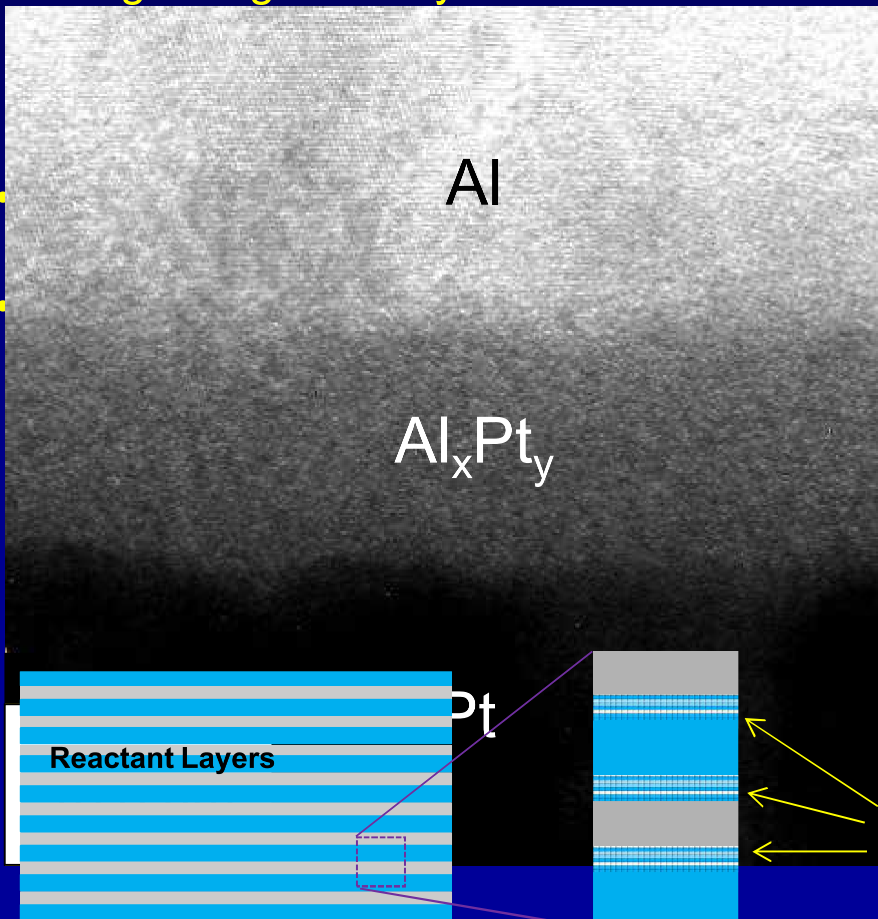


Fast release rate

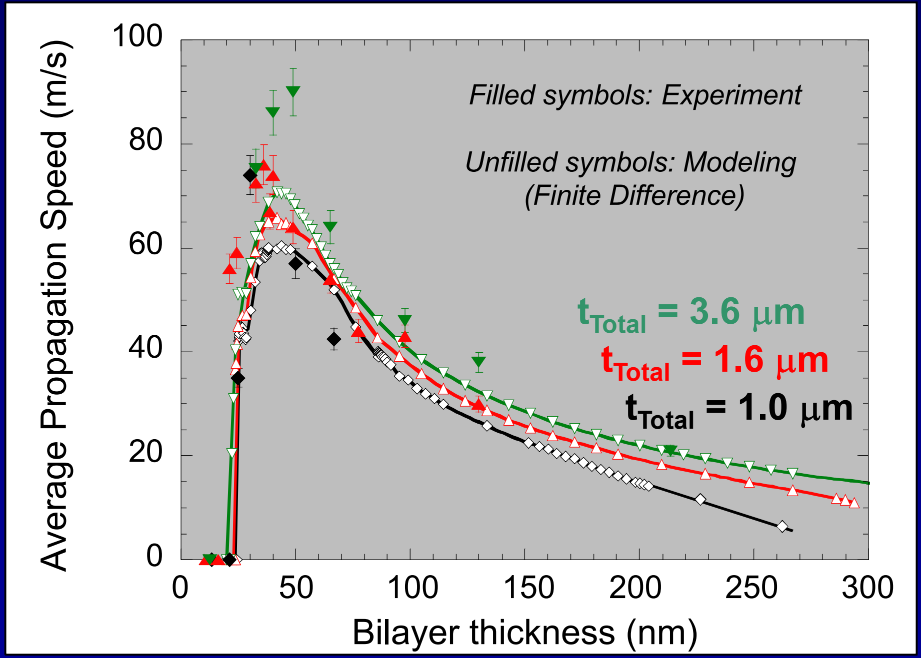


The general relationship between propagation speed and bilayer thickness is well established (through expt. and modeling).

- Large range of bilayer thickness in



Ex. Aluminum/Platinum on SiO_2



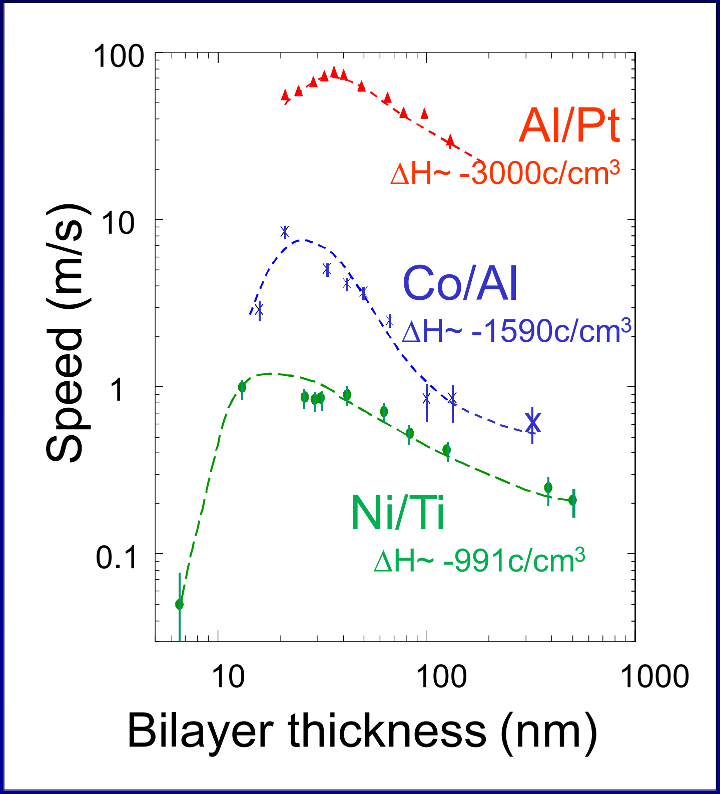
M. Hobbs, D.P. Adams, et al. 8th World Congress Comp. Mech. (2008).

Propagation speeds vary with bilayer thickness and with material system.

Average self-sustained speeds (in air)

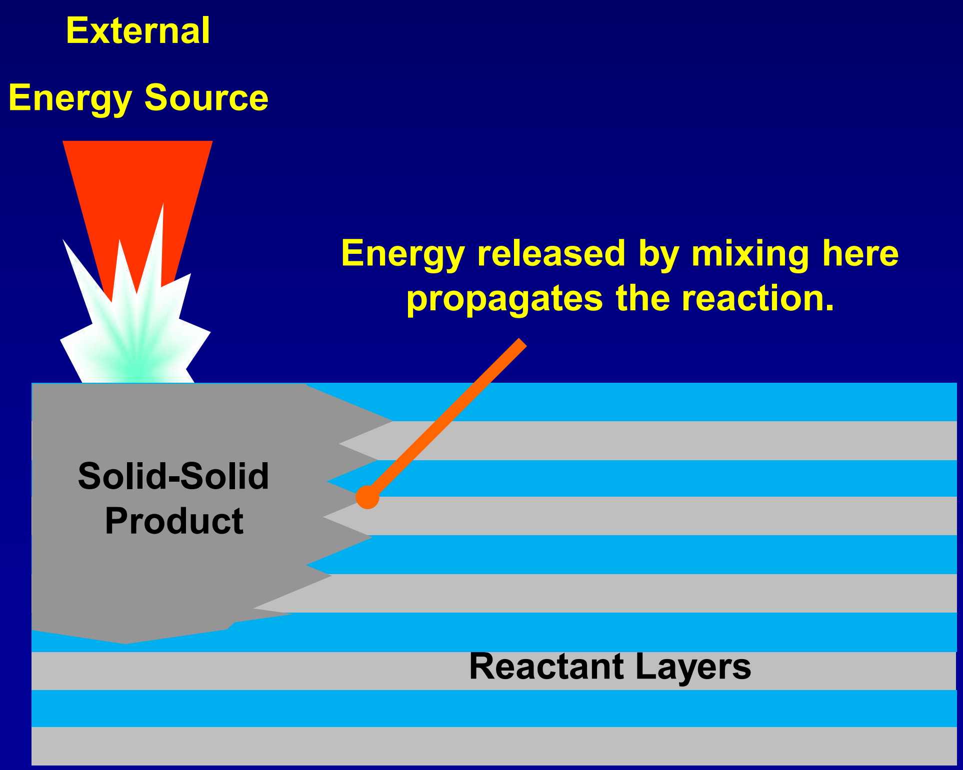
- The same general relationship between speed and bilayer thickness is found for different bi-metallic pairs.
- Speeds vary across a large range from ~0.1 to ~90 m/s (deflagration).
- Differences (between materials) are explained by heat release rate and this is affected by:

  heat of formation (ΔH)
  mass transport
  thermal transport



Y. Picard, J. P. McDonald, D.P. Adams, S. Yalisove Appl. Phys. Lett. 93 (2008).

What does it take to ignite various nanolaminates at a point?

