

# Steady and Unsteady Propagation in Exothermic Multilayers

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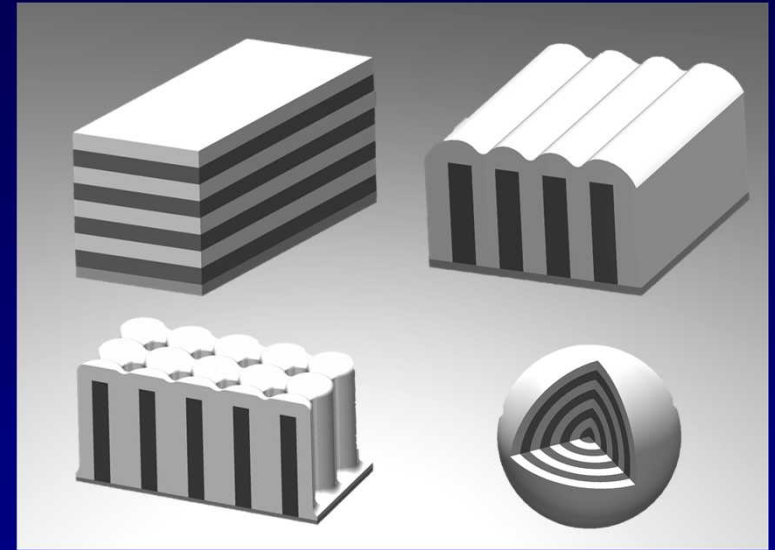


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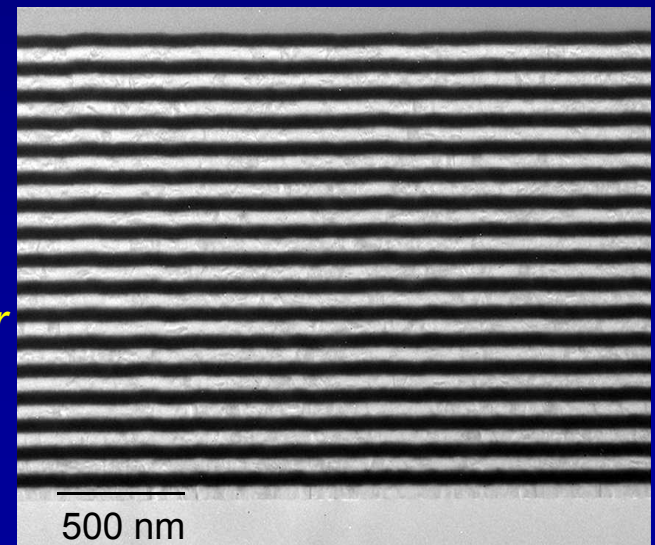


# Vapor deposition provides the desired level of control (thickness, composition, purity) for scientific study.

- Vacuum processes = high purity
- Different fabrication methods
  - Evaporative deposition
  - Sputter deposition
  - Atomic layer deposition
- Benefit from semiconductor industry tools
  - Ångström level precision
  - Uniform thickness, large areas
- Various symmetries
- Characteristic spacing 1-1000 nm
- Most exhibit deflagration reactions



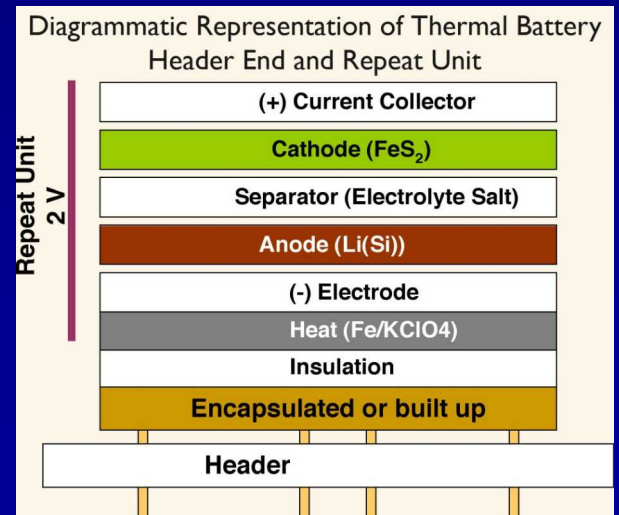
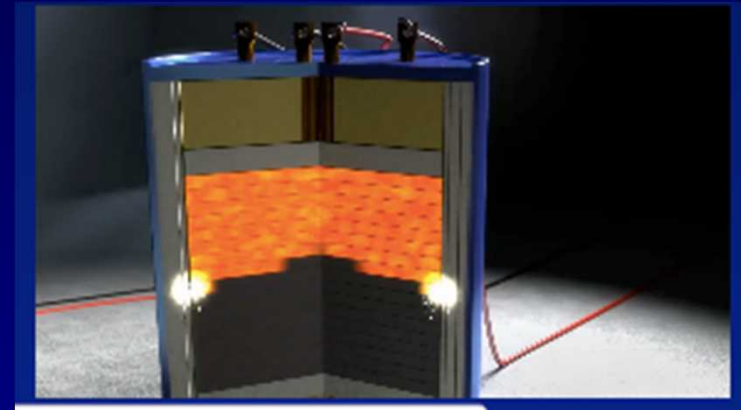
*Pt/Al  
Multilayer*



500 nm

# 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):
$$4\text{Fe} + \text{KClO}_4 \rightarrow 4\text{FeO} + \text{KCl} \quad (710 \text{ cal/g})$$
  - blends of Fe/KClO<sub>4</sub> are necessary
  - must be electronically conductive after burn so employ various compositions, e.g., 88/12 (w/w)



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

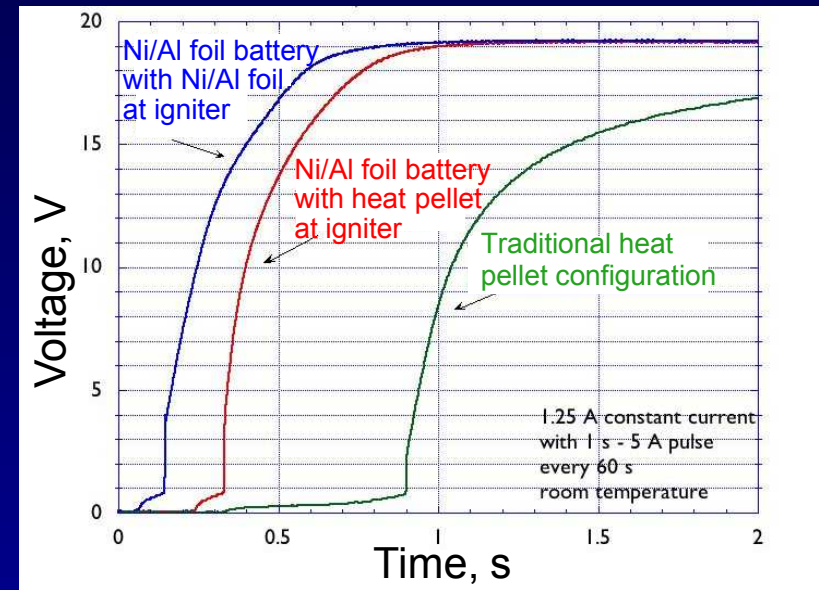
# Planar reactive multilayers (MLs) are replacement heat sources for reserve batteries.

- Comparable heats of reaction

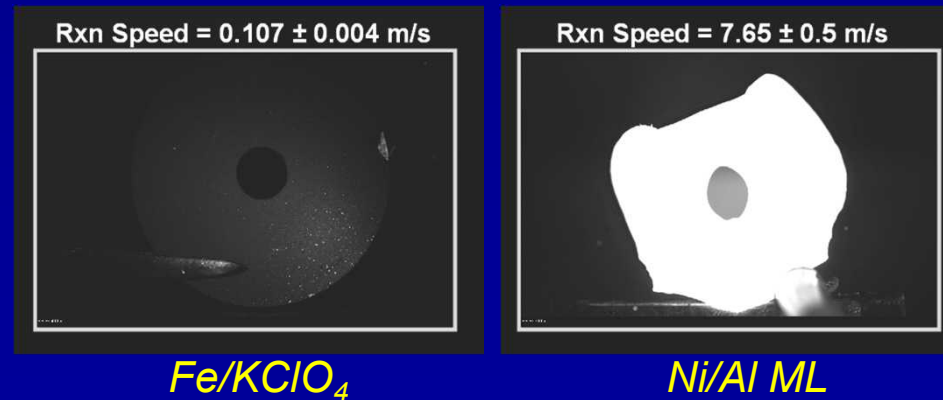
Composition	Calorific Output (cal/g)	Burn Rate (cm/s)
88/12 Fe/KClO <sub>4</sub>	221	7-12
86/14 Fe/KClO <sub>4</sub>	259	5-18
84/16 Fe/KClO <sub>4</sub>	292	12-20
equiat. Ni(V)/Al	250-298	~700

- Ni(V)/Al remains electronically conductive through reaction
- Original Reference for Deposited MLs  
J. Prentice, 1979 U.S. Patent  
“Heat sources for thermal batteries: exothermic intermetallic reactions”

## Battery rise time comparison

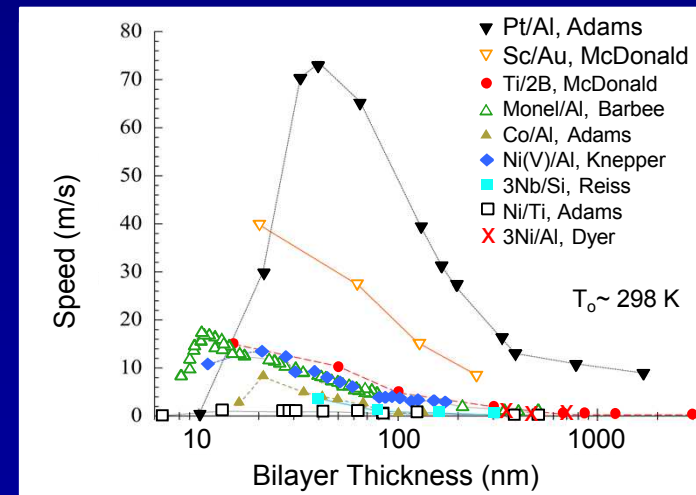
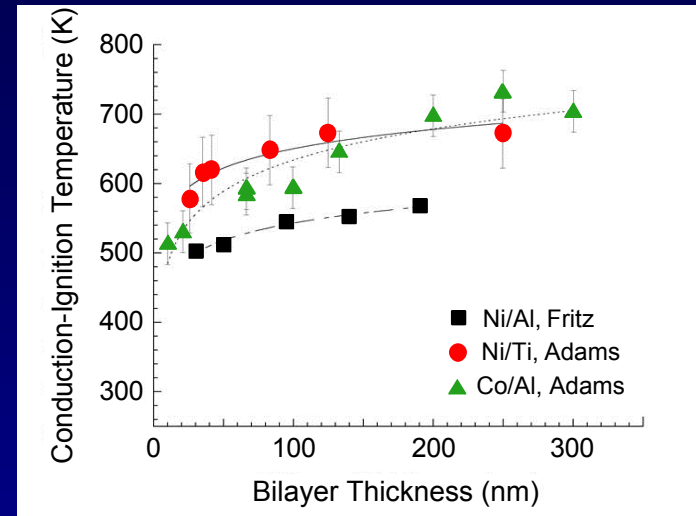


## Wavefront speed comparison in plan view



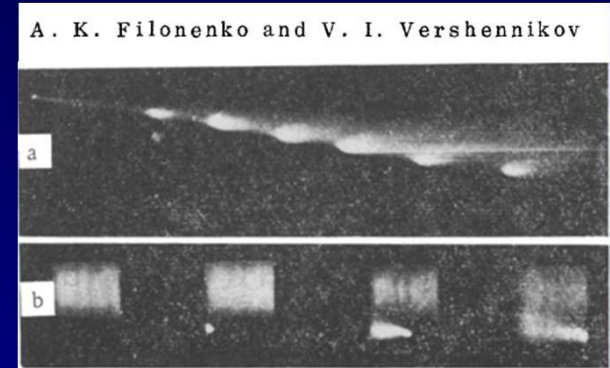
# Planar reactive multilayers exhibit several key material properties that can be tailored.

