

Steady and Unsteady Propagation in Exothermic Multilayers

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D.P. Adams

Sandia National Laboratories
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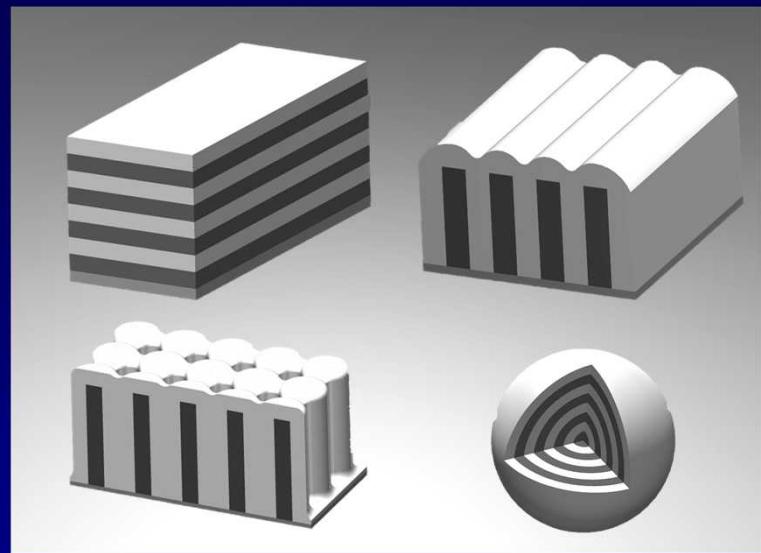


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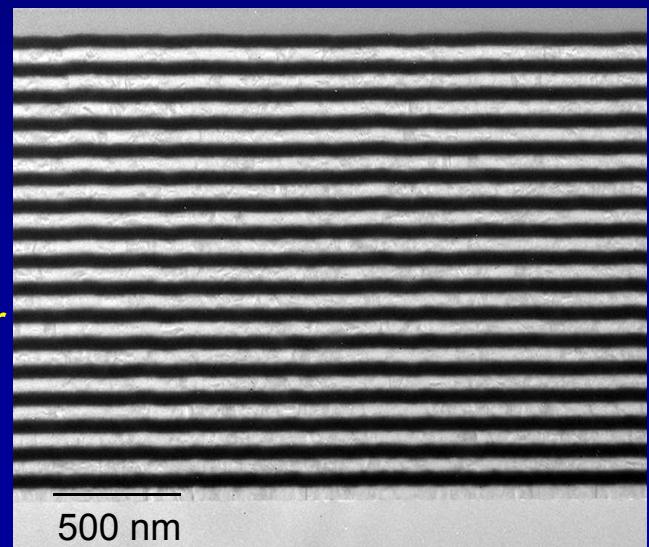


Vapor deposition provides the desired level of control (thickness, composition, purity) for scientific study.

- 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



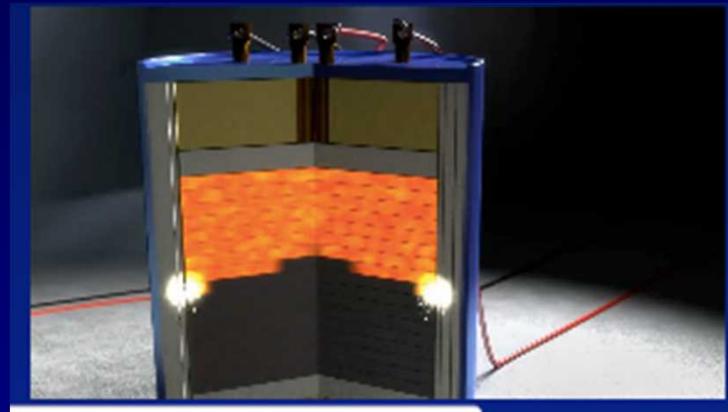
*Pt/Al
Multilayer*



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.