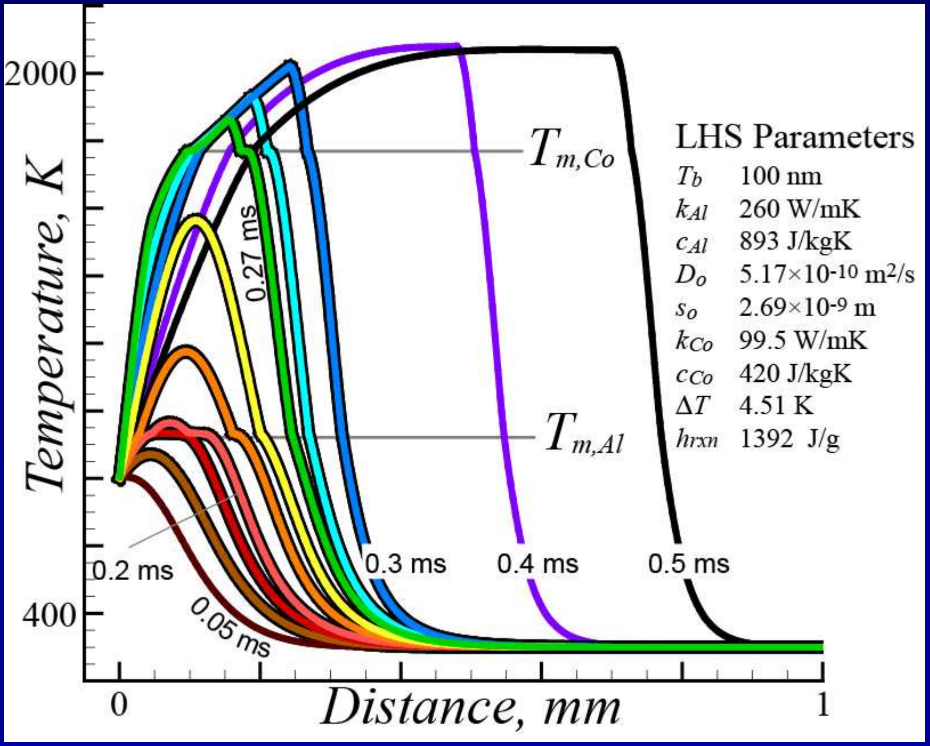


Ignition involves the rapid excitation of a volume of multilayer material such that a self-sustained reaction occurs to completion.

- Ignition involves an external energy source (light, heat, mechanical).
- Multilayers exhibit point ignition and global excitation.
- Material are mixed and raised to a high temperature quickly before energy dissipates away as heat.
- Models show:
  importance of T - dependent properties,
  a role of latent heat of melting, and
  effect of bilayer thickness

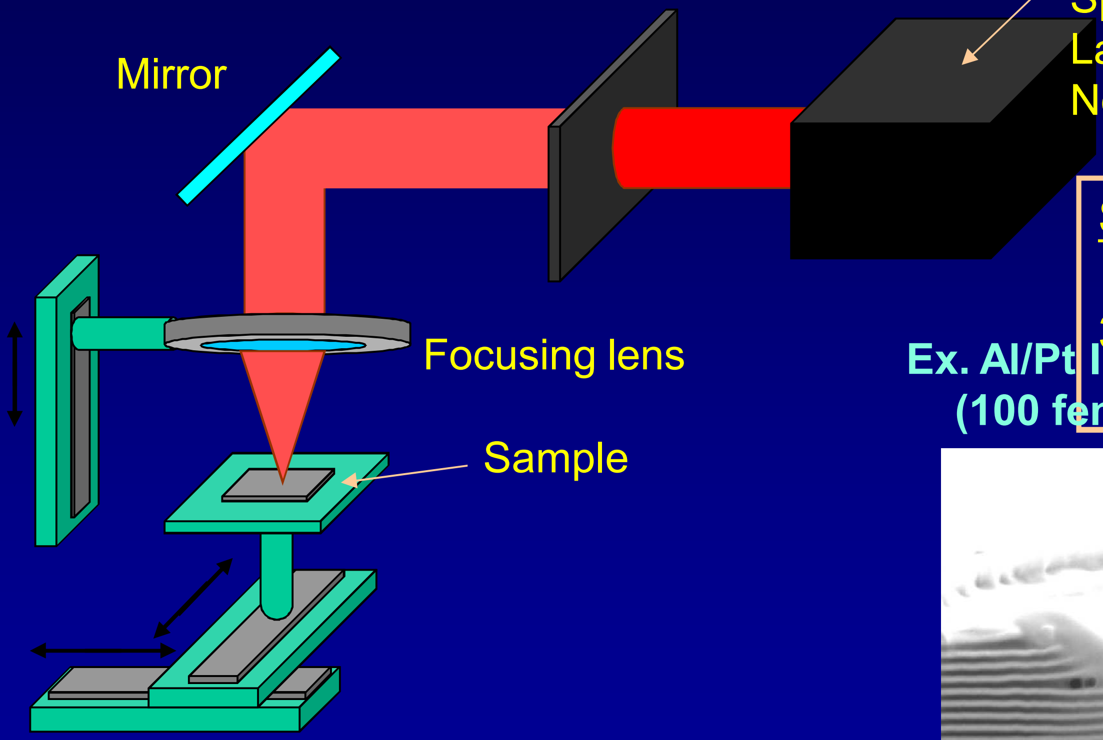
Ex. Finite difference modeling of Cobalt/Aluminum, edge ignition

Color lines are time steps.



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

Experimental schematic: quantifying point ignition thresholds



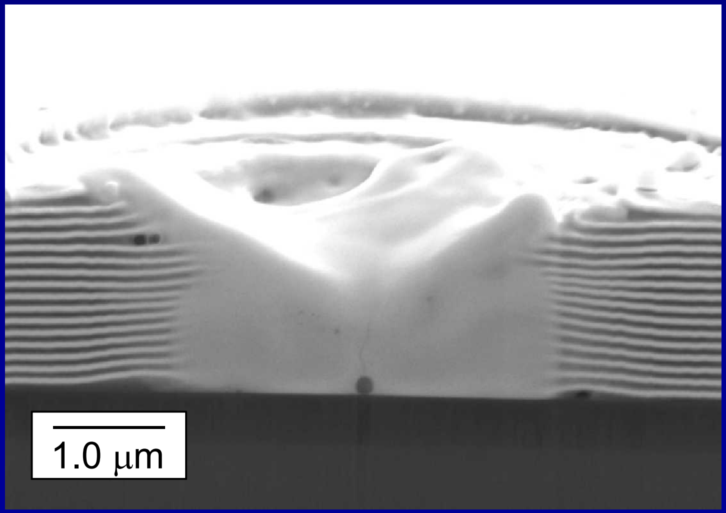
Laser systems:

Spectra-Physics Hurricane - Ti:sapphire
Lambda Physik LPX-300 – KrF Excimer
Northrup Grumman – Diode fiber

Single pulse laser ignition

150 fs, 1 ps, 30 ns; 800 nm
30 ns; 248 nm
1 ds – 10 µs; 808 nm.

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



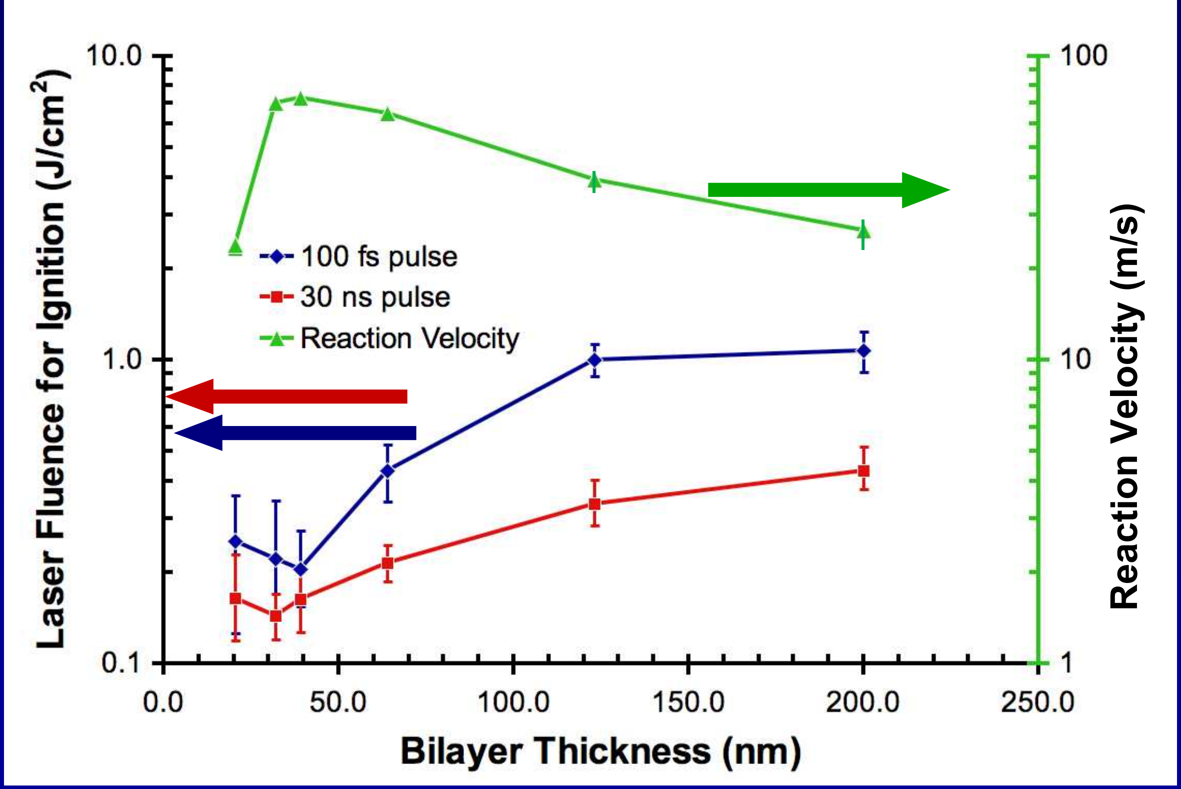
Cross section SEM (sectioned by focused ion beam)

Laser induced ignition show effects of multilayer design that mirror the propagation speed.

Example: Single pulse, ignition of Al/Pt using Ti:sapphire laser; 800 nm; ns and fs

- Thresholds are dependent on design (bilayer thickness).
- Threshold increases with bilayer thickness for a large range of this dimension.
- Fine bilayer designs are affected by premixed reactants.

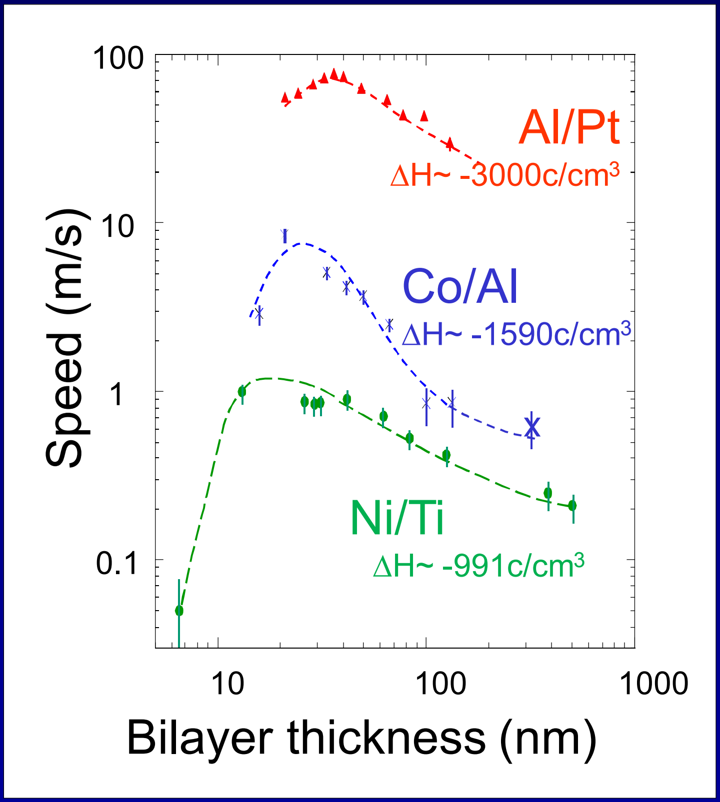
Similar trends are found for ignition temperature (global heating).