- Near term properties are tailored by deposition
  - ignition sensitivity (e.g.,  $T_{ig}$ )
  - reaction rate
  - total heat
- Questions remain about long term use:
  - changes in ignition sensitivity over time
  - changes in heat release rate over time
  - propensity to react and self-propagate
  - effects of environment (surrounding gases)

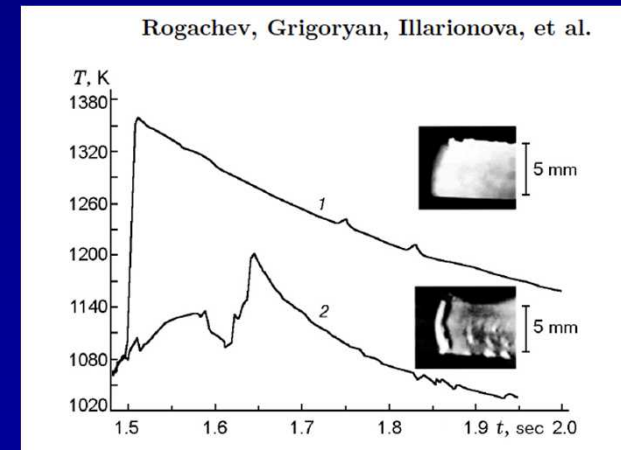


# Motivation: Understanding and controlling stability

- Instabilities can be detrimental to applications
- Effects of ambient temperature on stability
- Reactions with neighboring materials / gases can lead to thermal runaway
- Previous studies of self-propagating high temperature synthesis (SHS) show various types of reactions including
  - Steady
  - 1-D (auto-oscillatory) instability
  - 2-D (spin) instability
  - 3-D (chaotic) instability
  - Secondary reactions involving oxidation



Mechanism of Spin Burning of Titanium in Nitrogen, Fizika Goreniya i Vzryva 11 (1974).



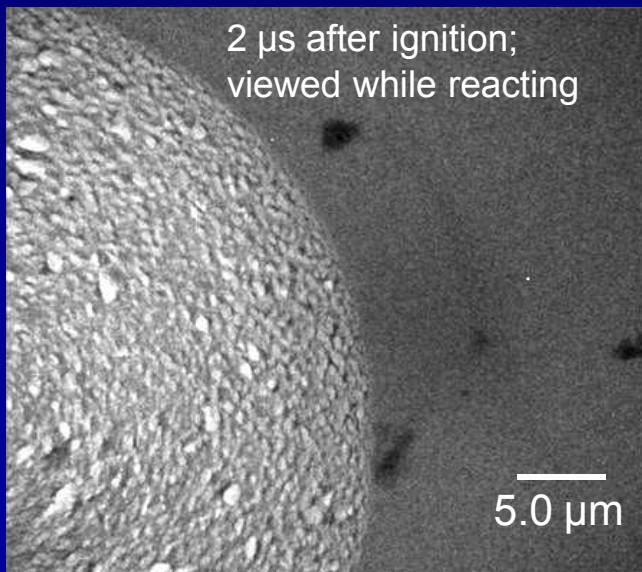
Gasless combustion of Ti-Al Bimetallic Multilayer Nanofoils Combust. Expl. Shock Waves 40 (2004).



# Many reactive multilayer systems exhibit a steady propagating reaction.

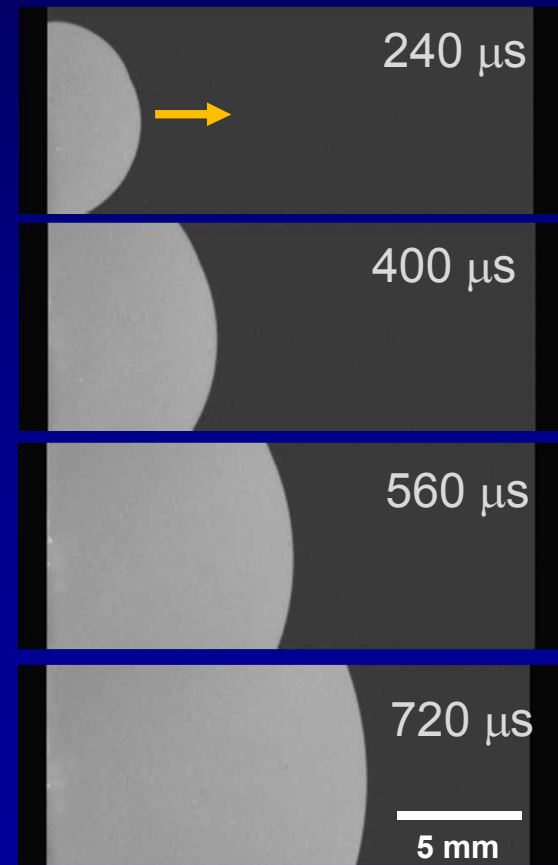
- Reaction front is smooth / uniform when observed at the micrometer or nanometer scale.
- Characterized by a single radial velocity.

*Ti/2B multilayer  
in plan view dynamic TEM*



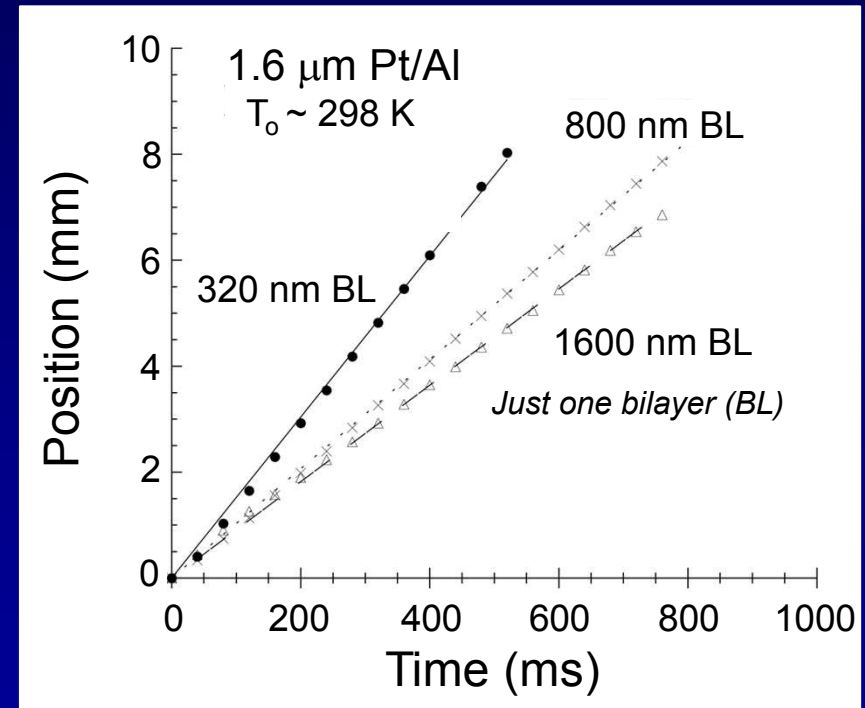
T. LaGrange, G. Campbell, A. Gash, D.P. Adams et al. *Microscopy & Microanalysis* 93 (2012).

*Al/Pt multilayer in plan view  
high speed optical microscopy*



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

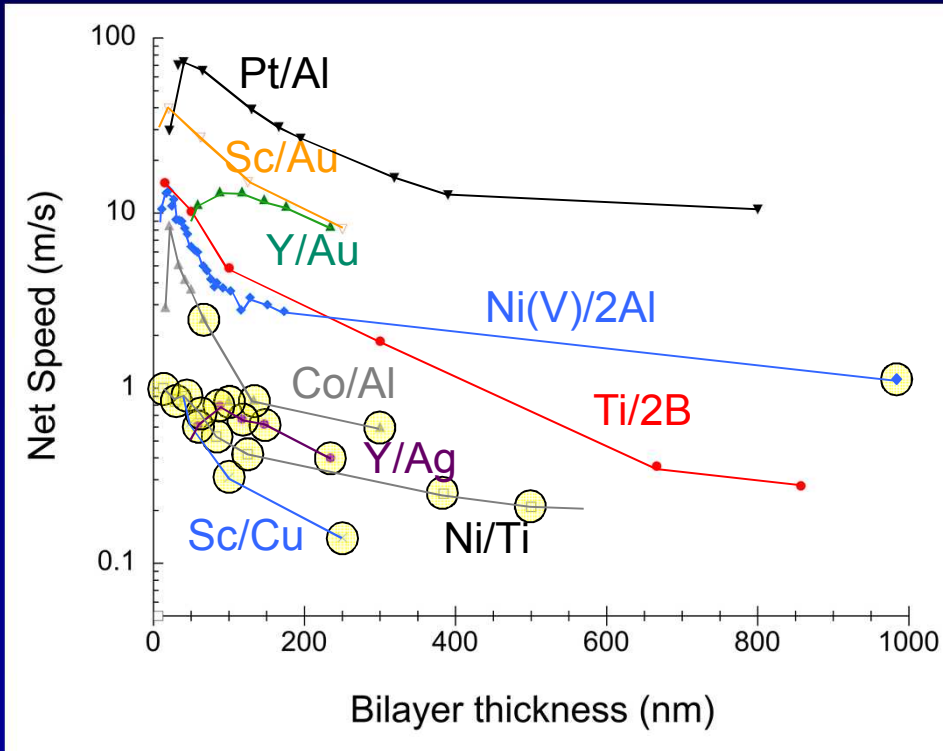
- Tests employ edge ignition.
- Position is characterized away from ignition zone (must be pre-determined)
- Measurements are made by high speed optical microscopy.
- Attribute the steady behavior to the high exothermicity, the enabled reaction kinetics, and the uniformity / purity of reactant layers.





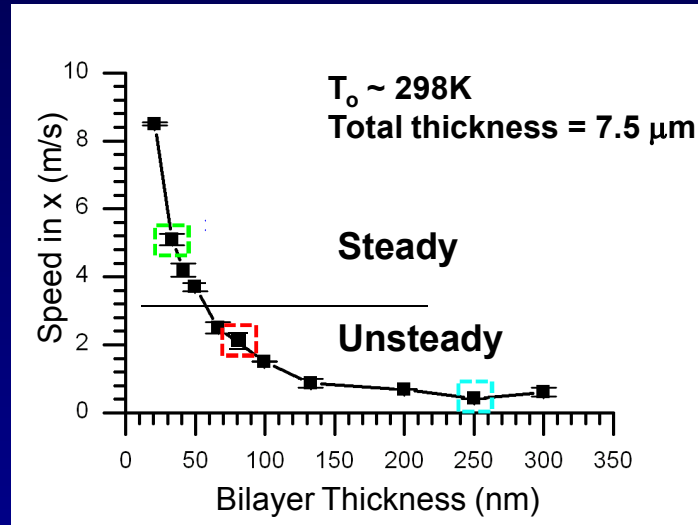
# Large exothermicity systems are generally found to exhibit steady propagation.

- Large  $\Delta H_o$  systems (Pt/Al, Sc/Au, Y/Au) exhibit steady propagating reactions.
- Low  $\Delta H_o$  systems (Ni/Ti, Sc/Cu, Sc/Ag) exhibit unsteady propagating reactions.
- A few systems (Co/Al and Ni/Al) are characterized by steady and unsteady reactions depending on multilayer design.



*Circled points  
indicate observed instability*

# Co/Al multilayers exhibit steady and unsteady propagating reactions depending on layer periodicity.



Bilayer  
thickness:  
33.2 nm

500  $\mu\text{m}$

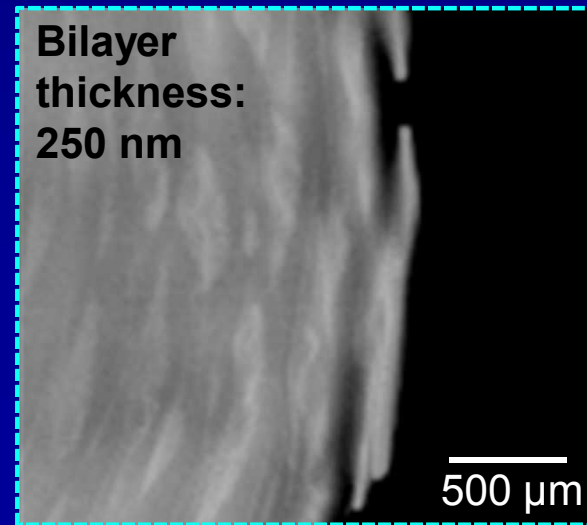
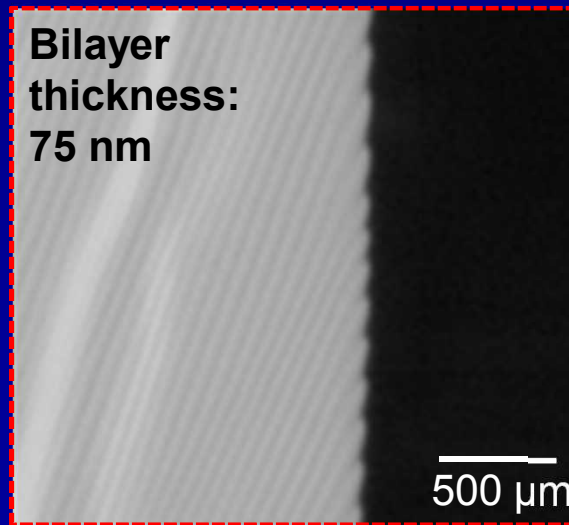
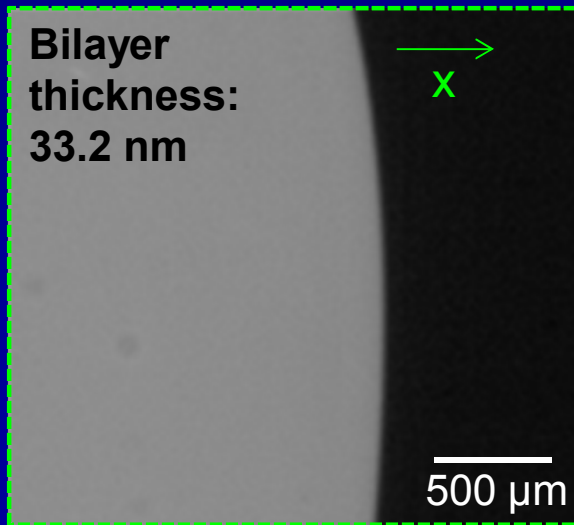
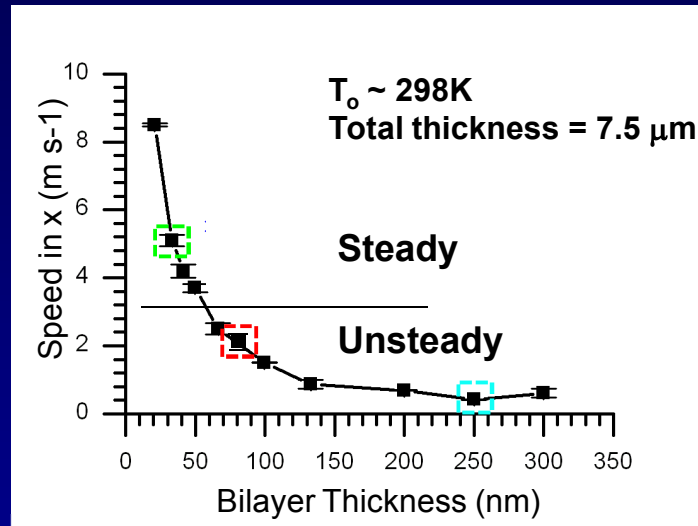
Bilayer  
thickness:  
75 nm