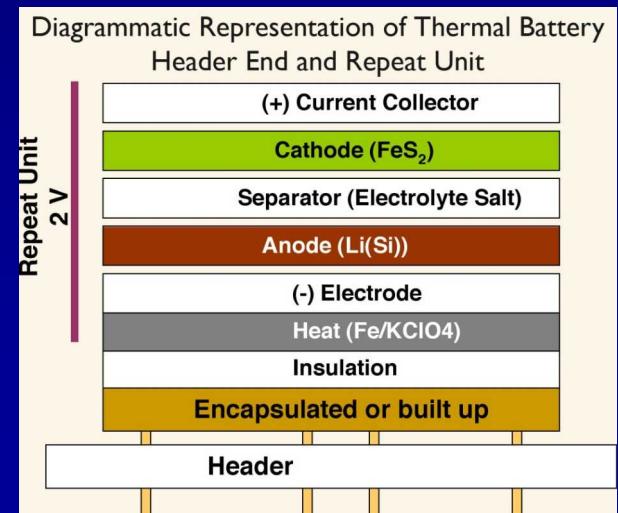
- Silver-zinc battery : electrolyte held in reservoir
 - A thermal battery : electrolyte is frozen



- Traditional heat source (thermal battery):



- blends of Fe/KClO₄ 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.

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

- Comparable heats of reaction

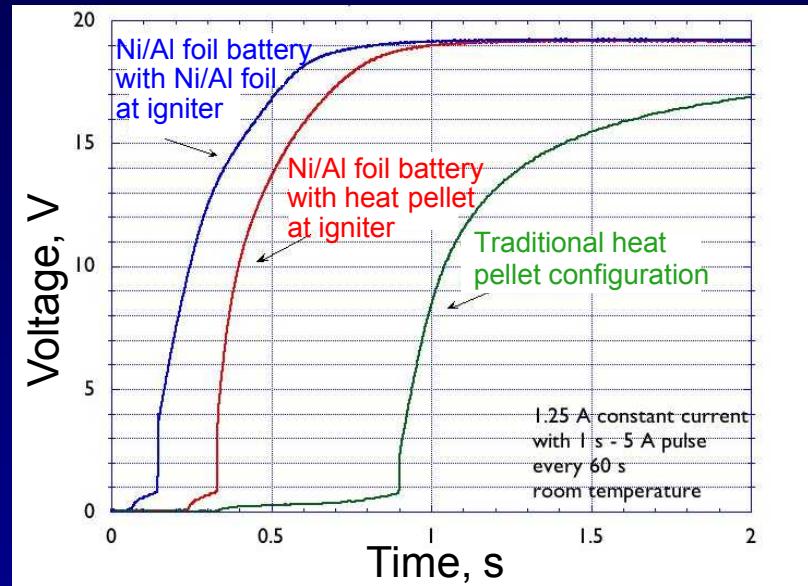
Composition	Calorific Output (cal/g)	Burn Rate (cm/s)
88/12 Fe/KClO ₄	221	7-12
86/14 Fe/KClO ₄	259	5-18
84/16 Fe/KClO ₄	292	12-20
equiat. Ni(V)/Al	250-298	~700