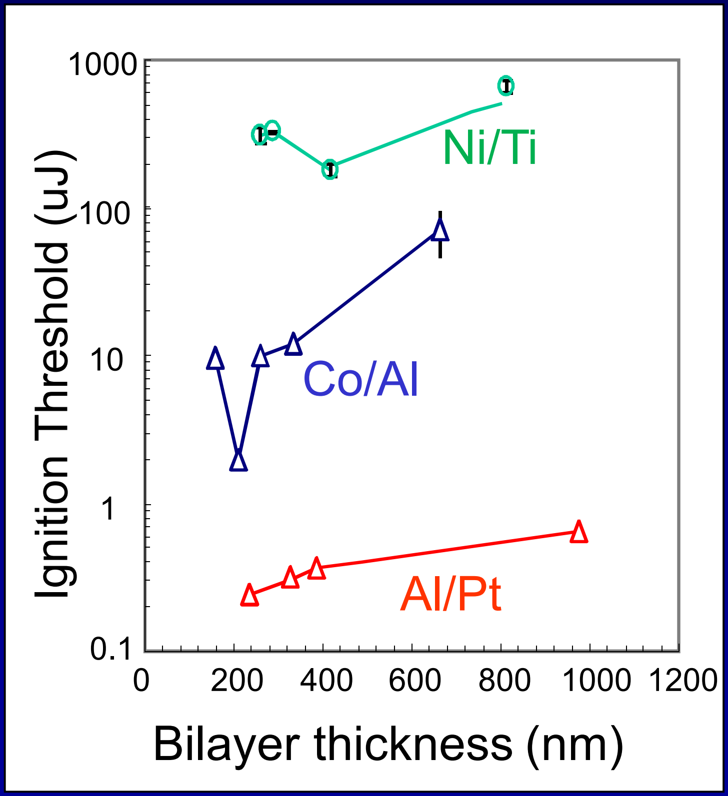
J. P. McDonald, D.P. Adams, Mat. Res. Soc. Symp. Proc. (2008).

Propagation speeds and ignition thresholds vary with bilayer thickness and material system.

Average self-sustained speeds (in air)



Single 30 nsec laser pulse ignition thresholds (in air)

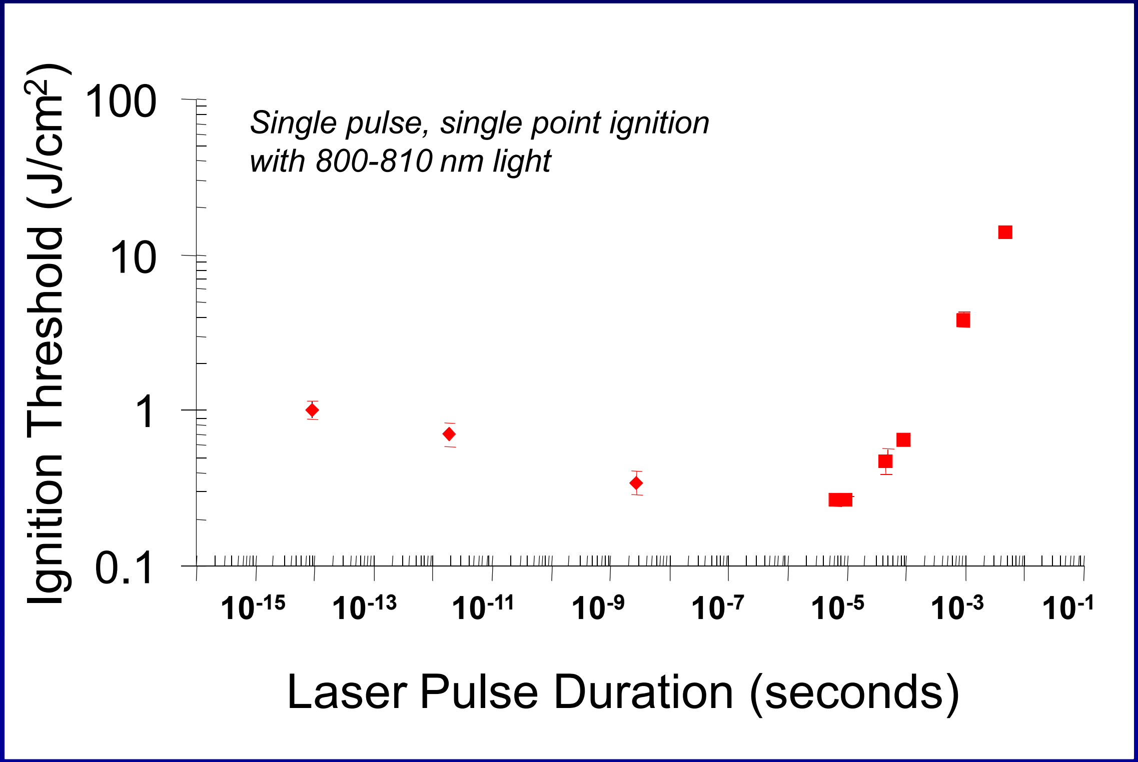


Y. Picard, J. P. McDonald, D.P. Adams, S. Yalisove Appl. Phys. Lett. 93 (2008).

Laser induced ignition: Effects of pulse duration

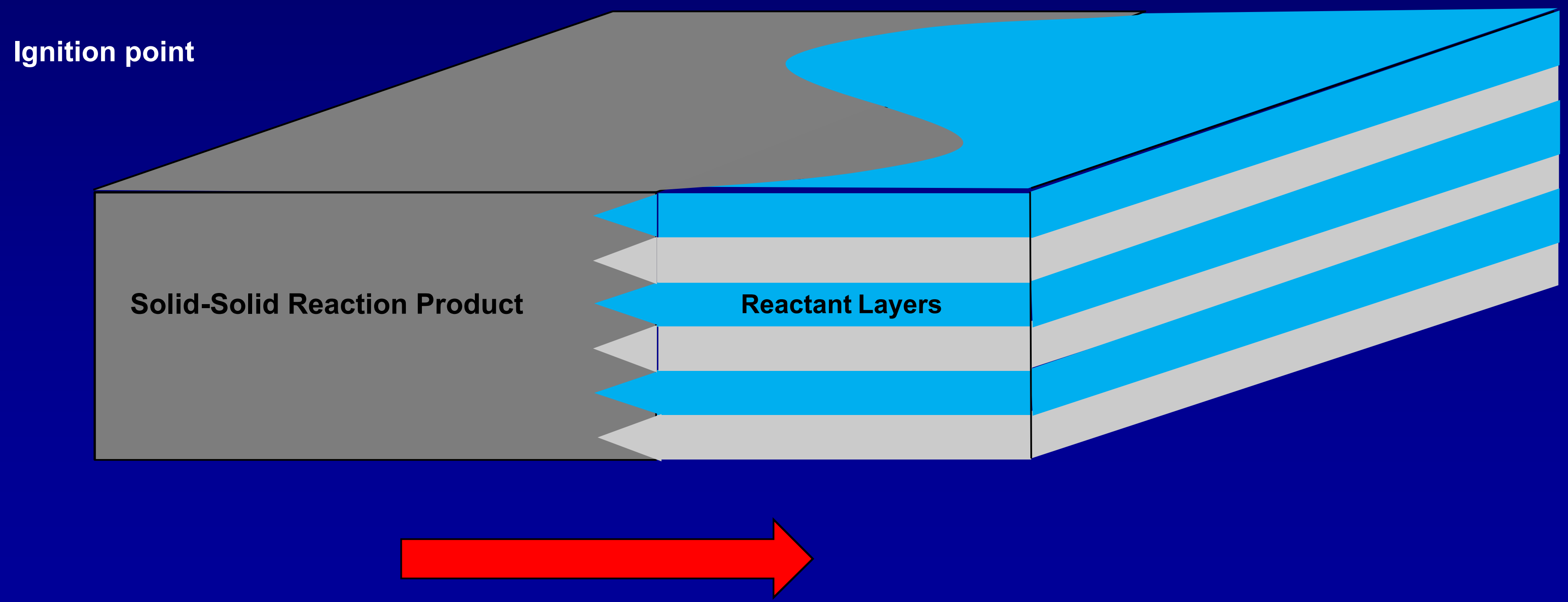
- Reduced thresholds for ignition when decreasing pulse duration from ds to ms to μs.
- Increased threshold when using ns, ps, fs light.
- Effects in the short and ultra-short domain are likely due to ablation, reduced heat affected depth and/or reflectivity differences.

Ex. Aluminum/Platinum
Fixed Bilayer thickness = 123 nm



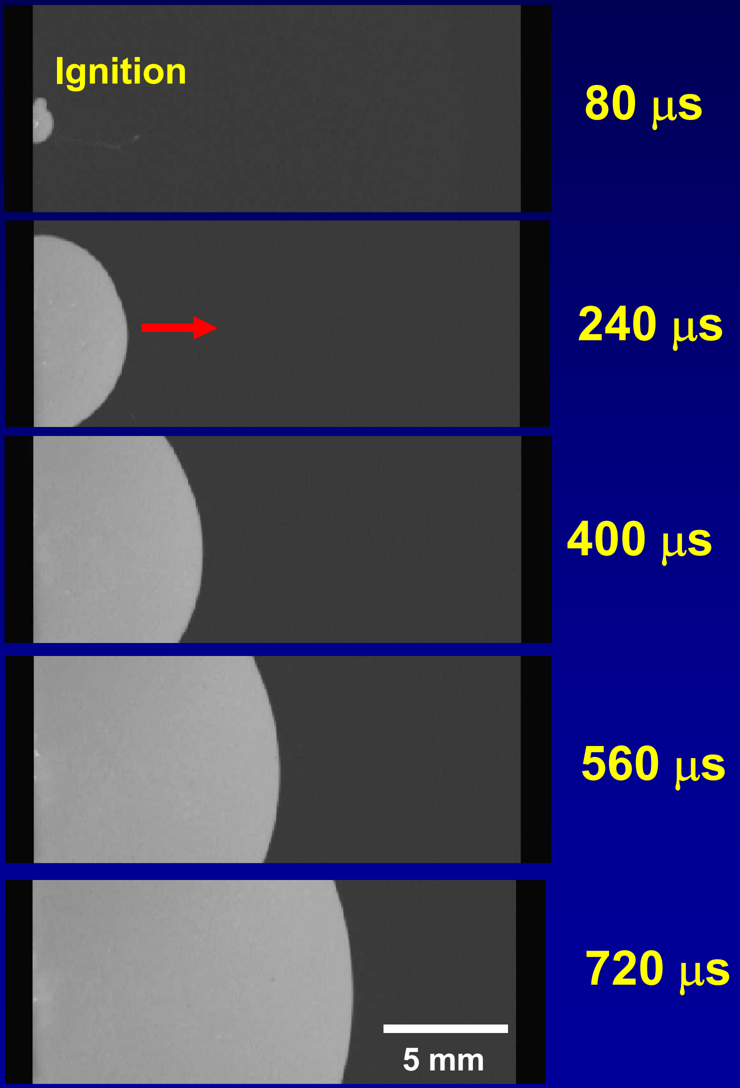
How do reactions propagate at the microscale?

post ignition



Many exothermic multilayer systems exhibit a stable reaction front.