500  $\mu\text{m}$

Bilayer  
thickness:  
250 nm

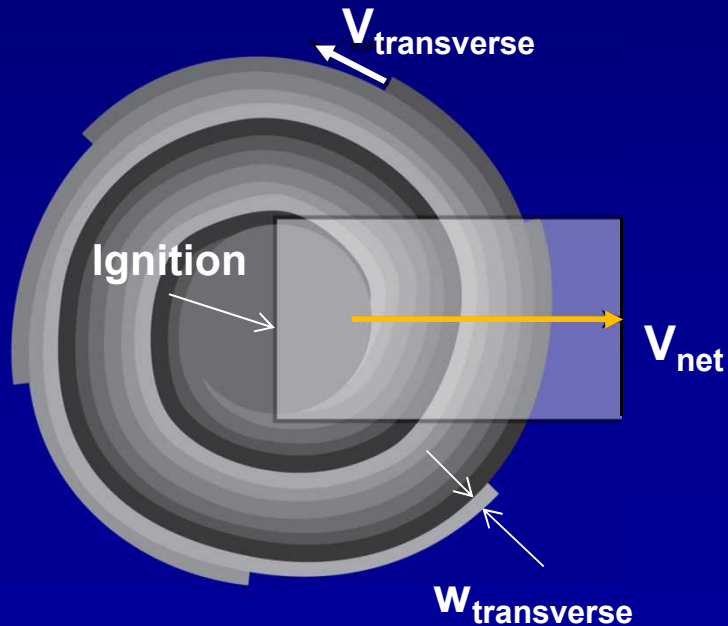
500  $\mu\text{m}$

# Co/Al multilayers exhibit steady and unsteady propagating reactions depending on layer periodicity.

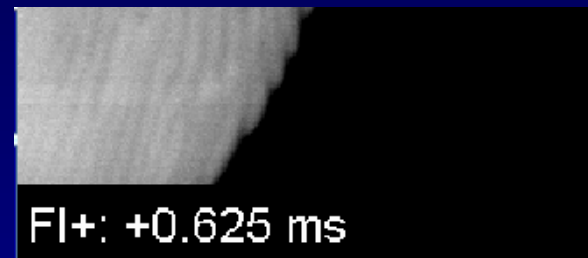


# Large bilayer thickness Co/Al multilayers are characterized by 2-D (spin-like) instabilities.

- Stalled fronts in net forward direction.
- Propagation of narrow transverse bands.
- Bands propagate in a common direction or in opposing directions.

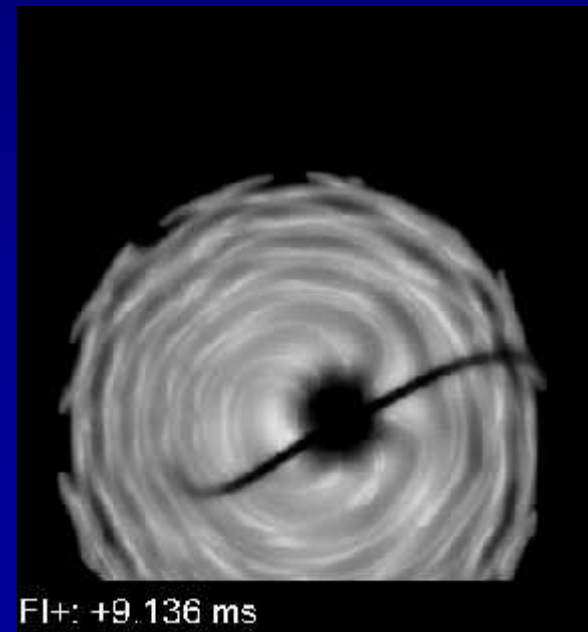


*Cobalt/Aluminum  
(in plan view)*



Bilayer:  
66 nm

200  $\mu\text{m}$

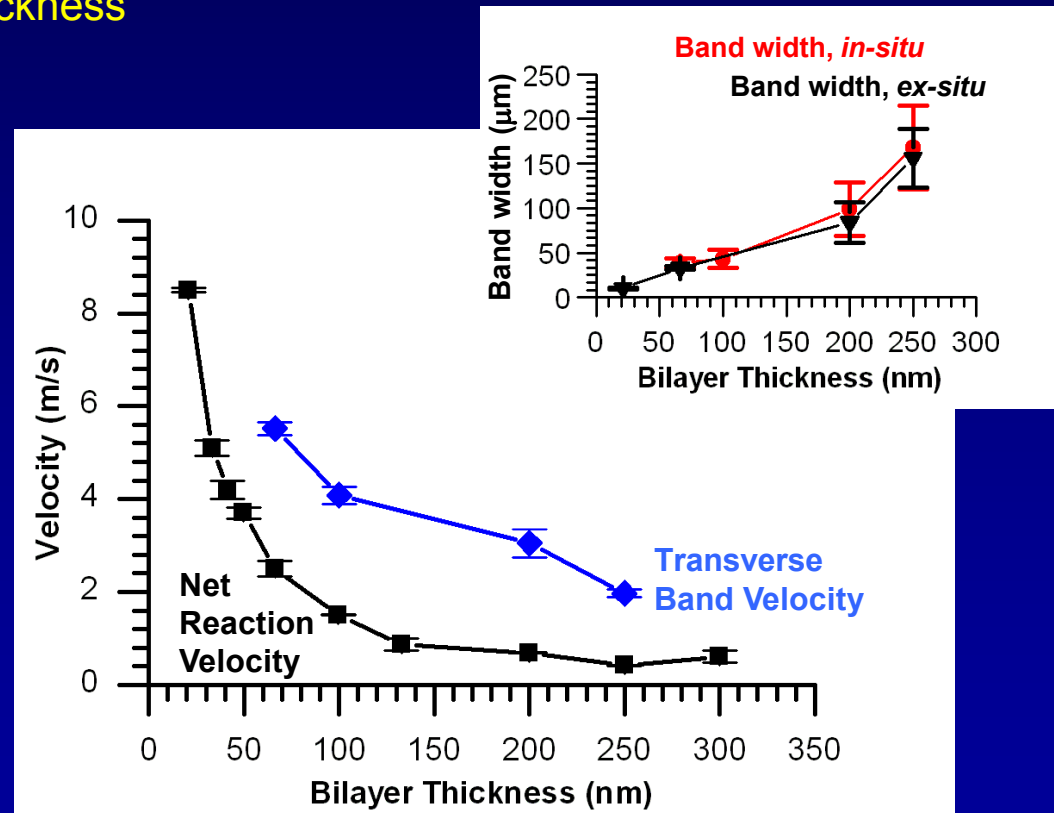
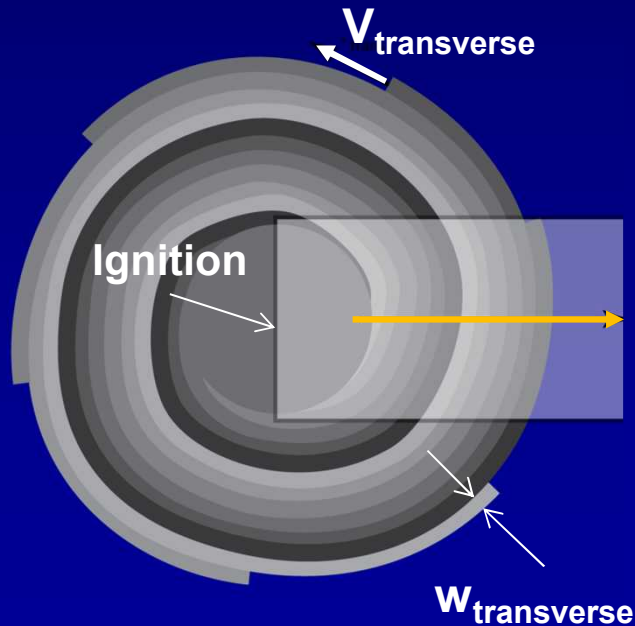


Bilayer:  
132 nm

1 mm

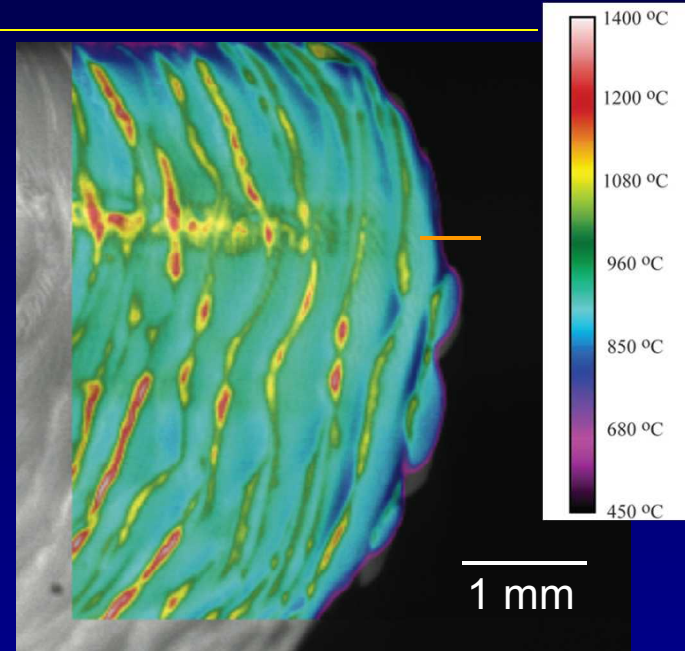
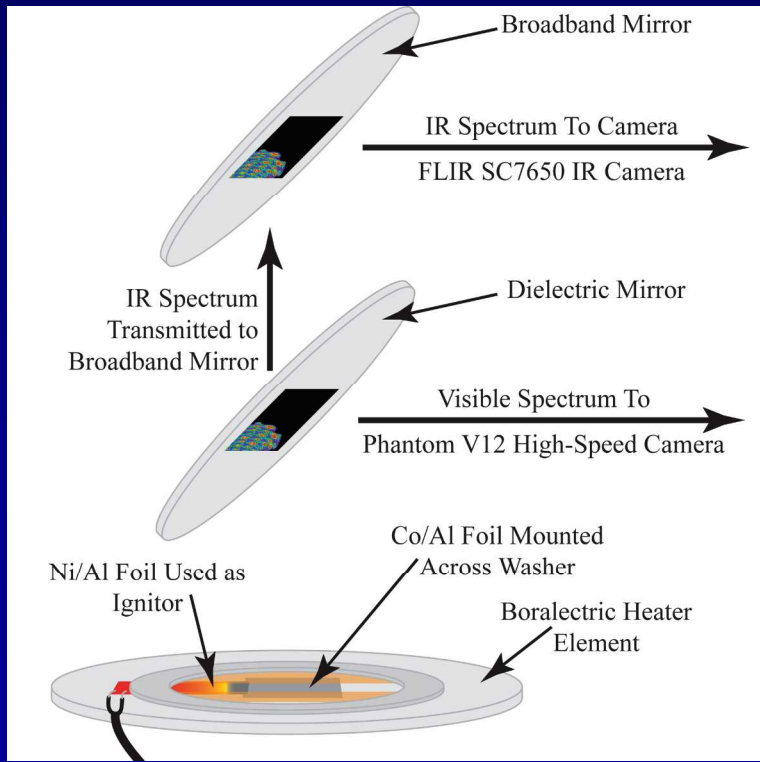
# Large bilayer thickness Co/Al multilayers are characterized by 2-D (spin-like) instabilities.