- Ni(V)/Al remains electronically conductive through reaction

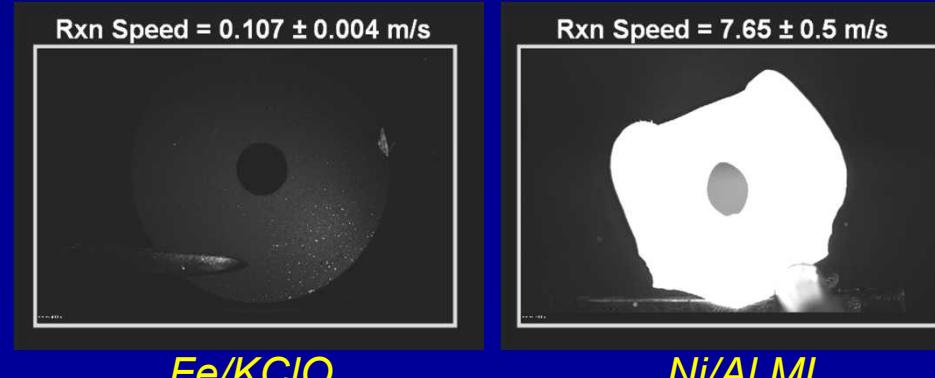
- Original Reference for Deposited MLs

J. Prentice, 1979 U.S. Patent
“Heat sources for thermal batteries:
exothermic intermetallic reactions”

Battery rise time comparison

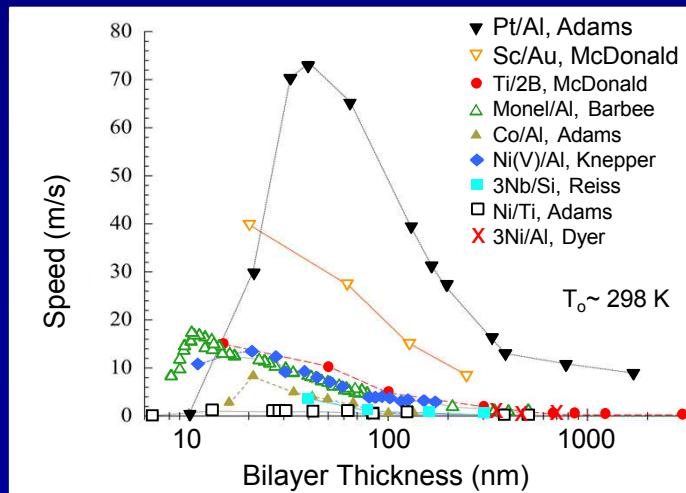
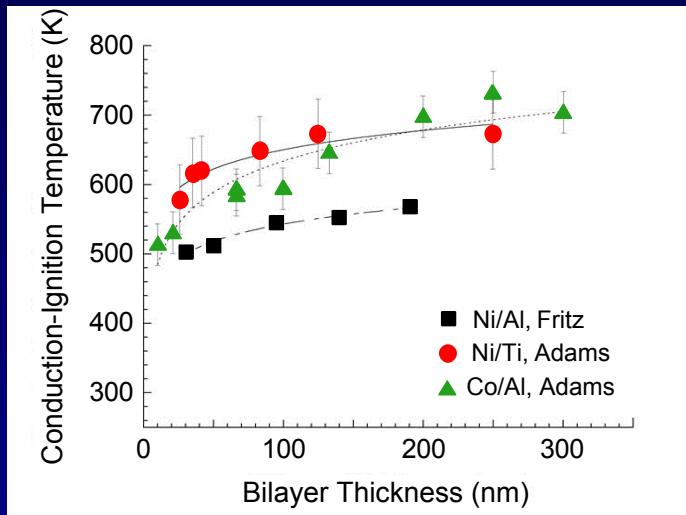


Wavefront speed comparison in plan view



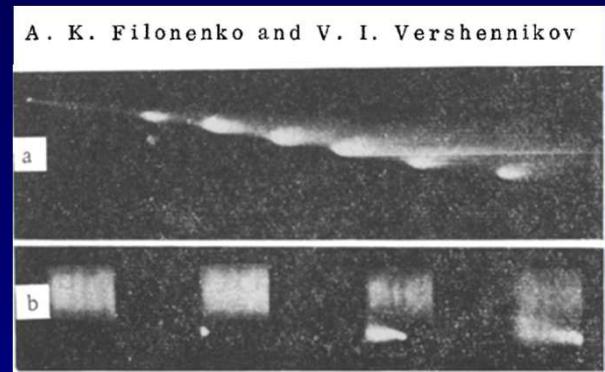
Planar reactive multilayers exhibit several key material properties that can be tailored.

- 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)

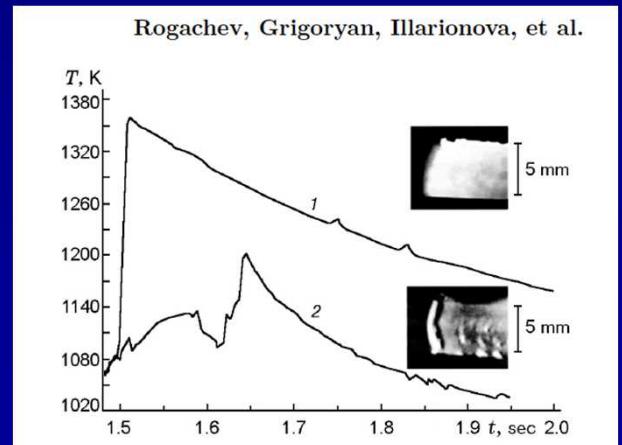


Motivation: Understanding and controlling stability

- 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



A. K. Filonenko and V. I. Vershennikov
Mechanism of Spin Burning of Titanium in Nitrogen, Fizika Gorenija i Vzryva 11 (1974).