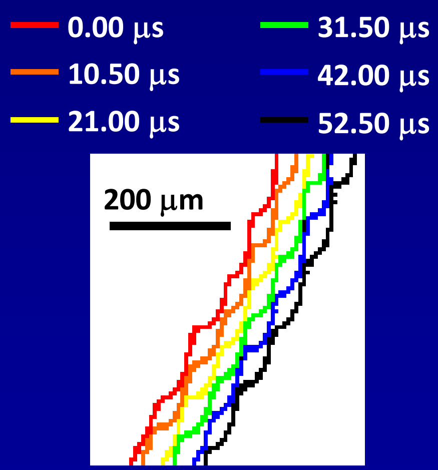
- Reaction front is smooth / uniform when observed at the micrometer scale.
- Reaction wave is characterized by a single radial velocity.
- Origin is the ignition site.
- Verified smooth front on nanoscale by Dynamic TEM.



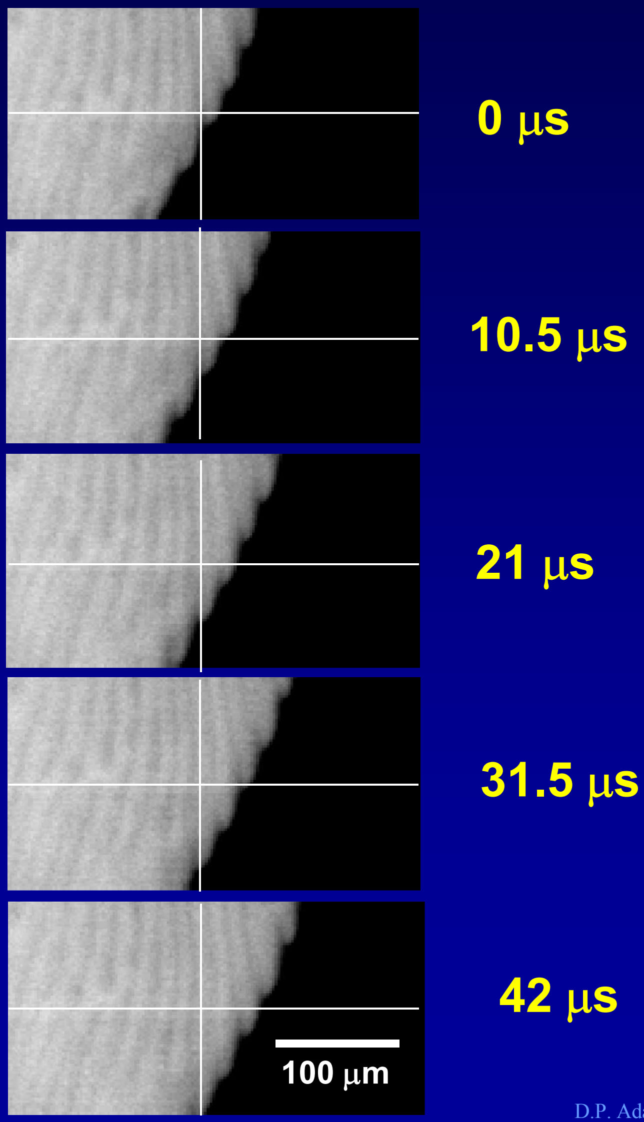
Ex. Al/Pt multilayer
(21 nm bilayer)
in plan view

Other exothermic multilayer systems exhibit an reaction front instability.

- Reaction front is not smooth / uniform when observed at the micrometer scale in the net forward direction.
- Characterized by stalled front (in net forward direction) and propagation of transverse bands.



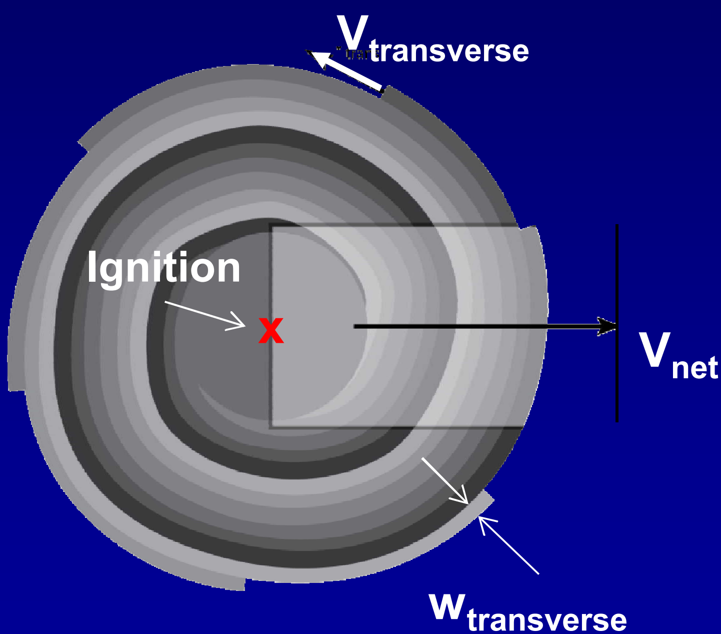
Ex. Co/Al multilayer (66 nm bilayer) in plan view



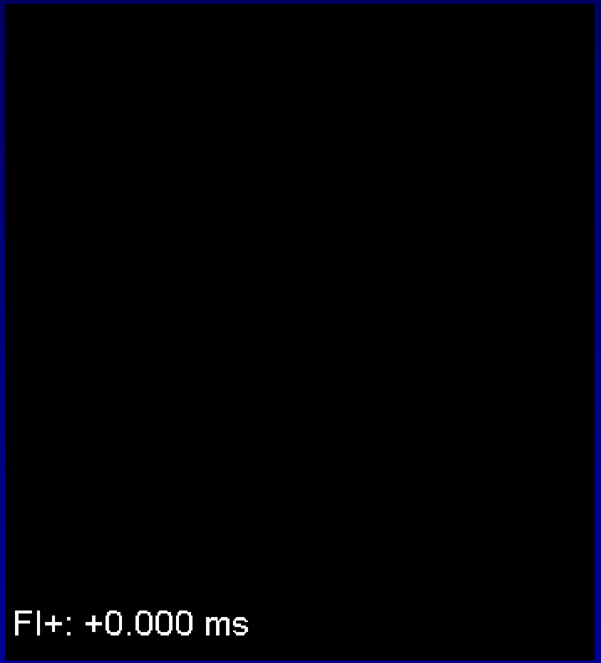
- Bands may propagate in a common rotation direction or in back-and-forth in two directions.

Spin-like front instability is exhibited by several reactive metal multilayers.

All movies and depiction are in plan view with multilayer periodicity in the plane of page



Ex. Cobalt / Aluminum (7.5 μm)



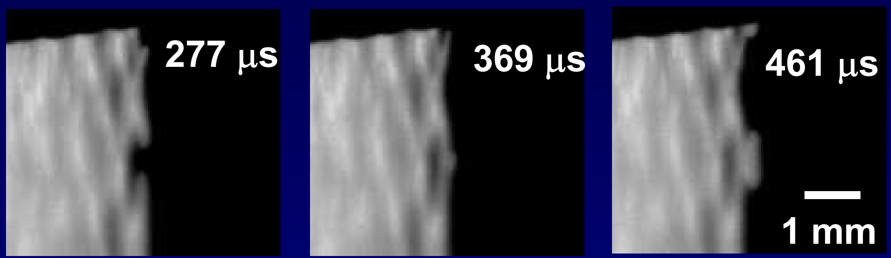
BL = 132 nm

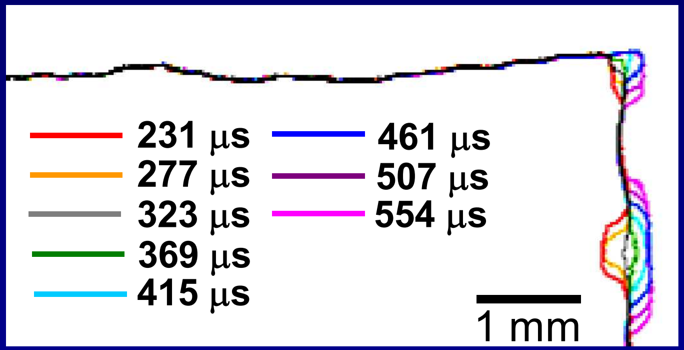
1 mm

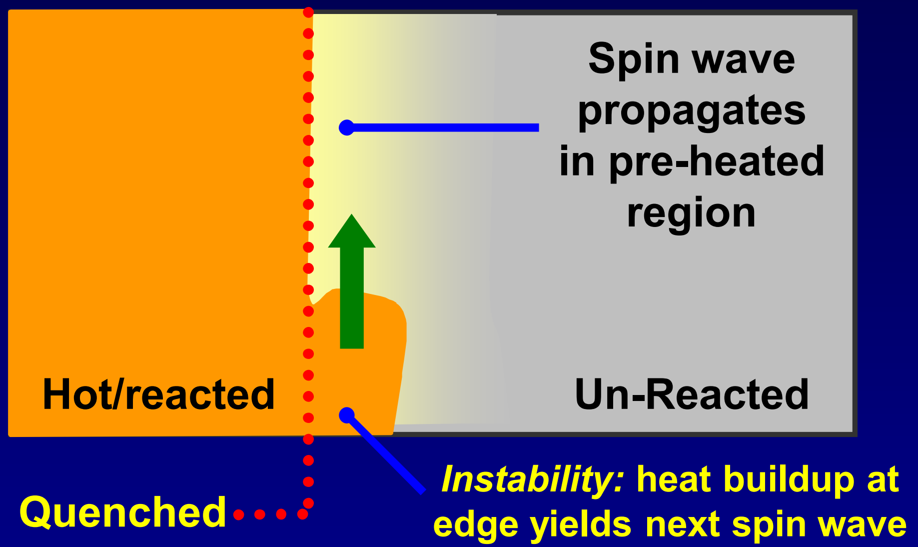
BL = 66 nm

200μm

Reaction front instability is characterized by stalled fronts and propagation along previous transverse bands.