- Transverse band speed decreases with bilayer thickness.
- Band width increases with bilayer thickness

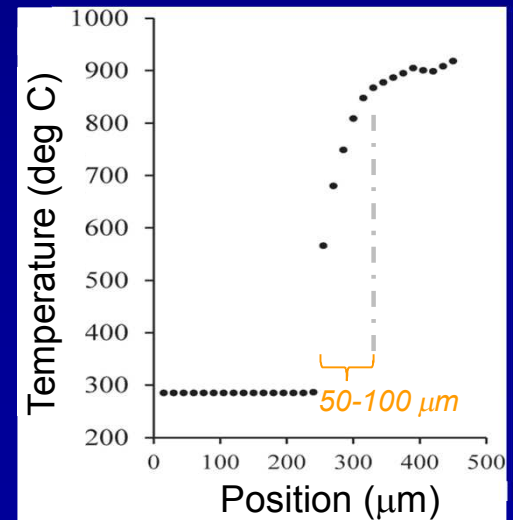


# Spin mode is characterized by large temperature variations and chemical kinetics that vary over micron scales.

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



*Temperature profile across line drawn above*

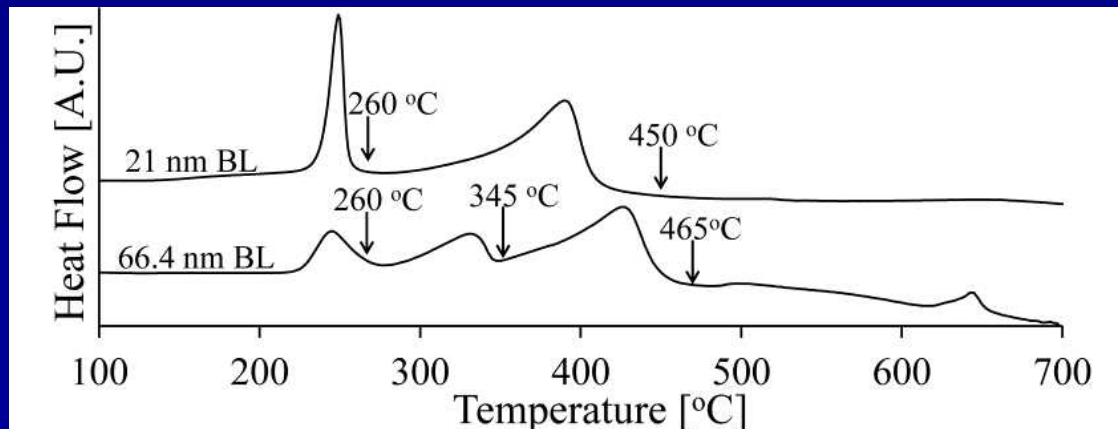




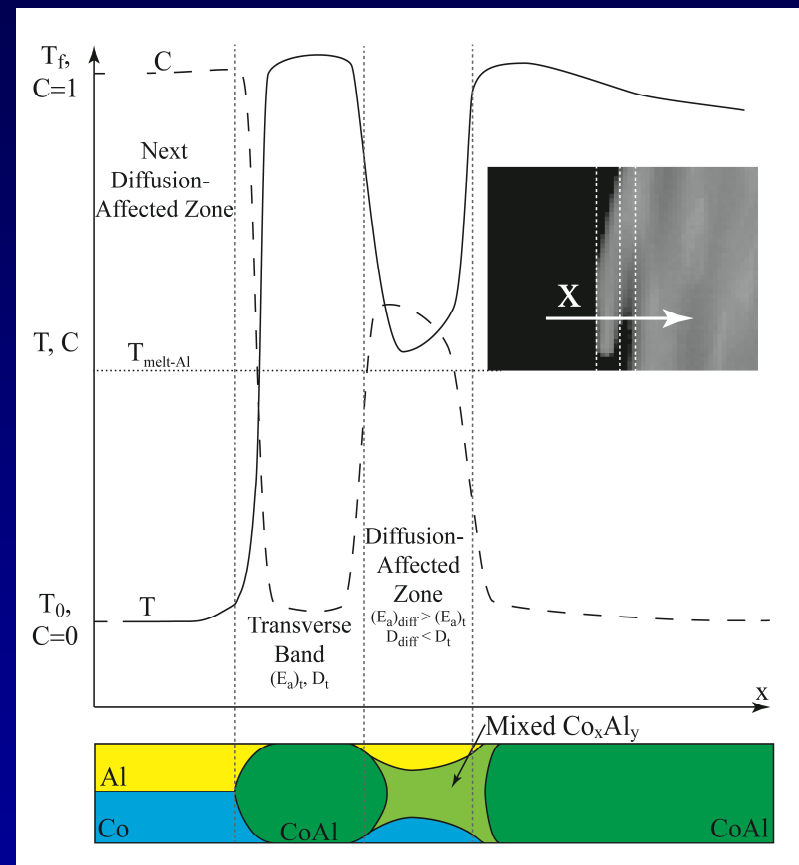
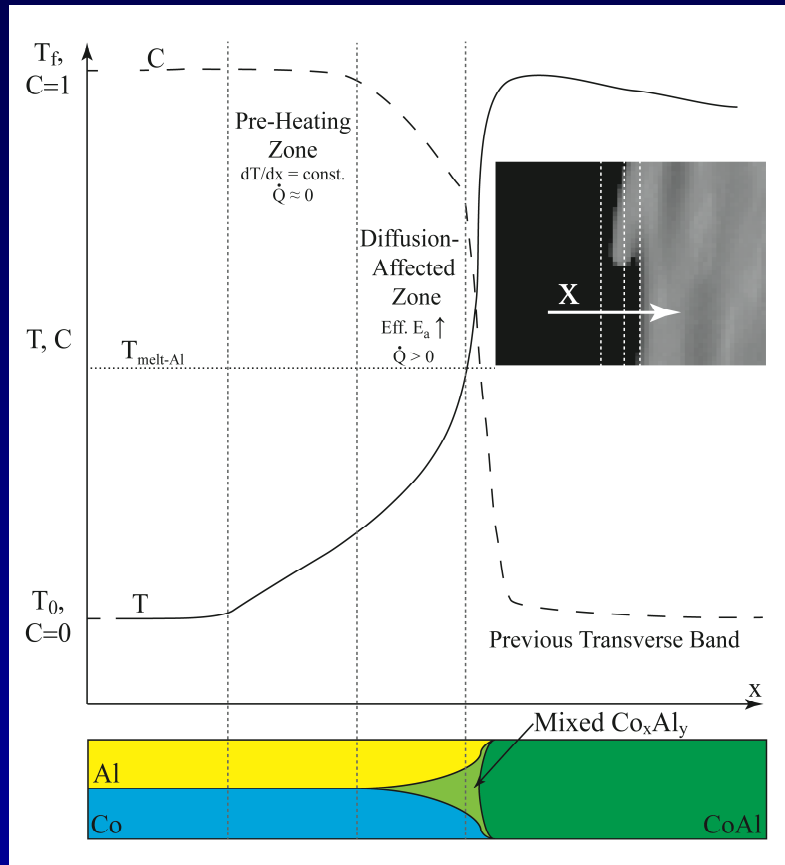
# Quenched Samples Phase ID (after slow heating)

		Co	Al	Co <sub>2</sub> Al <sub>9</sub>	Co <sub>4</sub> Al <sub>13</sub>	Co <sub>2</sub> Al <sub>5</sub>	CoAl
BL ≤ 33.2 nm	Initial	x	x				
	Exotherm 1	x		x	o	o	
	Exotherm 2						x
BL ≥ 66.4 nm	Initial	x	x				
	Exotherm 1	x	x	x	o	o	
	Exotherm 2	x		o	o	o	
	Exotherm 3						x

- Rates of heating just ahead of stalled front are expected to be similar to those used in DSC.
- If true, can expect that phase formation sequence is similar.



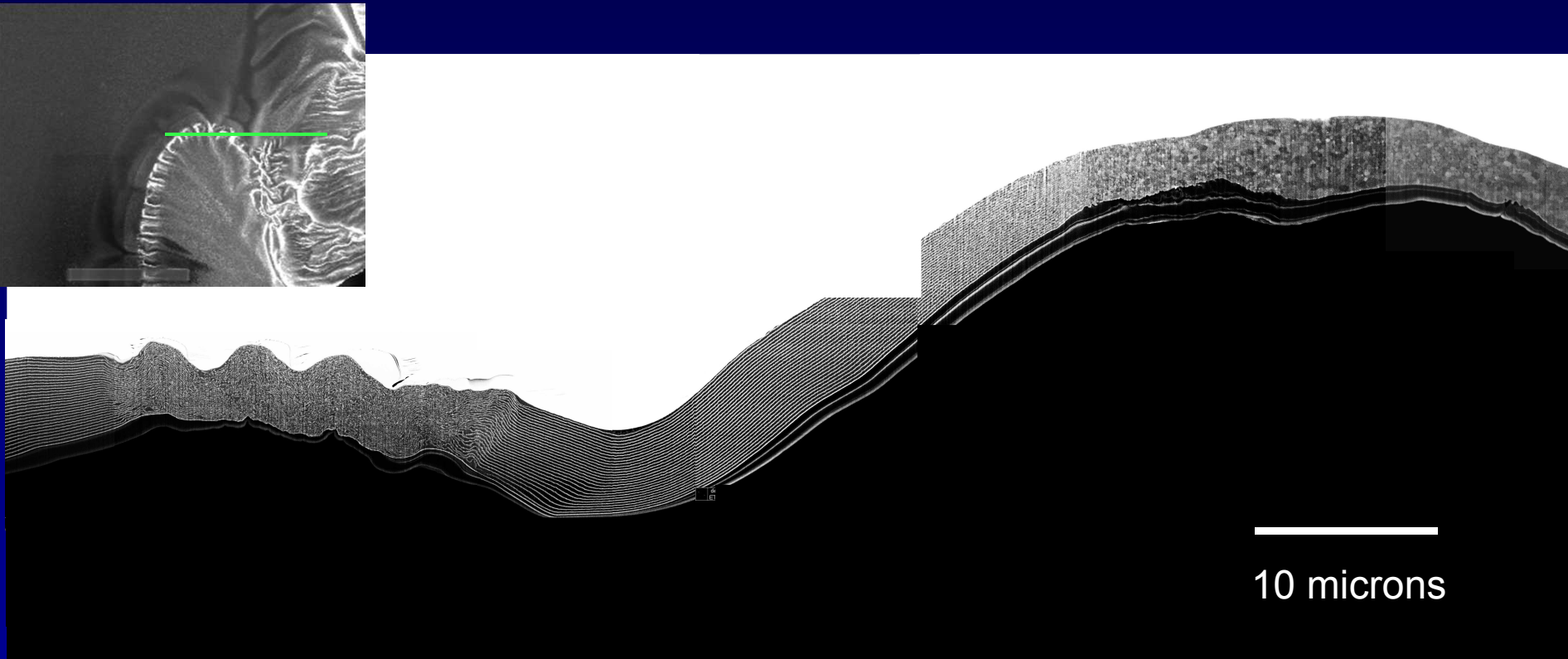
# Proposed mechanism for unsteady propagation



- 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

Evidence for diffusion affected zones is suggested by quenched samples.

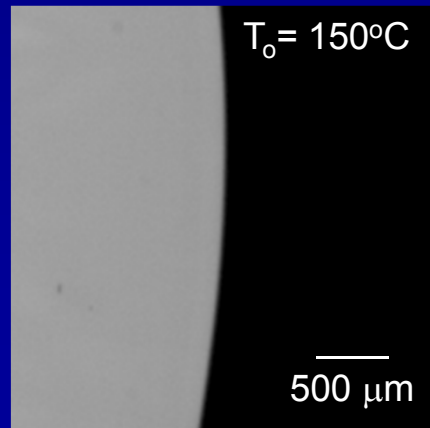
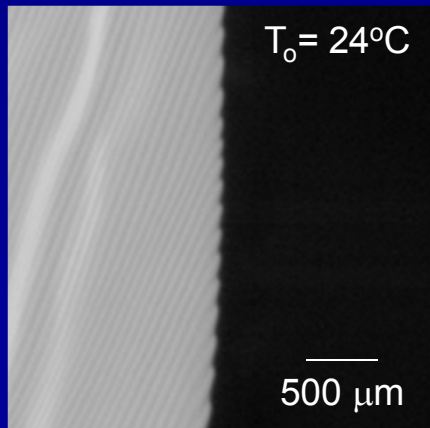
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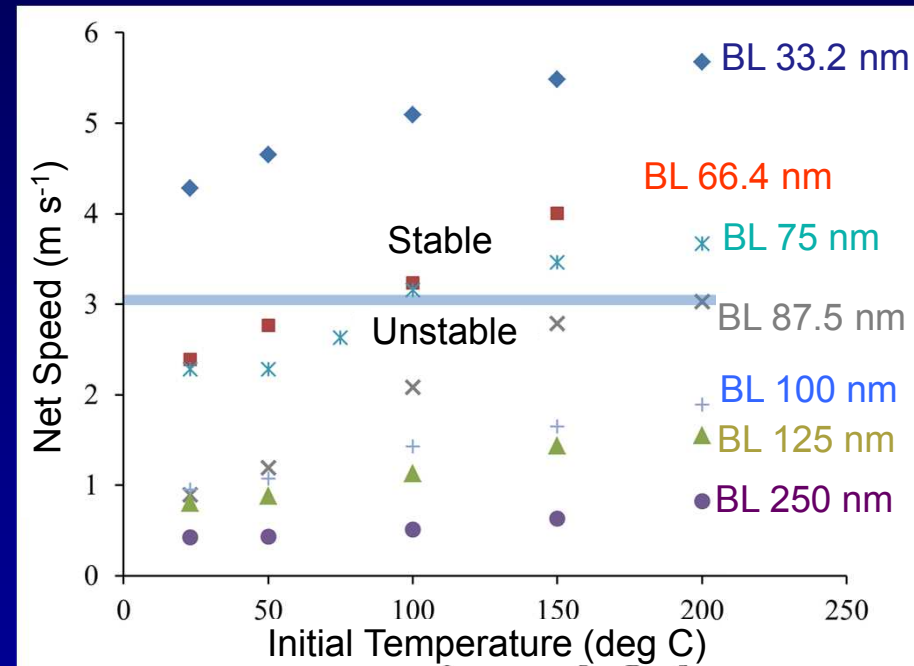
- Intermediate area in quenched sample is characterized by a mixture of reactants (Co, Al) and  $\text{Co}_2\text{Al}_9$
- Evidence supports proposed model of a diffusion affected zone.