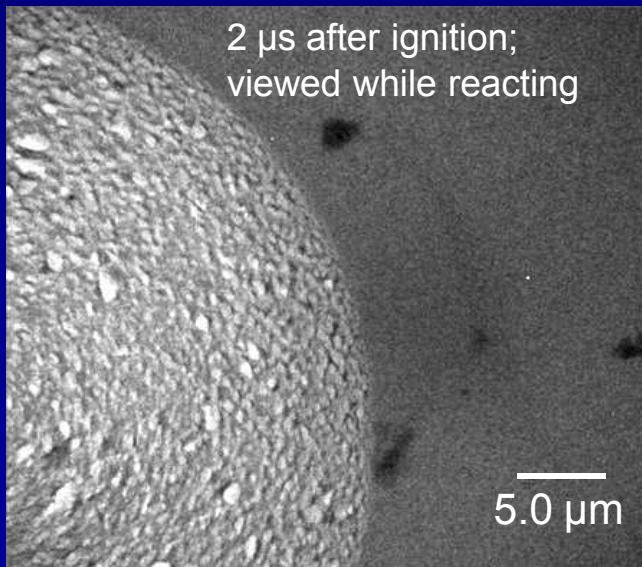


Gasless combustion of Ti-Al Bimetallic Multilayer Nanofoils Combust. Expl. Shock Waves 40 (2004).

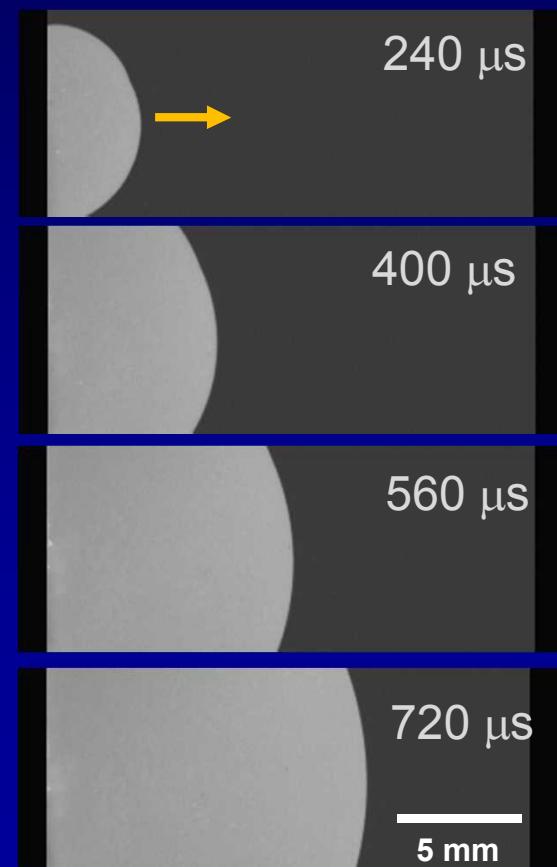
Many reactive multilayer systems exhibit a steady propagating reaction.