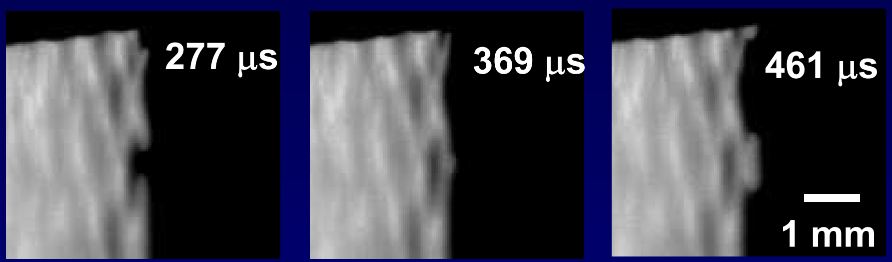


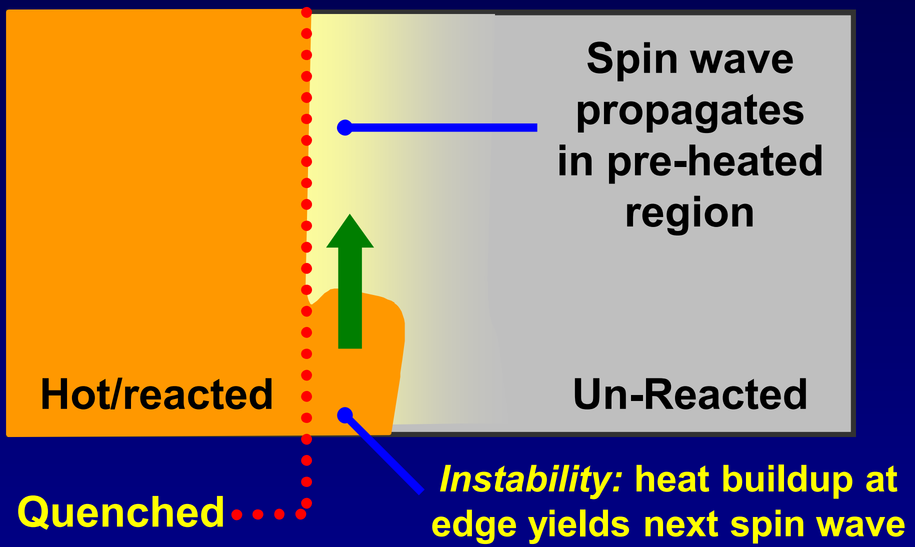


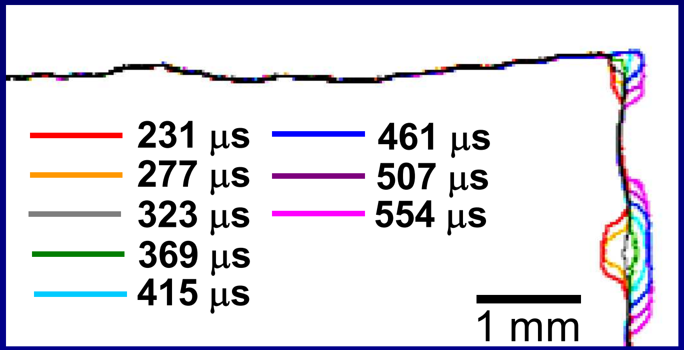


J. Mcdonald, D.P. Adams, Appl. Phys. Lett. 94 (2009).

Reaction front instability is characterized by stalled fronts and propagation along previous transverse bands.

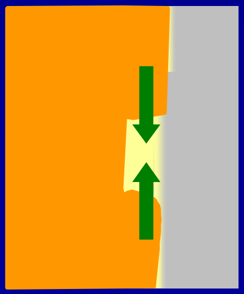




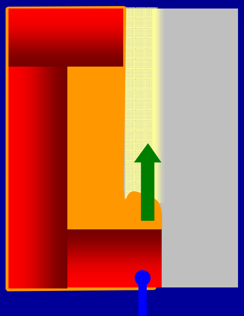


J. Mcdonald, D.P. Adams, Appl. Phys. Lett. 94 (2009).

Observed origins

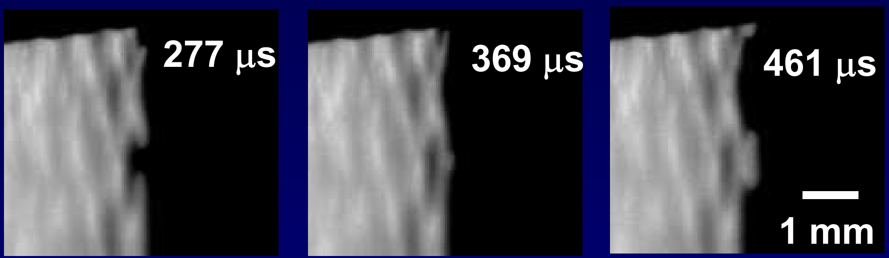


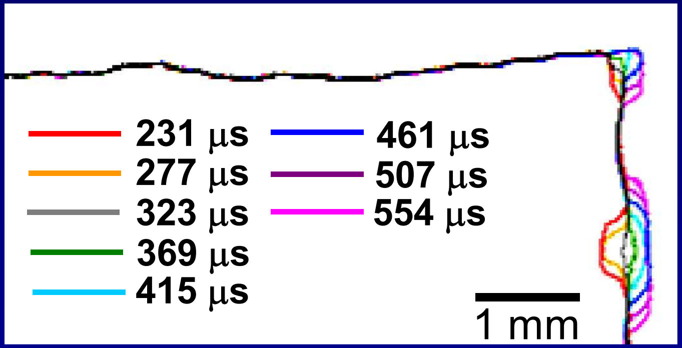
1. Collision of spin waves



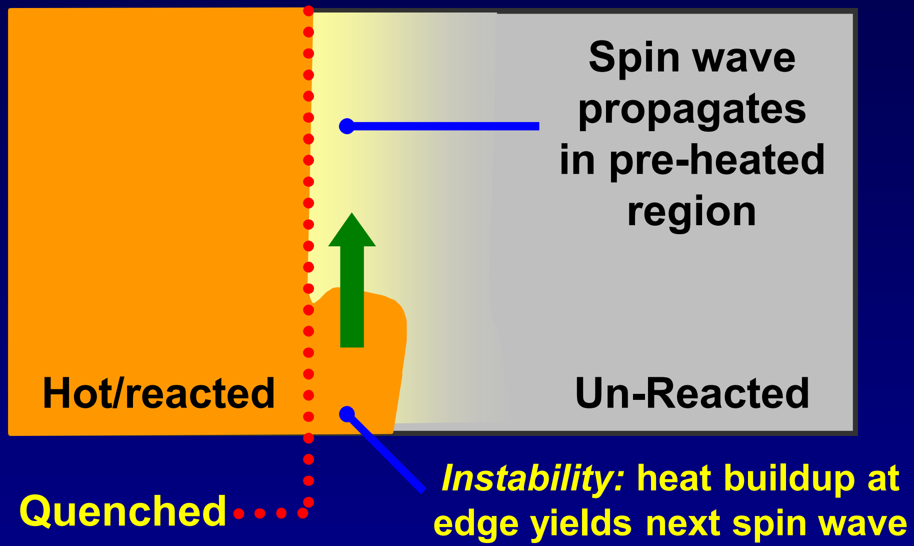
2. Heat buildup at foil edge

Reaction front instability is characterized by stalled fronts and propagation along previous transverse bands.

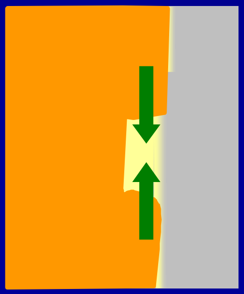




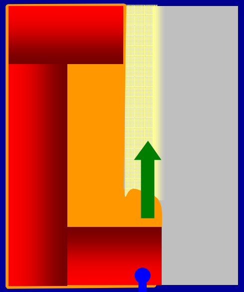
J. Mcdonald, D.P. Adams, Appl. Phys. Lett. 94 (2009).