# Preheat experiments demonstrate stability with increasing initial 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 boundary.



## Cobalt/Aluminum

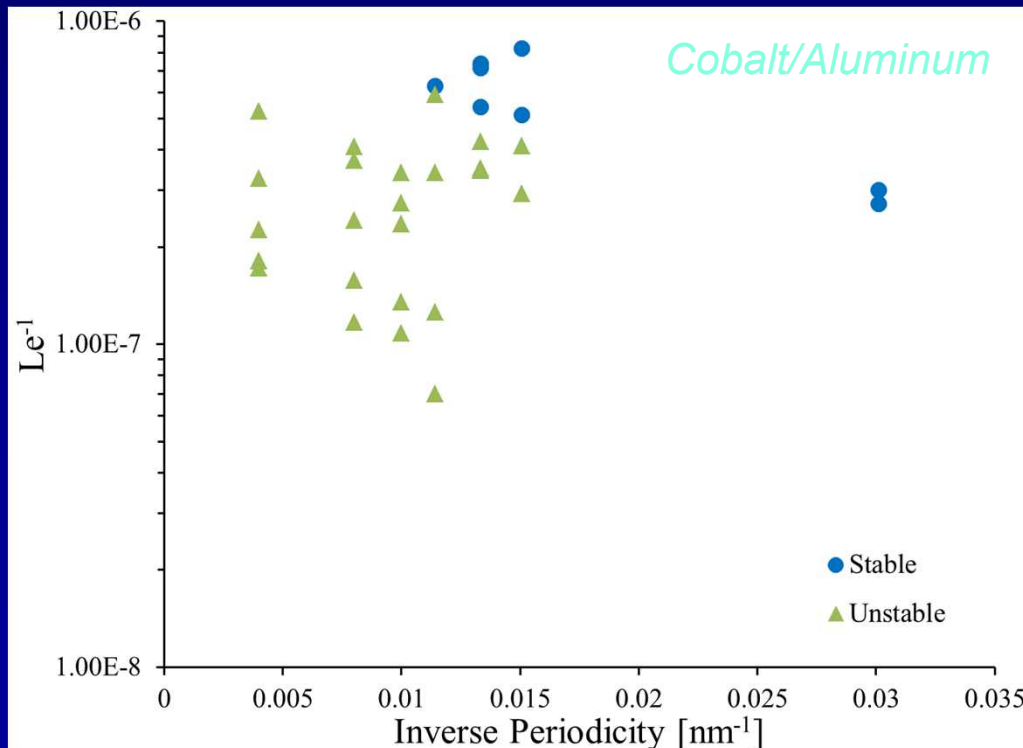


Bilayer thickness: 75 nm  
Total thickness: 7.5  $\mu\text{m}$

# $Le^{-1}$ at Transition to Stability

Using Armstrong's relationship\*,

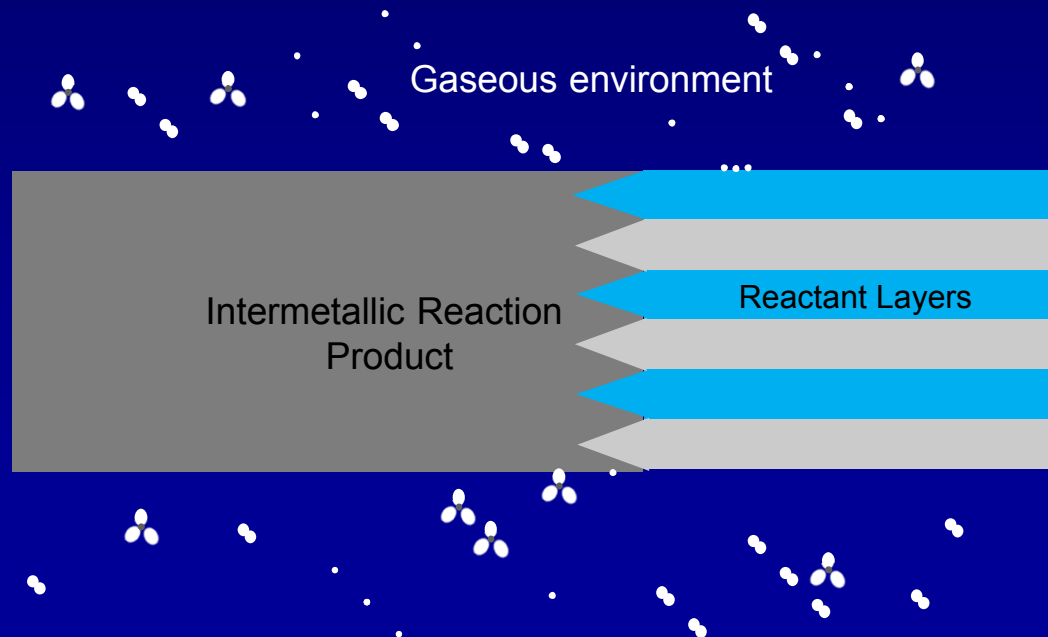
$$Le^{-1} = D/\lambda = \frac{u^2 \delta^2 E_a (T_{max} - T_o)}{3 \lambda^2 T_{max}^2 R} = A \exp(-E_a/RT_{max})$$



- Thinner bilayers exhibit stable front at lower  $Le^{-1}$
- Assuming constant  $\lambda$ , thicker bilayers require higher mass diffusivity (reaction rates) for stability
- Fits with idea of critical heat transfer rate

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

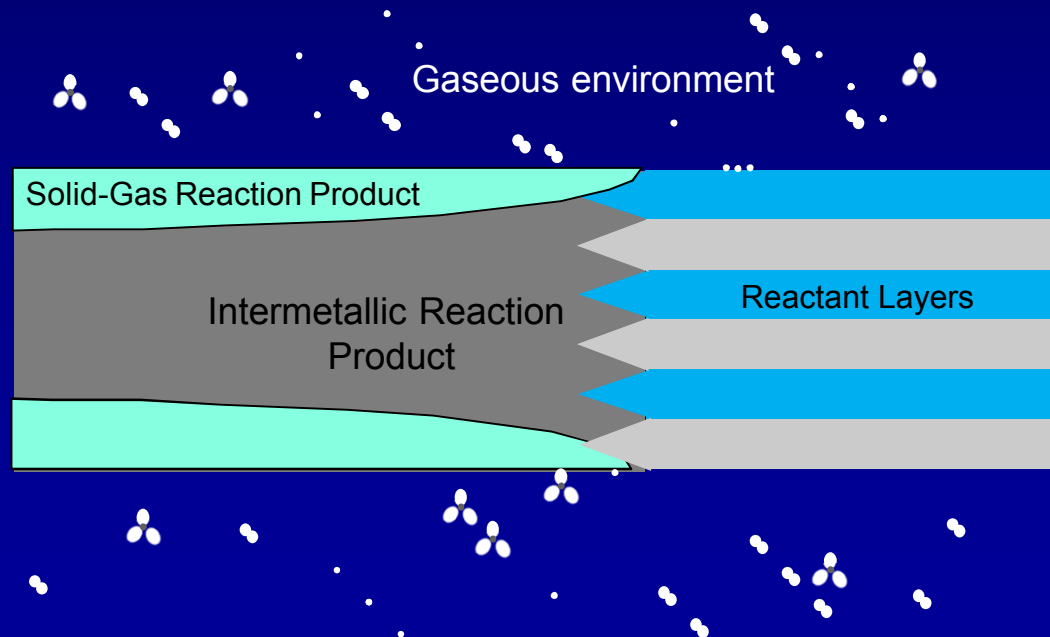
If so, how?





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

If so, how?



# Many reactive multilayers form the same, targeted intermetallic compound when reacted in air vs. vacuum.

## Cobalt / Aluminum

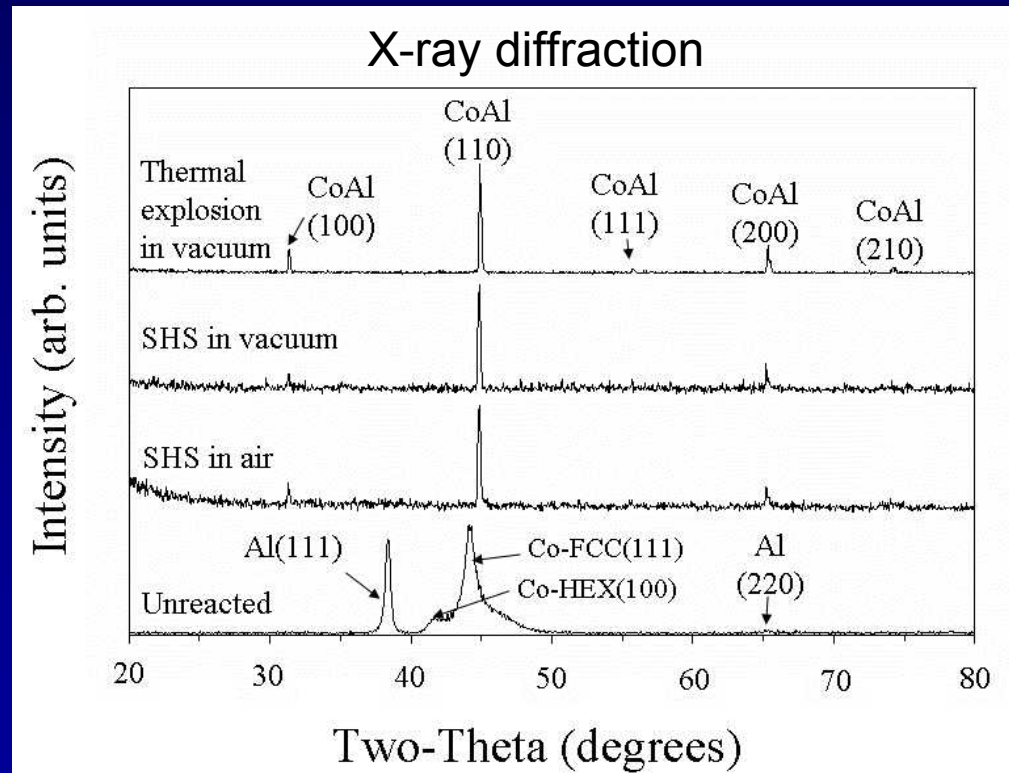
- B2 Structure (CsCl type) independent of multilayer design, ignition conditions, and surrounding gaseous environment.