- 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*

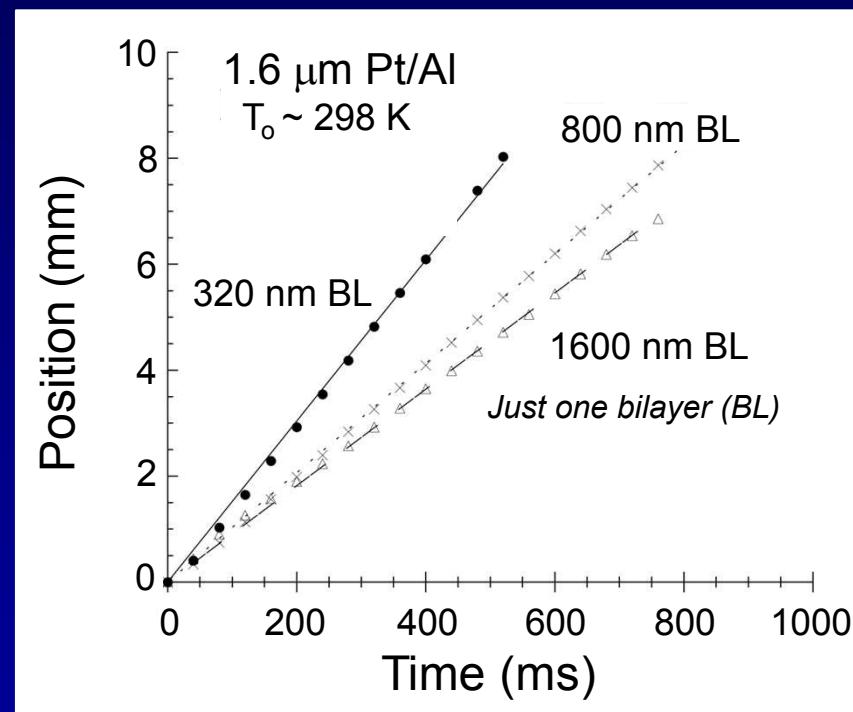


*Al/Pt multilayer in plan view
high speed optical microscopy*



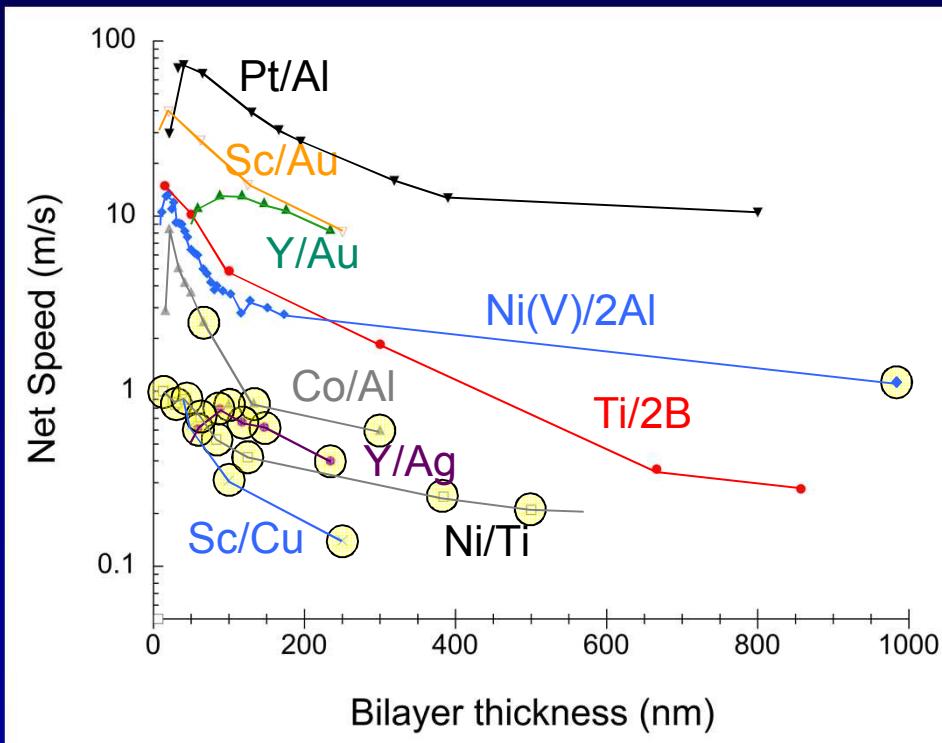
Evidence for steady propagation comes from plots of front position vs. time.

- 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.