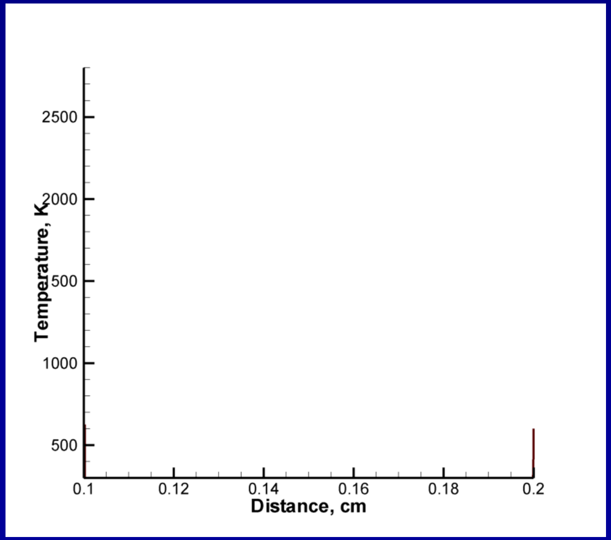
Observed origins



1. Collision of spin waves

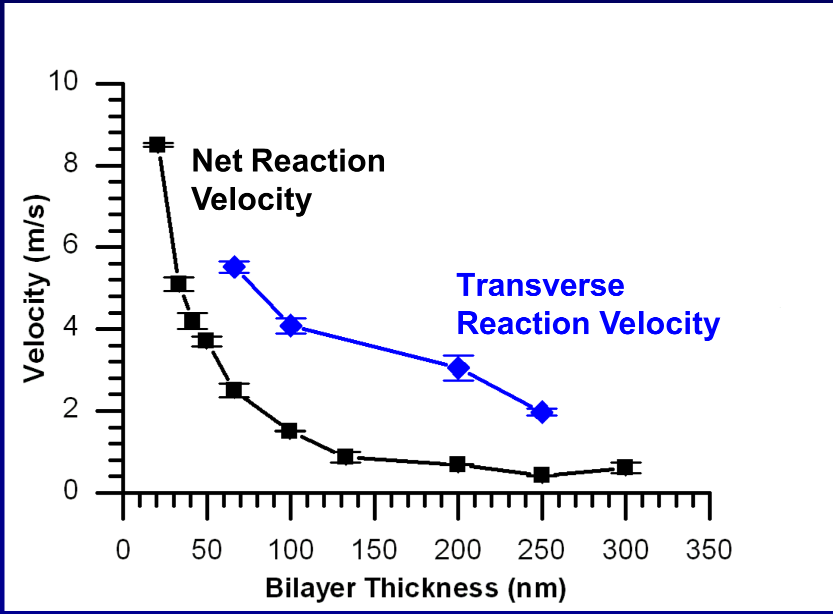


2. Heat buildup at foil edge

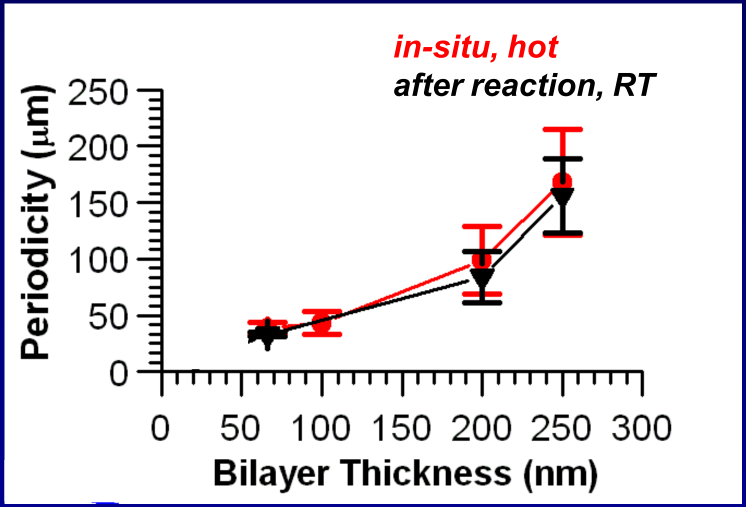


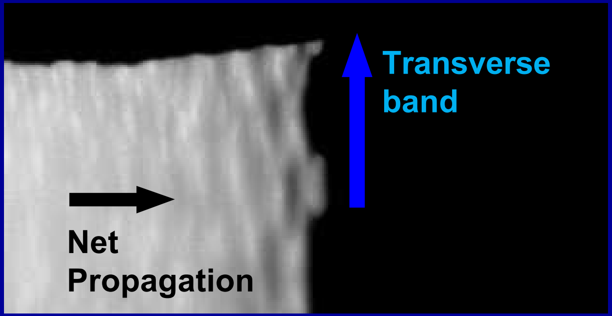
Co/Al multilayers exhibit a change in propagation mode with multilayer design

Speeds of reaction wave



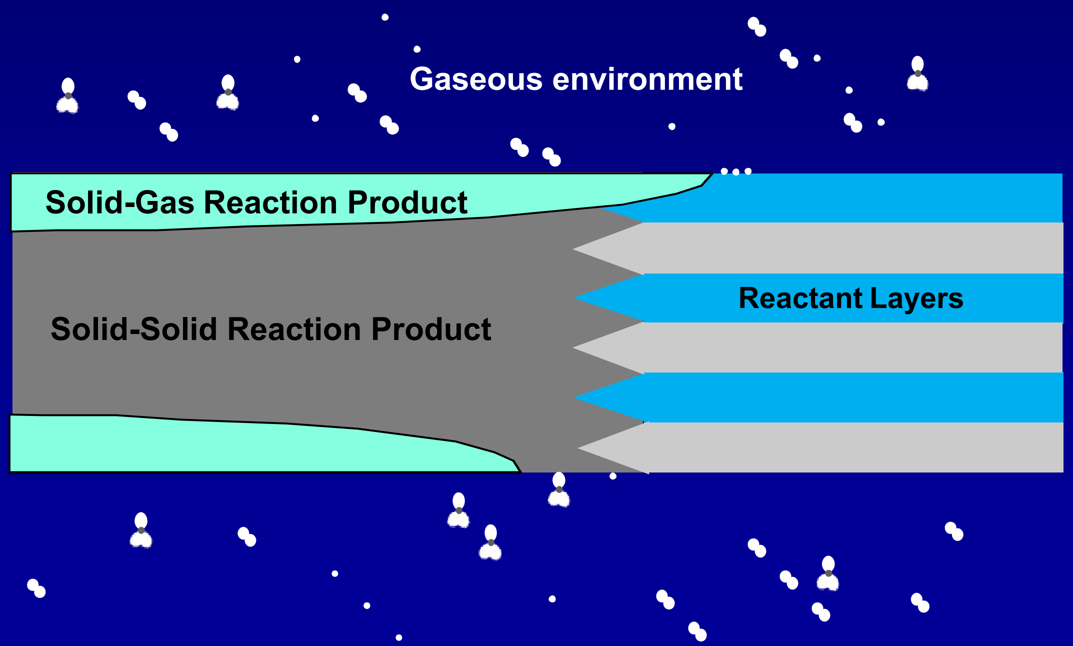
Widths of transverse bands





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

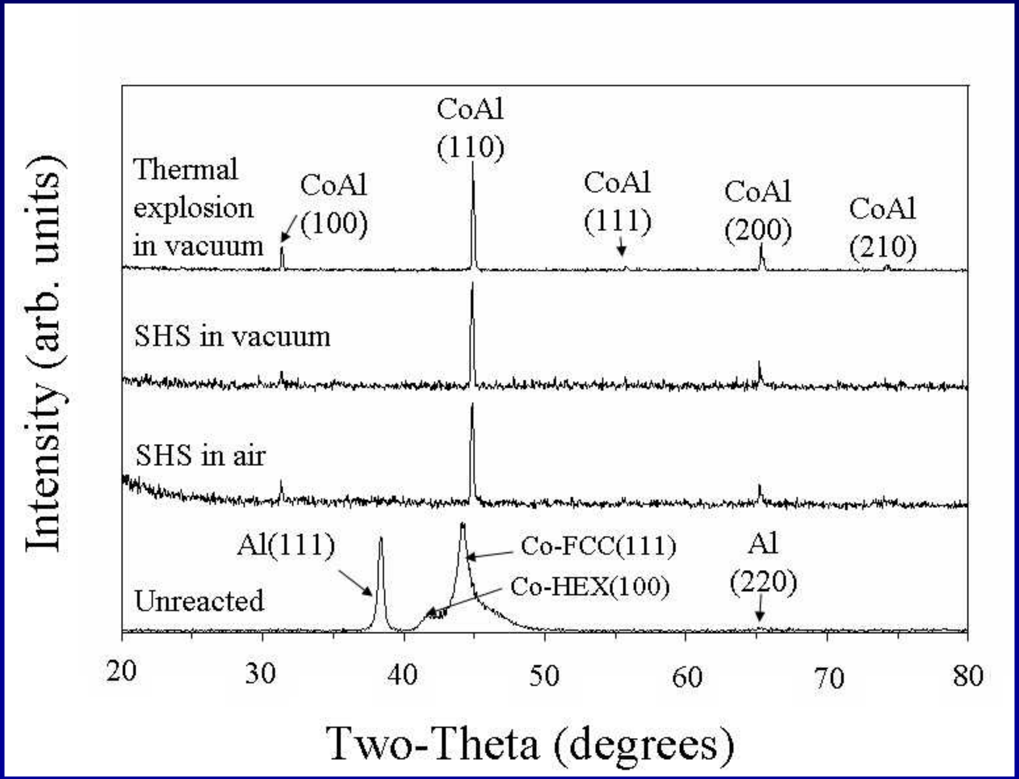
If so, how?



Many exothermic multilayers form intermetallic compounds when reacted in air.

Ex. Cobalt / Aluminum

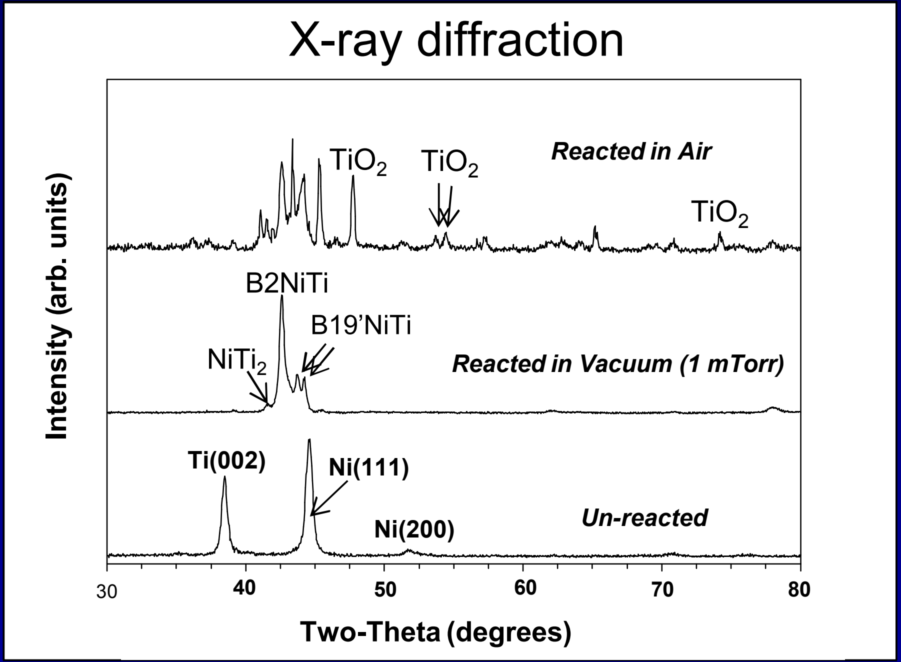
- XRD shows that final phase is independent of design, ignition conditions and surrounding gaseous environment.
- Compare heat of formation for Co/Al to that of Al_2O_3.



Other systems are affected by and react with the surrounding gaseous environment.

Ex. Nickel/ Titanium

- As-deposited multilayers are composed of elemental Ni and Ti.
- Foils reacted in vacuum generally form a mixture of B2 NiTi (or hexagonal NiTi) and B19' NiTi with evidence for other intermetallic compounds Ni_3Ti, $NiTi_2$).
- Foils reacted in air form a mixture of Ni-Ti intermetallic compounds and crystalline TiO_2 (rutile and anatase).