- Compare Gibbs free energies

$$\Delta G_{\text{CoAl}} (1400 \text{ K}) = -70.8 \text{ kJ/mol comp.}$$

$$\Delta G_{\text{Al}_2\text{O}_3} (1400\text{K}) = -1399 \text{ kJ/mol comp.}$$

$$\Delta G_{\text{CoO}} (1400\text{K}) = -111 \text{ kJ/mol comp.}$$



# Other reactive multilayers form a very different mixture of phases when reacted in air vs. vacuum.

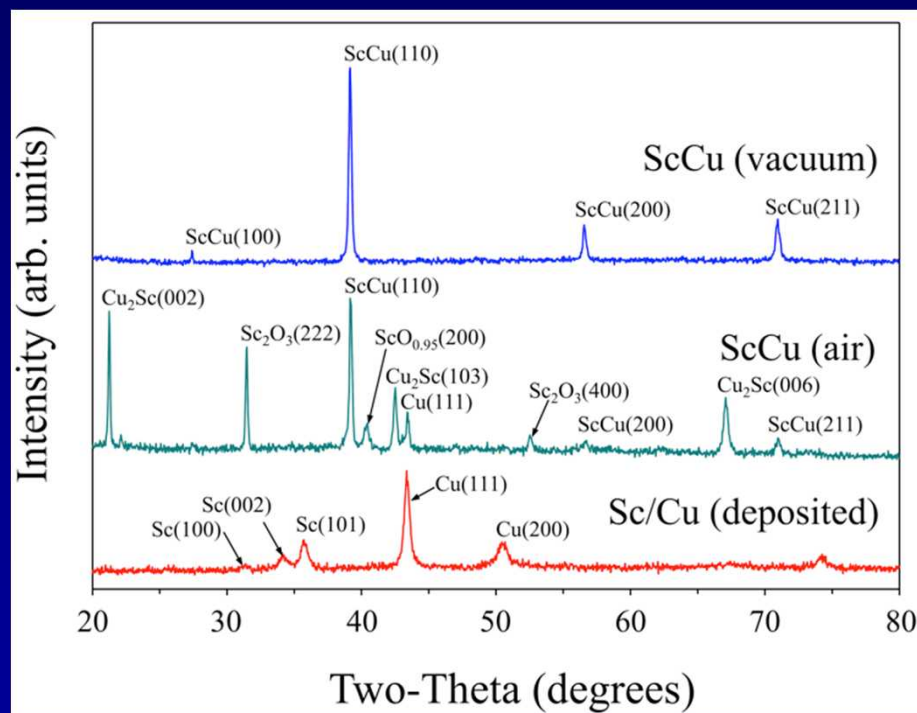
## Scandium/Copper

- B2 Structure (CsCl type) is the single phase formed when reacted in vacuum.
- A mixture of metal oxides and intermetallic compounds is formed when reacted in air.
- Compare heats of formation

$$\Delta G_{\text{ScCu}} (1400 \text{ K}) \sim -80.8 \text{ kJ/mol comp.}$$

$$\Delta G_{\text{Sc}_2\text{O}_3} (1400\text{K}) = -1908 \text{ kJ/mol comp.}$$

$$\Delta G_{\text{CuO}} (1400\text{K}) = -110 \text{ kJ/mol comp.}$$

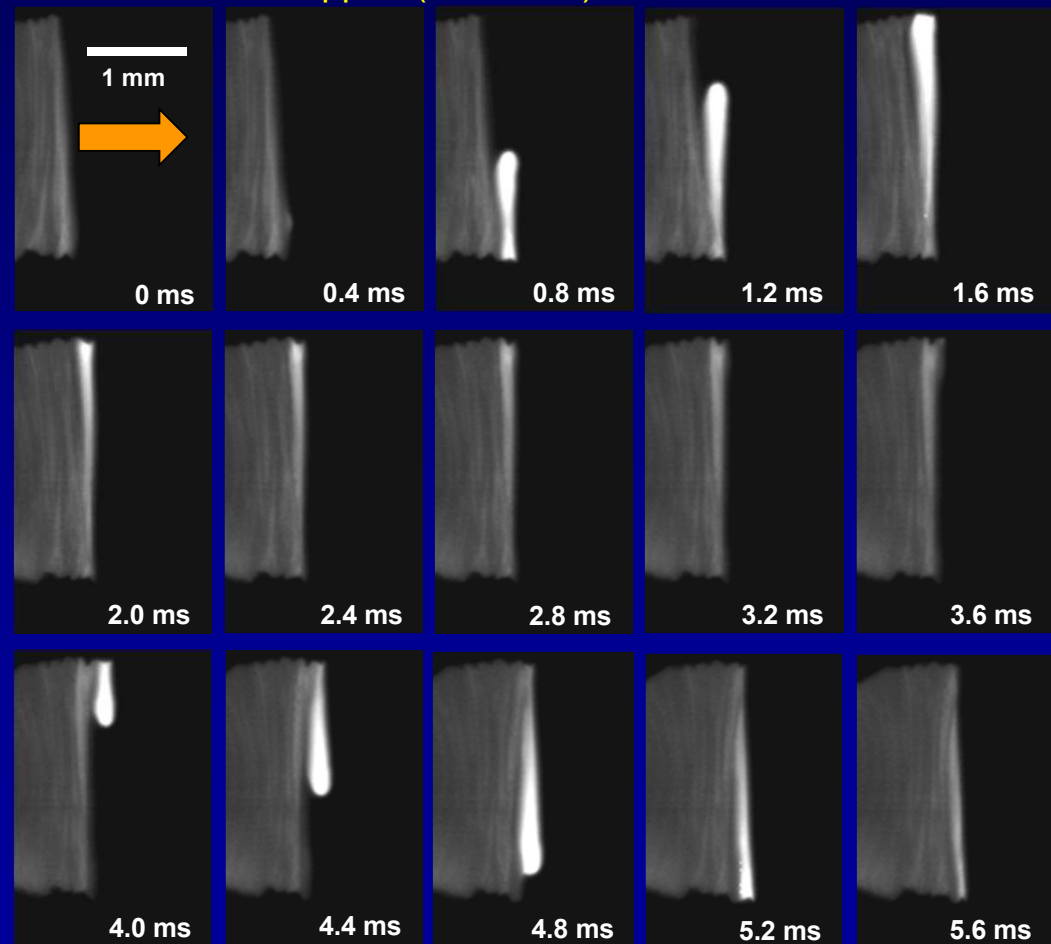


# Ni/Ti exhibits a 2-D reaction front instability when reacted in vacuum.

## Nickel / Titanium

Bilayer thickness = 4730 Å; Total thickness =  $\sim 5.0 \mu\text{m}$   
Ti capped (two sides); P = 300 mTorr

- 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
- Similar in many respects to Co/Al



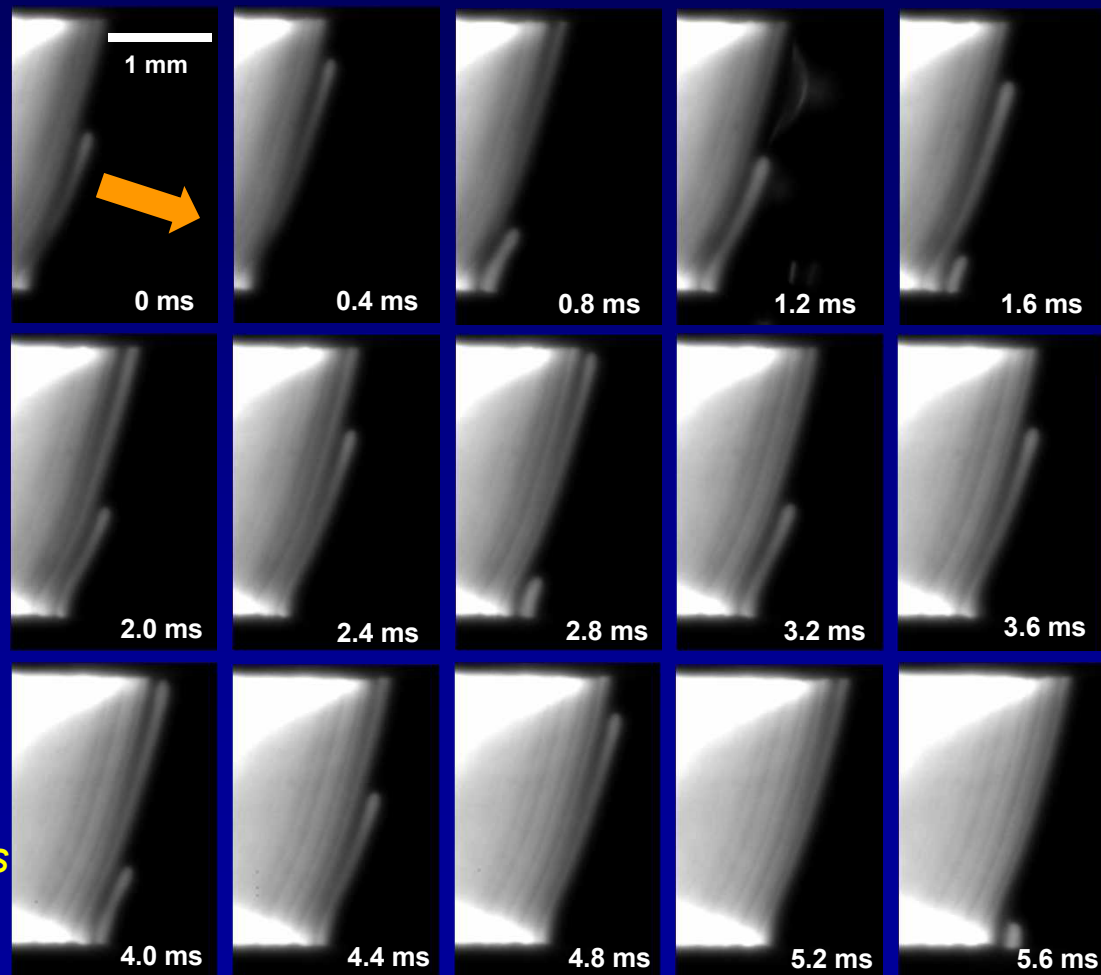
*Plan view images*

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

## Nickel / Titanium

Bilayer thickness = 4730 Å; Total thickness =  $\sim 5.0 \mu\text{m}$   
Ti capped (two sides); P = 670 mTorr 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*

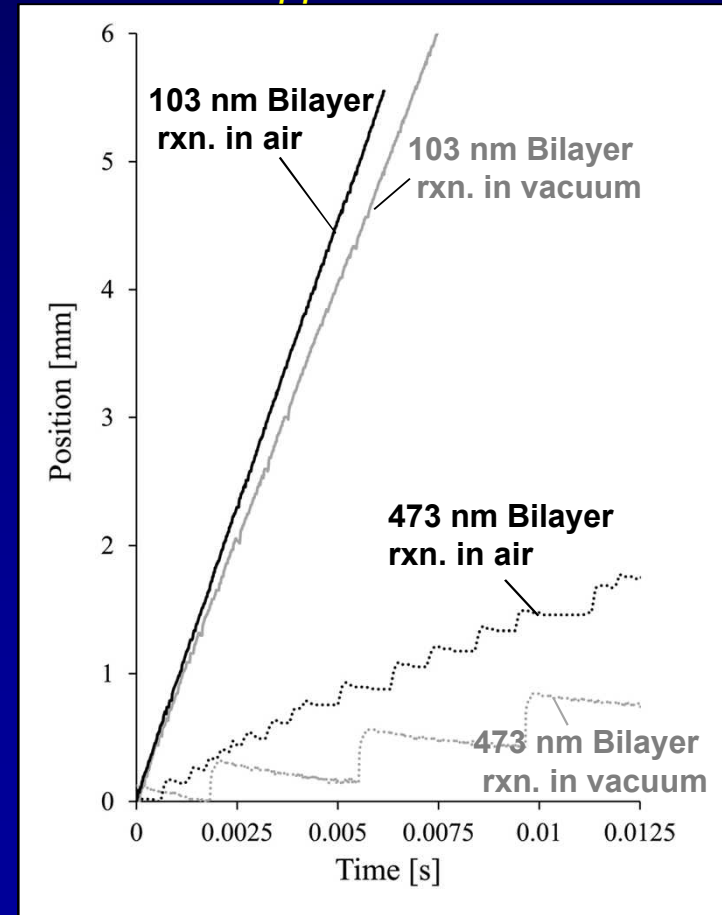
# Experiments reveal how air increases the average propagation speed of some Ni/Ti multilayers (having large bilayer thickness).

- Frequency of transverse bands is increased when air is present.
- Air does not change the transverse band speed in Ni/Ti.
- Conclude that 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 =  $5.0\ \mu\text{m}$

Ti capped both sides

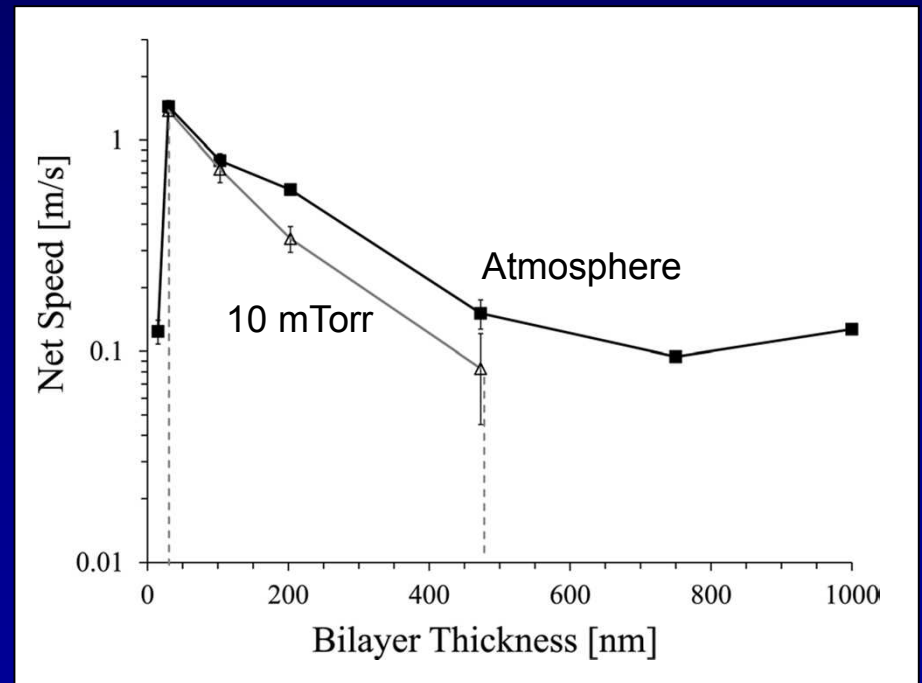




# The reactive gaseous environment (air) affects average propagation speed.

- Average propagation speed of Ni/Ti is affected by reaction environment for large bilayer thickness multilayers.
- Increased average propagation speed at atmospheric pressure for these designs.
- Oxidation extends the range of self-propagating designs.