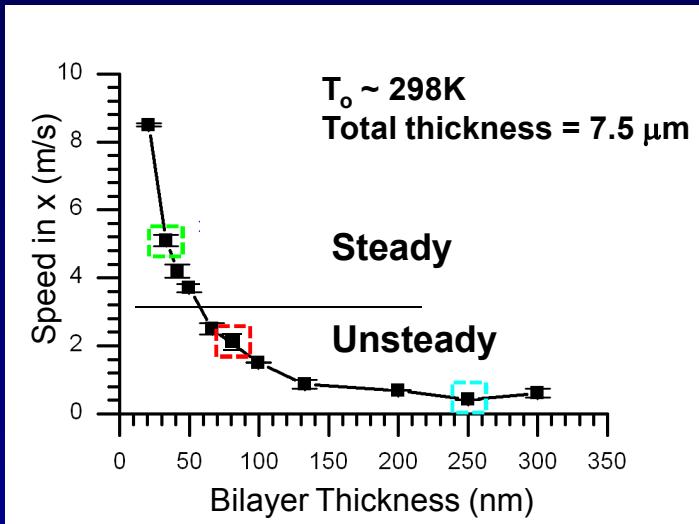
Large exothermicity systems are generally found to exhibit steady propagation.

- Large ΔH_0 systems (Pt/Al, Sc/Au, Y/Au) exhibit steady propagating reactions.
- Low ΔH_0 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 μm

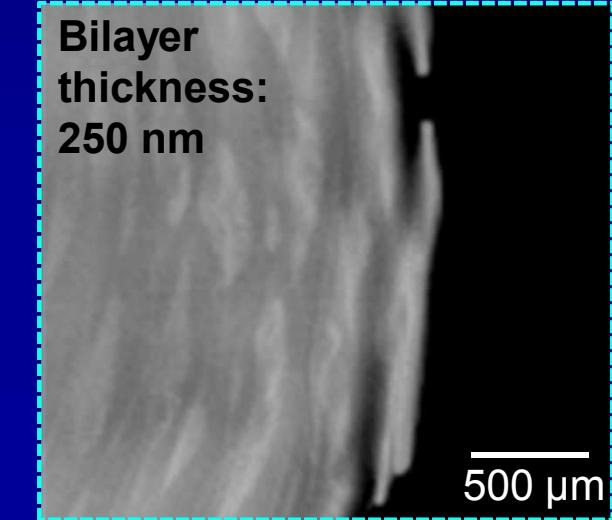
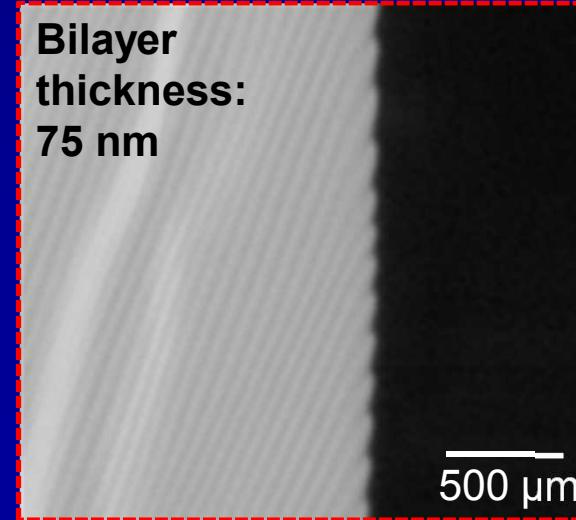
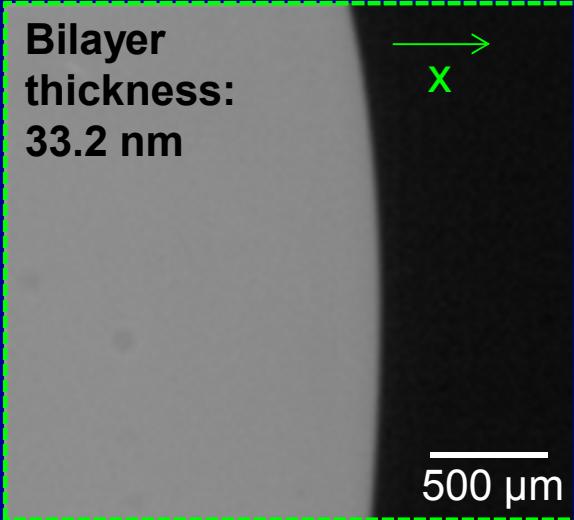
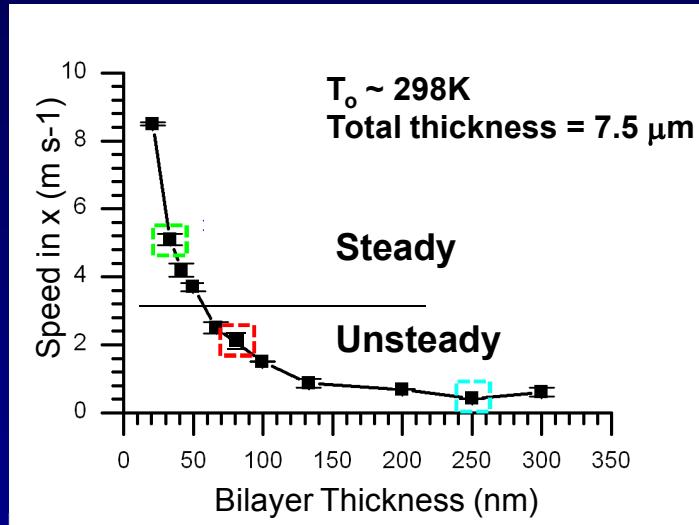
Bilayer thickness:
75 nm