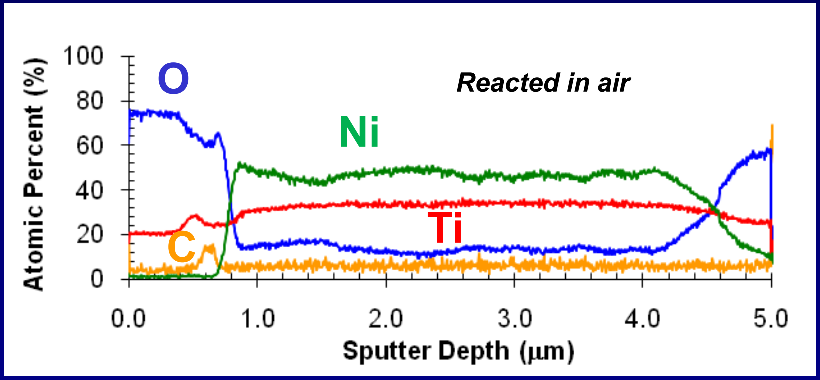
Single foil design evaluated (above):
Bilayer thickness = 625 Å
Total thickness = ~ 5.0 μm

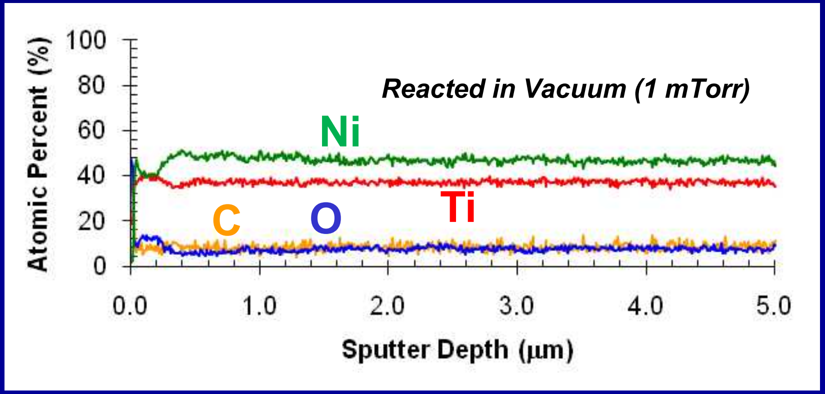
D.P. Adams, M.A. Rodriguez, J. Appl. Phys. (2009).

Reacted Ni/Ti foil composition is affected by reaction environment.

Depth-resolved composition profiles from Auger electron spectroscopy

- TiO_2 forms to a depth of approx. 800 nm on both sides when reacted in air.
- Minimal amounts of oxygen are present within foils reacted at 1 mTorr.
- Similar behavior is observed regardless of capping layer (Ni or Ti).

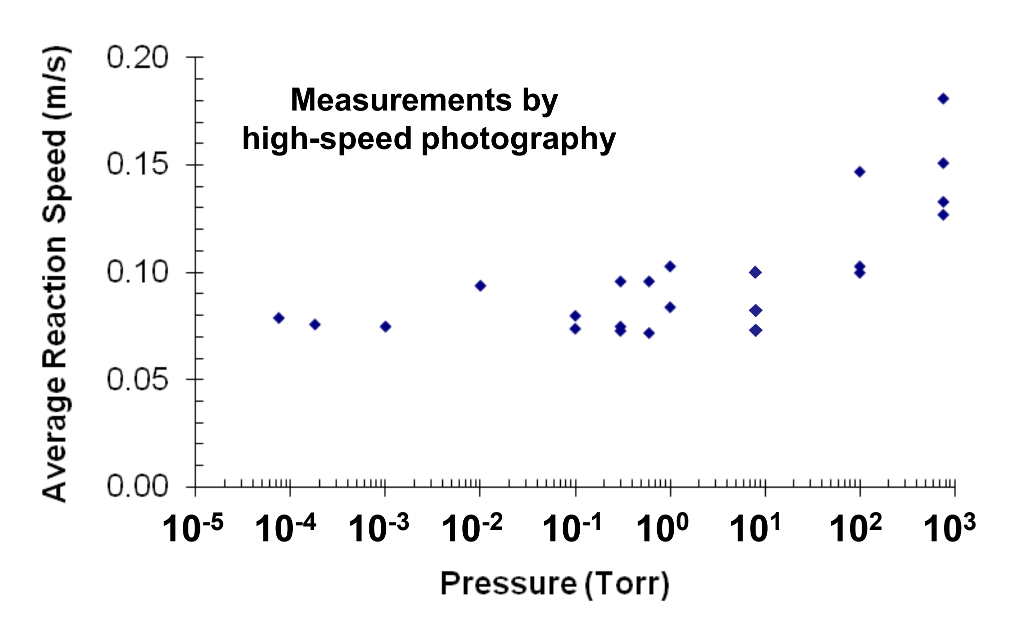




Single foil design evaluated (above):
Bilayer thickness = 4730 Å
Total thickness = ~ 5.0 µm
Ti capped (two sides) initially

Nickel / titanium foils exhibit SHS in vacuum, but average speed is affected by surrounding gas.

Ex. Nickel / Titanium
Bilayer thickness: 4730 Å, Ti capped
5 μm total thickness

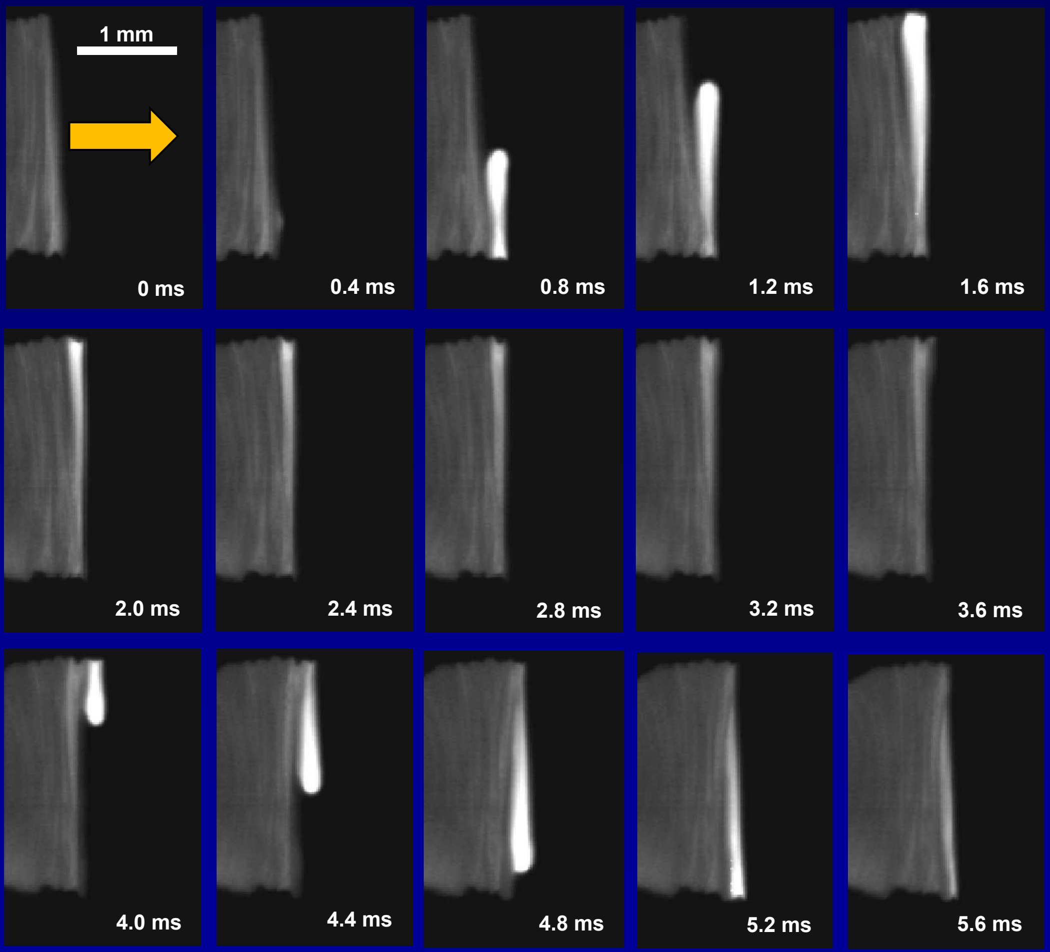


- Average propagation speed of Ni/Ti is affected by reaction environment.
- Maximum average propagation speed at atmospheric pressure (for our tests).
- Average propagation speed appears to be constant for pressure < 1 Torr.

High-speed photography reveals that Ni/Ti exhibits an unstable propagation mode (when tested in vacuo).

- Reactions occur by the propagation of transverse reaction bands (this resembles spin modes in cylindrical compacted powder samples).
- Transverse reaction bands nucleate at foil edges and, occasionally, via the 'collision' of bands.
- Transverse band speed exceeds average propagation speed.

Ex. Equiatomic Nickel / Titanium
Bilayer thickness = 4730 Å; Total thickness = ~ 5.0 μm
Ti capped (two sides); P = 300 mTorr

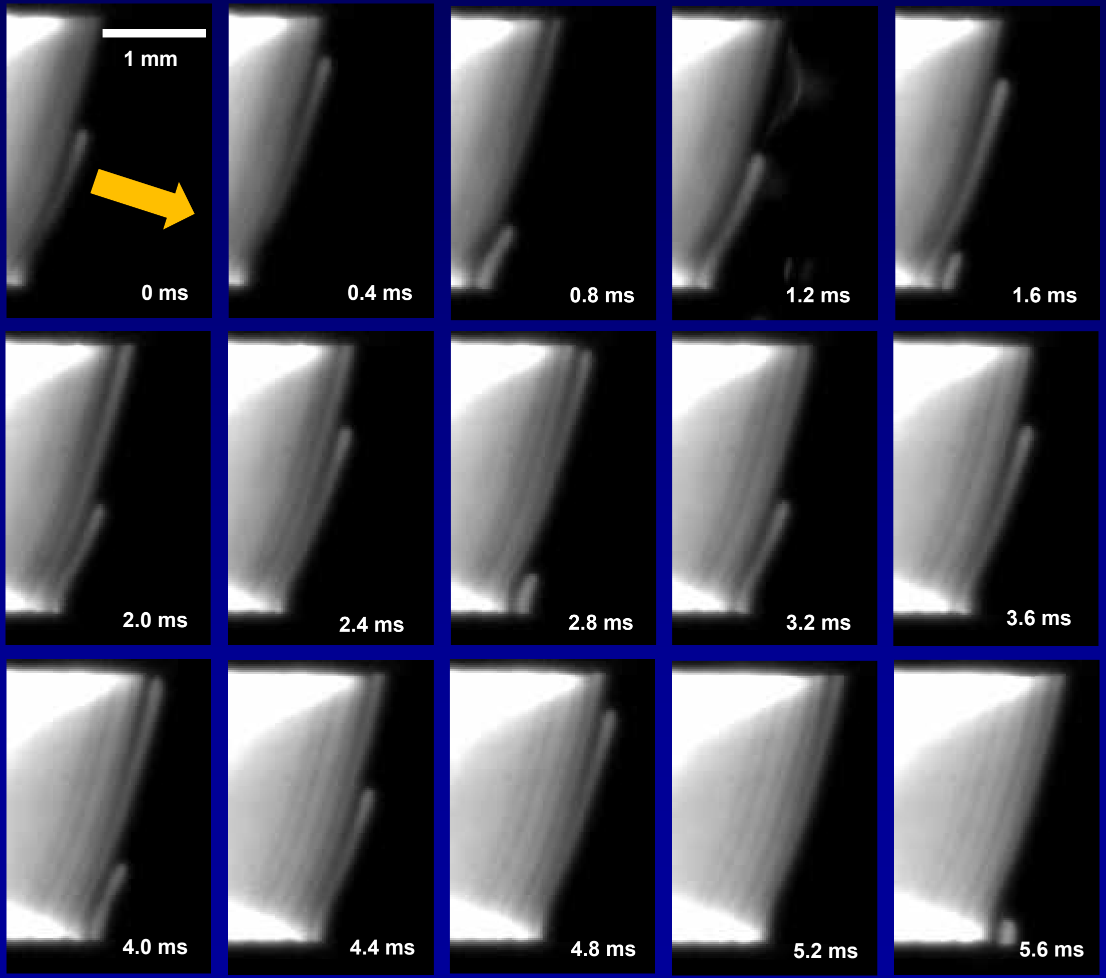


Plan view images

High-speed photography shows that Ni/Ti exhibits unstable reaction modes when reacted in air.