## Nickel/Titanium



*With oxidation expected to add energy to the film how does an increase in speed occur?*

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

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- Intermetallic formation reaction moves at  $v_{\text{net}} \sim 0.9$  m/s and exhibits a 2-D instability.
- Oxidation wave trails intermetallic with  $v = 0.036 \pm 0.012$  m/s.
- Oxidation wave disturbs initial periodic morphology resulting from spin waves.
- Oxidation wave increased in speed as Sc-Cu bilayer was made larger.

*Scandium/Copper*

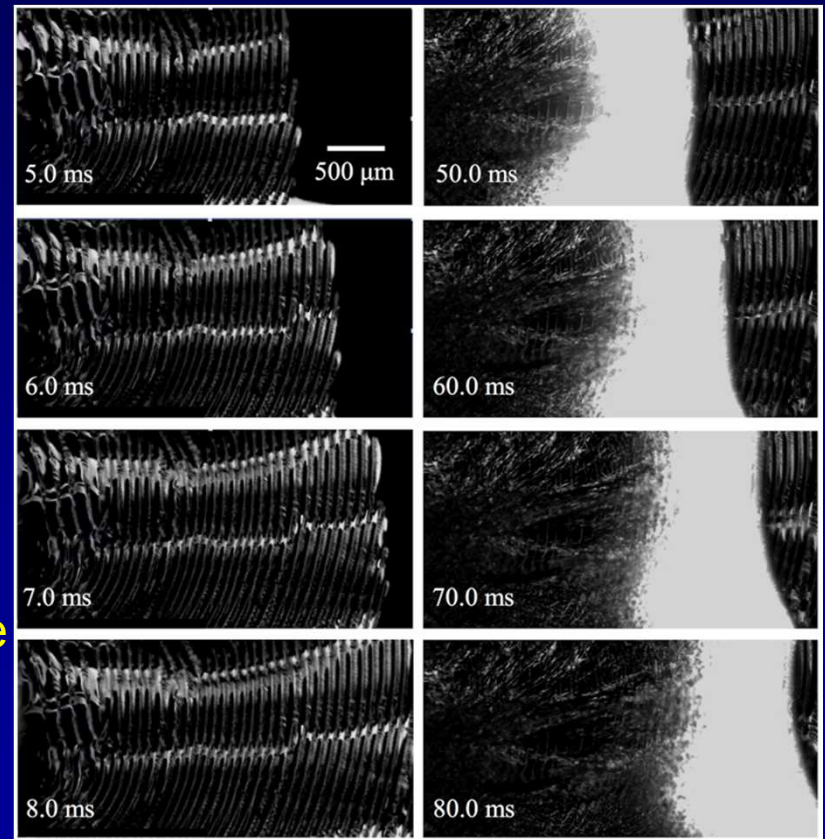


Bilayer thickness: 41 nm  
Total thickness = 2.5  $\mu\text{m}$ .

# Oxidation waves interfere with the intermetallic front of certain Sc/Cu multilayers.

- Relatively slow intermetallic reaction characterized by 2-D (spin) instability
- Trailing oxidation wave which does not proceed past intermetallic front
- Intermetallic front pushed forward when sacked by a trailing oxidation wave
- Net effect: a pulsating, spinning front.

## *Scandium/Copper*



# Summary

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- Sputter-deposition provides the required level of control (purity, density, composition, interfacial area) that is required for scientific study and various applications.
- 2-D instabilities are prevalent in low exothermicity bimetallic multilayers (now includes eight chemistries such as Ni/Al, Co/Al, Ni/Ti, Zr/Al), but the reason for this prevalence is not known.
- Two types of reaction kinetics characterize the propagating wave associated with 2-D (spin) instabilities (fast reaction at leading edge of transverse band and slower diffusion limited kinetics between bands)
- A critical forward heat transfer rate defines the stability boundary for 2-D (spin) unsteady behaviors in reactive multilayers.

# Summary continued

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- Many bimetallic multilayers undergo secondary reactions with oxygen-containing species that are present in air. This can lead to a mixture of phases that includes metal oxides.
- Secondary oxidation reactions can be distinct from the propagating intermetallic front and self propagate (although little is known about the ignition of these second waves).
- Secondary oxidation reactions can interfere with propagating intermetallic reaction waves and give rise to a variety of different behaviors including:
  - increased spin band nucleation rates (Ni/Ti) which leads to higher net propagation speeds
  - pulsating effects on intermetallic front (certain Sc/Cu designs)

# Acknowledgements

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I sincerely thank all of these folks:

Robert Reeves

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Joel McDonald

Carter Hodges

David Ingersoll

Mark Rodriguez

Joe Michael

Paul Kotula

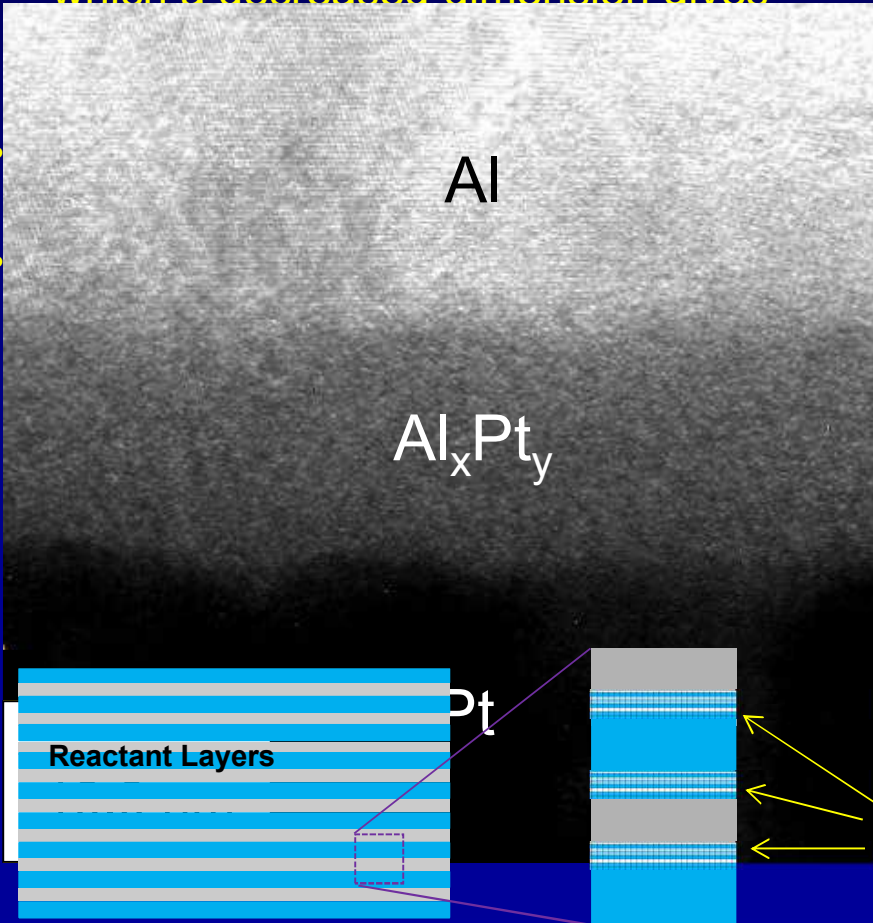




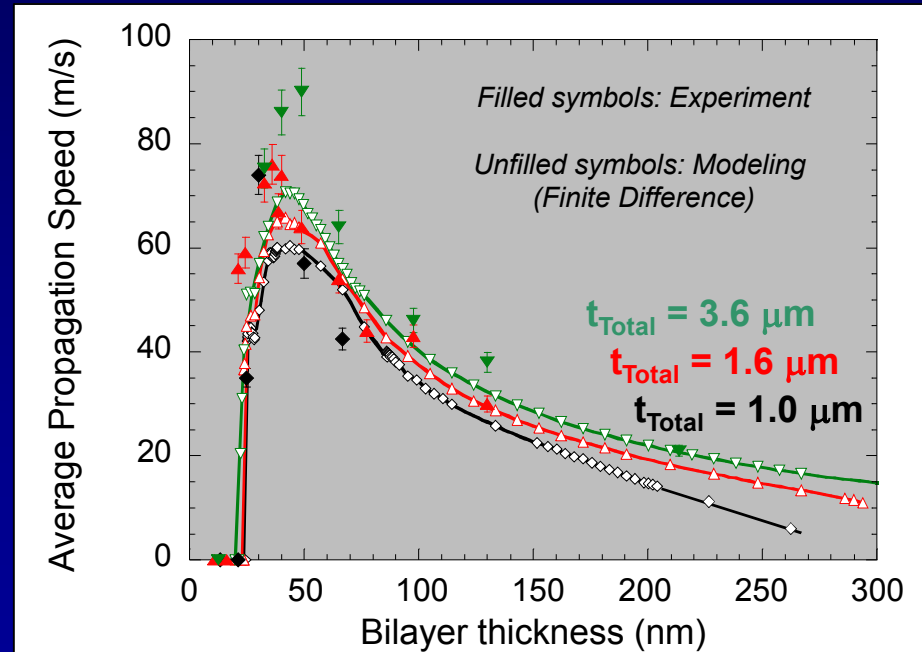
# EXTRA SLIDES

# Equiatomic Al/Pt multilayers react at high rates, up to 100 m/s, that vary with bilayer thickness.

- Large range of bilayer thickness over which a decreased dimension gives



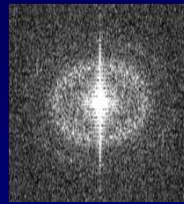
## Ex. Equiatomic Aluminum/Platinum on SiO<sub>2</sub>



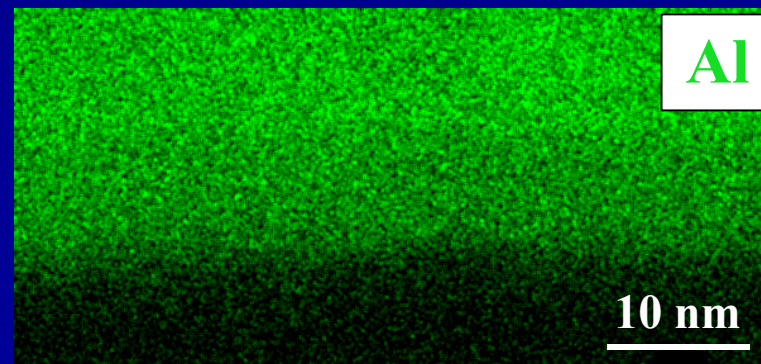
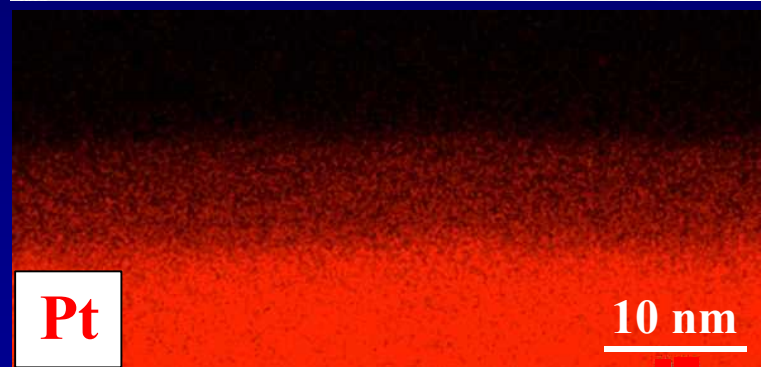
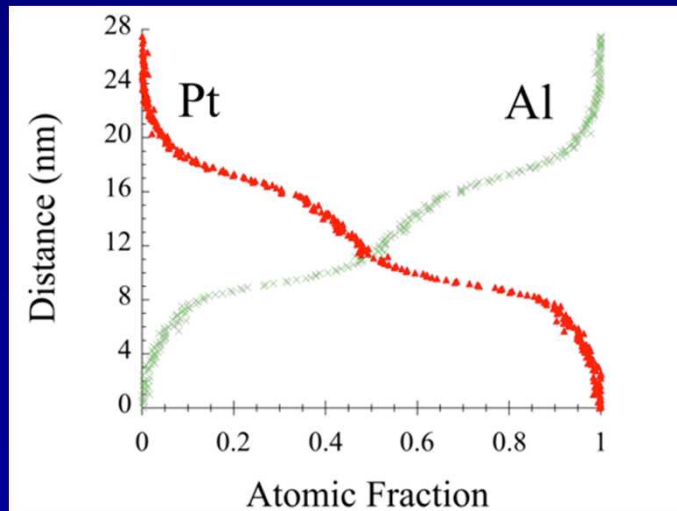
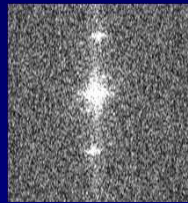
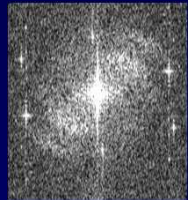
M. Hobbs, D.P. Adams  
et al. 8<sup>th</sup> World Congress  
Comp. Mech. 2008).

# Direct evidence for premixing along interfaces is provided by EDS with AC-TEM.

- Equiatomic AlPt.
- Evaluated prior to ignition.
- Premix thickness  $\sim 10$  nm.



Al-Pt



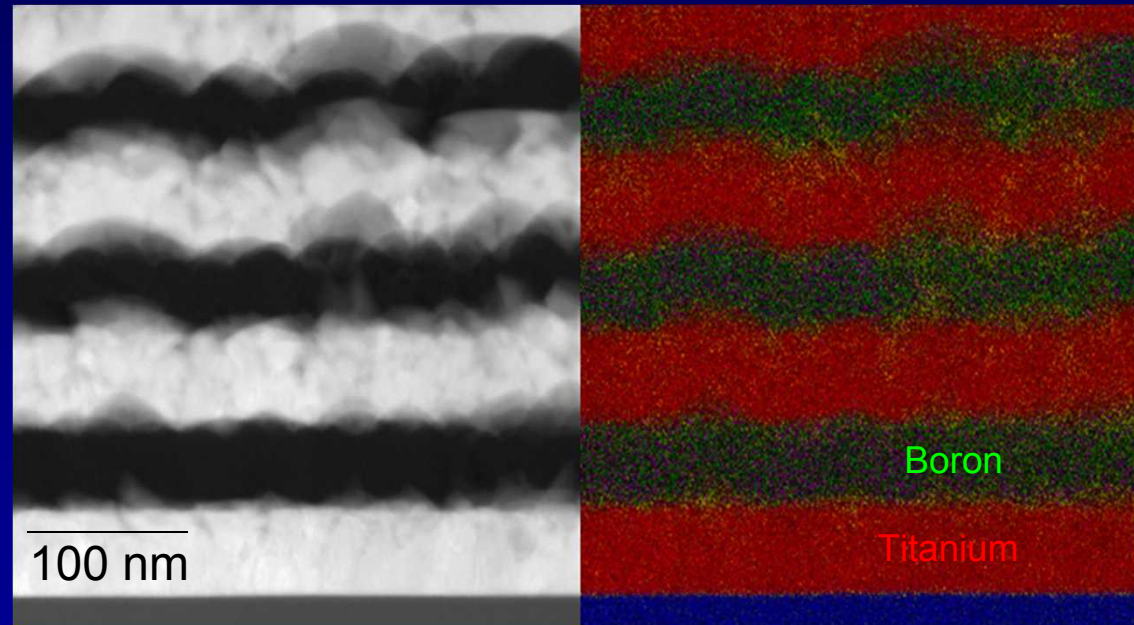
# Vapor deposition plays a vital role in fabricating multilayers for research and application.

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Sputter multilayers include

- two or more reactants
- hundreds, thousands of layers
- single, out-of-plane periodicity
- tailored interfacial area
- tailored composition

*Ti/2B multilayer imaged/mapped using AC-TEM/EDS*

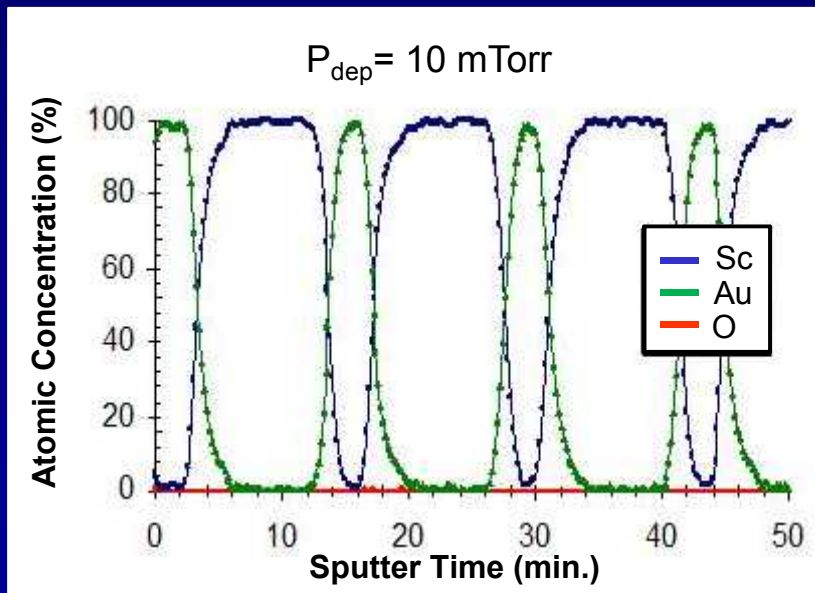


Trace Oxygen: yellow

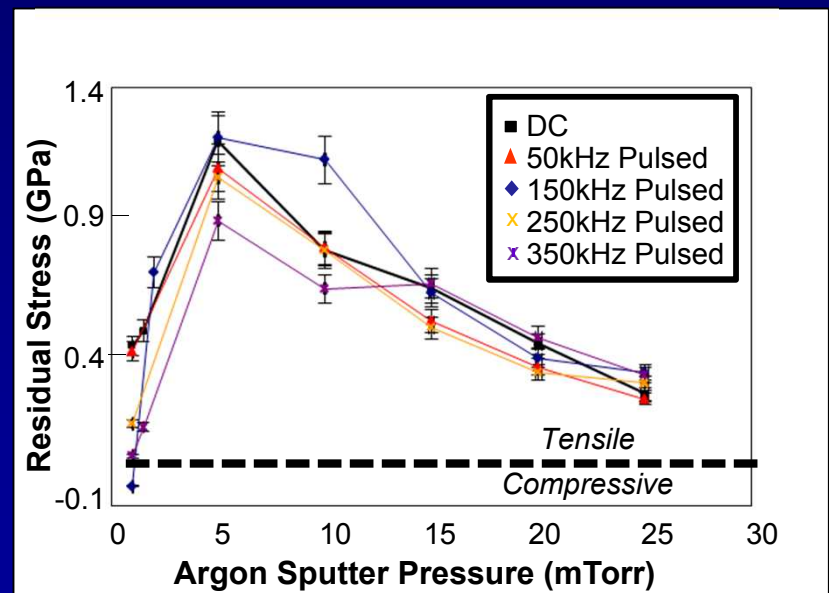
*Well-defined structure enables reliable ignition and tailorable heat release rates.  
Nanometric multilayers can be ignited with no preheating above  $T_{room}$ .*

# Sputter deposition has been used to achieve the desired purity and minimize film stress.

*Purity evaluated by  
Auger electron  
spectroscopy*



*Residual Stress  
evaluated by  
wafer curvature techniques*





# This idea was conceived several decades prior to our research.

## United States Patent [19]

Prentice

[11] 4,158,084

[45] Jun. 12, 1979

[54] HEAT SOURCES FOR THERMAL  
BATTERIES: EXOTHERMIC  
INTERMETALLIC REACTIONS

[75] Inventor: Jack L. Prentice, Ridgecrest, Calif.

[73] Assignee: The United States of America as  
represented by the Secretary of the  
Navy, Washington, D.C.

[21] Appl. No.: 770,246

[22] Filed: Feb. 18, 1977

[51] Int. Cl.<sup>2</sup> ..... H01M 6/20

[52] U.S. Cl. .... 429/112; 126/263

[58] Field of Search ..... 126/263; 252/70;  
429/112, 218, 104

### [56] References Cited

#### U.S. PATENT DOCUMENTS

2,968,932	1/1961	Vance et al. ....	126/263
2,980,103	4/1961	Scribner et al. ....	126/263
3,093,514	6/1963	McCallum et al. ....	429/218
3,335,246	10/1970	Crowell, Jr. et al. ....	252/70
3,558,363	1/1971	Franklin ..... 429/112	
3,575,714	4/1971	Bennett et al. .... 429/112	
3,625,767	12/1971	Clark et al. .... 429/112	
3,669,748	6/1972	McCullough et al. .... 429/112	

3,885,989	5/1975	Bush .....	429/104
4,041,220	8/1977	Armand .....	429/218

#### OTHER PUBLICATIONS

Combustion and Flame (2), pp. 77-89 (1973), Hardt, A. P. and Phung, P. V. "Propagation of Gasless Reactions in Solids-I, Analytical Study of Exothermic Intermetallic Reaction Rates".

Combustion and Flame (2), pp. 91-97 (1973), Hardt, A. P. and Holsinger, R. W., "Propagation of Gasless Reactions in Solids-II, Experimental Study of Exothermic Intermetallic Reaction Rates".

Primary Examiner—Ronald C. Capossela  
Attorney, Agent, or Firm—R. S. Sciascia; W. Thom  
Skeer; Lloyd E. K. Pohl

#### [57] ABSTRACT

An intimate mixture of two or more finely divided metals is formed into a heat pad or pellet for a thermal battery. The metals are chosen to react exothermically in a self-sustaining manner to provide a heat source for the battery whereby the battery electrolyte, normally a solid, is melted and the battery generates current.

11 Claims, 1 Drawing Figure

Present day heat sources using iron fuel have the further drawback of requiring at least 150 msec to attain operating temperature. This is an excessive delay for

Another method involves vapor deposition. One metal may be deposited on particles or foils of another or both metals may be co-deposited on a suitable substrate, such as quartz gauze or plates. The sputtering rates of the various metals must be adjusted to allow them to be deposited in the proper proportions. For instance boron has much lower sputtering rate than titanium, and Ti/2B mixtures deficient in boron were found to be difficult to initiate. This problem may be circumvented by depositing alternate layers of the desired metals.

# A variety of metal-metal multilayers have been evaluated at Sandia

Exothermic Materials (2-50 micron thick foils)	Composition of foil	Heat of reaction (kJ/mol atoms)	Propagation speeds (m/s)	Ignition Temperatures (°C)
Sc/Au	ScAu	-111 #	10 - 40	tbd
Y/Au	YAu	-110 #	8 - 15	tbd
Ti/B	TiB <sub>2</sub>	-102 #	10 - 30	tbd
Al/Pt	AlPt	-100	15 - 95	tbd
Ni/Al	NiAl	-60 #	6 -10	200 - 300
Co/Al	CoAl	-58	0.3 – 10	280 - 450
Y/Ag	YAg	-44 #	0.5 – 0.8	tbd
Sc/Ag	ScAg	-43 #	0.2 – 0.5	tbd
Ni/Ti/B	Ni <sub>.43</sub> Ti <sub>.48</sub> B <sub>.09</sub>	-38	0.5 - 4.5	340 - 500
Ni/Ti/C	Ni <sub>.43</sub> Ti <sub>.48</sub> C <sub>.09</sub>	-37	1 – 5.0	320 - 480
Sc/Cu	ScCu	-36	0.2 - 0.9	tbd
Ni/Ti	NiTi	-34	0.1 – 1.0	280 - 400
Y/Cu	YCu	-32 #	0.2 – 0.4	tbd

Nanofoil from  
Reactive Nanotech.,  
Inc.

Compare with

$\Delta H_o$  (Al<sub>2</sub>O<sub>3</sub>) =  
-1670 kJ/mol



# A variety of metal-metal multilayers have been evaluated at Sandia

Exothermic Materials (2-50 micron thick foils)	Composition of foil	Heat of reaction (J/g)	Propagation speeds (m/s)	Adiabatic reaction temperatures (°C)
Ti/B	TiB <sub>2</sub>	-4403 to -5240	10 - 30	3275
Al/Pt	AlPt	-1505 to -1870	15 - 95	2798
Ni/Al	NiAl	-1400 to -1680	6 - 10	>1637
Co/Al	CoAl	-1120 to -1350	0.3 – 10	>1639
Sc/Au	ScAu	-917	10 - 40	unknown
Ni/Ti/B	Ni <sub>.43</sub> Ti <sub>.48</sub> B <sub>.09</sub>	-772	0.5 - 4.5	unknown
Y/Au	YAu	-769	8 - 15	unknown
Ni/Ti/C	Ni <sub>.43</sub> Ti <sub>.48</sub> C <sub>.09</sub>	-751	1 – 5.0	unknown
Sc/Cu	ScCu	-663	0.2 - 0.9	unknown
Ni/Ti	NiTi	-637	0.1 – 1.0	1568
Sc/Ag	ScAg	-562	0.2 – 0.5	unknown
Y/Ag	YAg	-447	0.5 – 0.8	unknown
Y/Cu	YCu	-419	0.2 – 0.4	unknown

Compare with  
 $\Delta H_o$  (Fe/KClO<sub>4</sub>) ~  
 -1560 J/g