Ex. Equiatomic Nickel / Titanium
Bilayer thickness = 4730 Å; Total thickness = ~ 5.0 μm
Ti capped (two sides); P = 670 mTorr

- Similar to reactions in vacuum, reaction bands propagate transversely.
- A second reaction 'wave' appears behind the intermetallic reaction front.
- Frequency of transverse bands is increased when air is present.

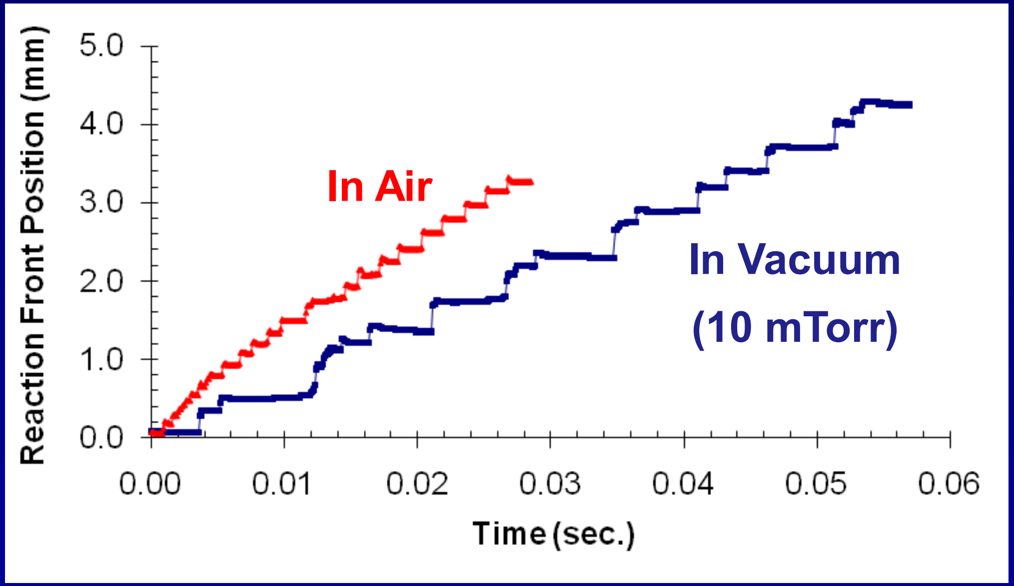


Plan view images

High-speed photography shows how air increases the average propagation speed of Ni/Ti.

Ex. Ni/Ti foil (equiatomic)
Bilayer thickness = 4730 Å;
Total thickness = ~ 5.0 μm; Ti capped (two sides)

- Frequency of transverse bands is increased when air is present.
- Detailed measurements suggest that reaction advances solely by propagation of transverse bands.
- Other Ni/Ti multilayer designs exhibit similar behavior.



Some systems exhibit a fast intermetallic wave and a slow, self-propagating combustion wave

Ex. Sc/Cu multilayer – shown in plan view

- Second reaction wave is an oxidation reaction

  - not observed when reacted in vacuum.

  - crystalline Sc_2O_3 phases observed after cooldown when reacted in air.

  - single intermetallic compound forms when reacted in vacuum.

500 μm

J. Mcdonald, D.P. Adams, J. Mater. Res. (2010).

Summary

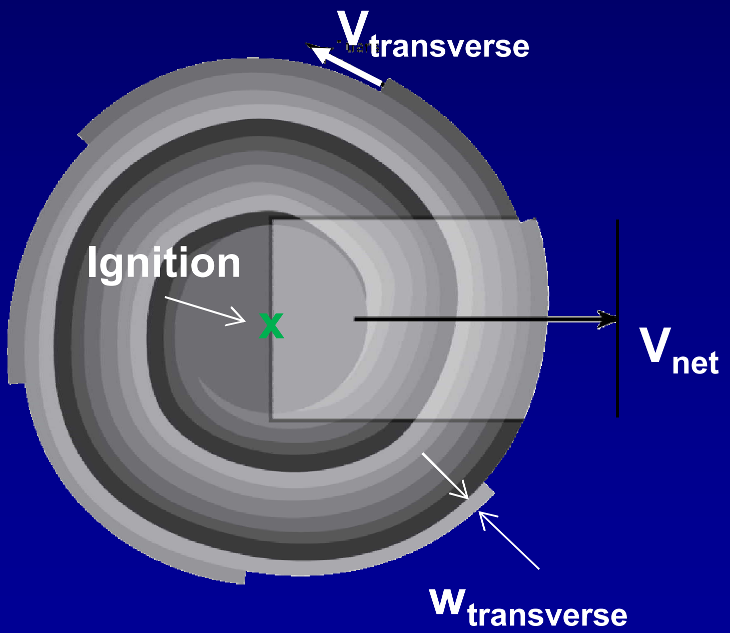
- Sputter-deposition provides the control needed for these studies, but care must be taken to maintain purity, etc.
- Laser ignition threshold fluences are affected by multilayer design, stored chemical energy and laser pulse duration.
- A spin-like reaction front instability has been observed in several moderate enthalpy systems (Co/Al, Ni/Ti, Sc/Cu).
- Several (but not all) material systems are affected by chemical reactions with the surrounding gaseous environment. These secondary reactions can affect phase, but also reaction speed, heat output and reaction front stability.

EXTRA SLIDES

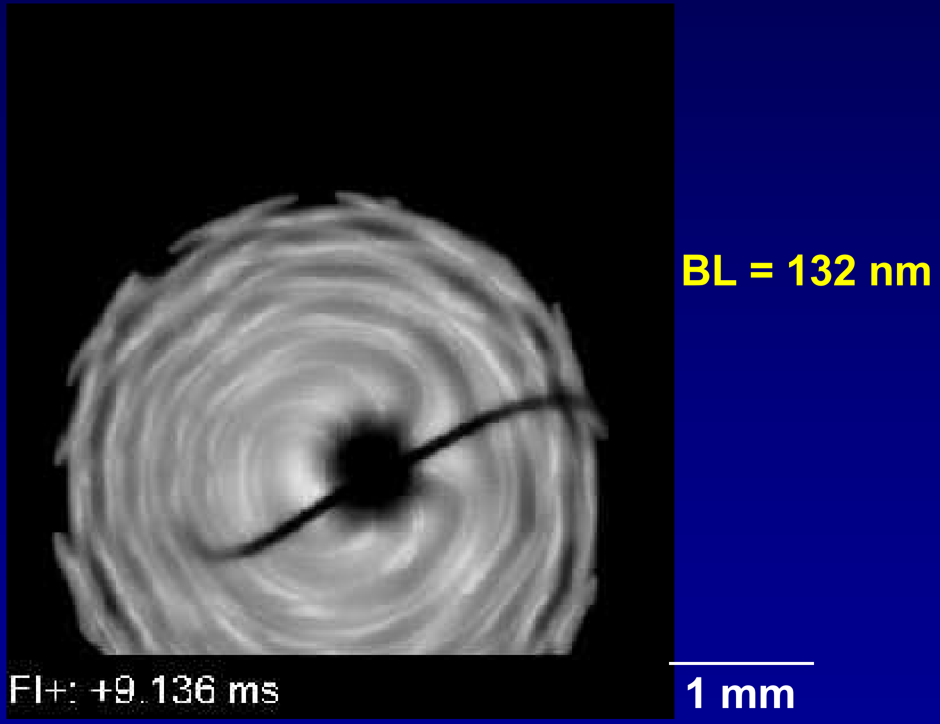
A few materials systems (Co/Al, e.g.) show a reaction front morphology dependence on bilayer thickness.

Spin-like front instability is exhibited by several reactive metal multilayers.

All movies and depiction are in plan view with multilayer periodicity in plane of page



Cobalt / Aluminum (7.5 μm)



Tasks of this research

High level: Determine if vapor-deposited, equiatomic Ni/Ti multilayers exhibit self-propagating reactions with no pre-heating (above room temperature)

Focus: examine how the surrounding gaseous environment affects

- propagation speed
- reaction mode
- final phase

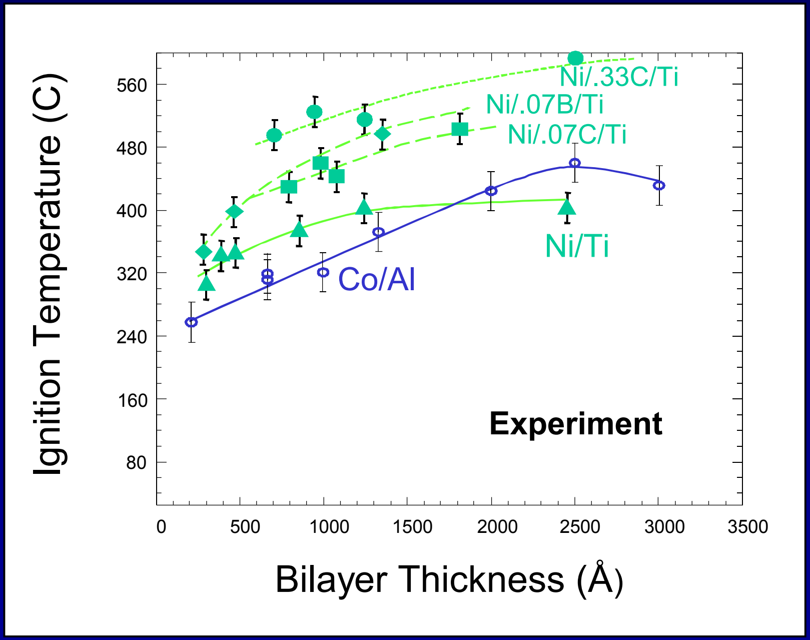
Global annealing leads to high-temperature reaction (potentially thermal explosion)

- Reactive foils ignite at temperatures far below the melting point of their constituents.

  compare with bulk Ni - Ti powder (with μm periodicity) $T_{ig} \sim 910 \pm 10^{o}C$
  - *reference Yi and Moore Scr. Met. 1988*

- Ignition temperatures vary with bilayer thickness (i.e., periodicity) with more coarse multilayers having higher T_{ig}.

.



Estimated heating rate ~ 1-10 deg./ms