500 μm

Bilayer thickness:
250 nm

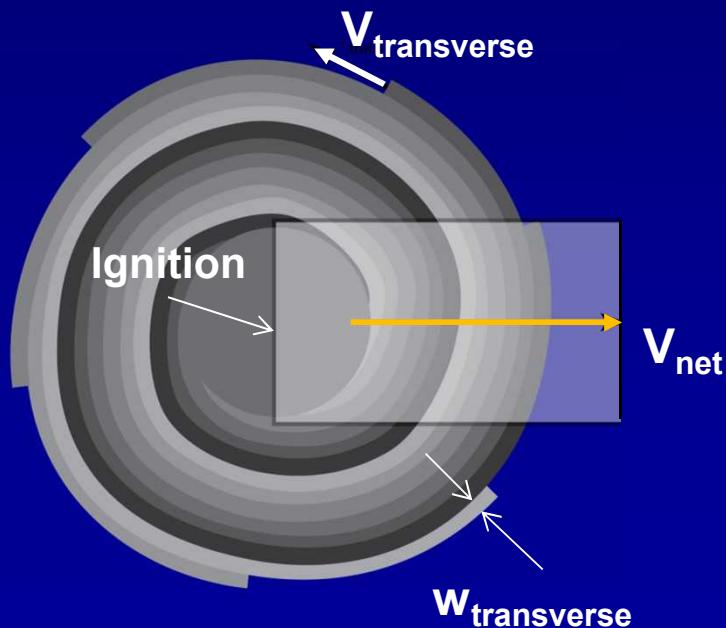
500 μm

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

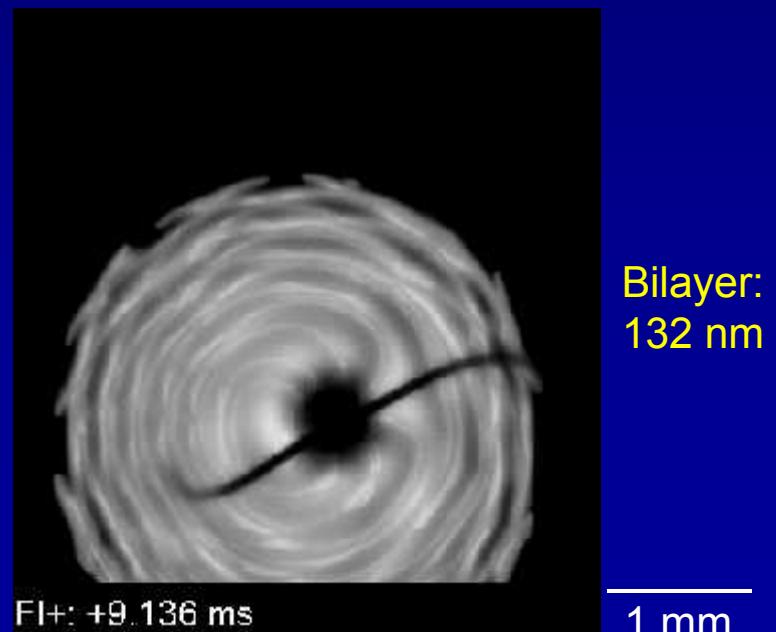
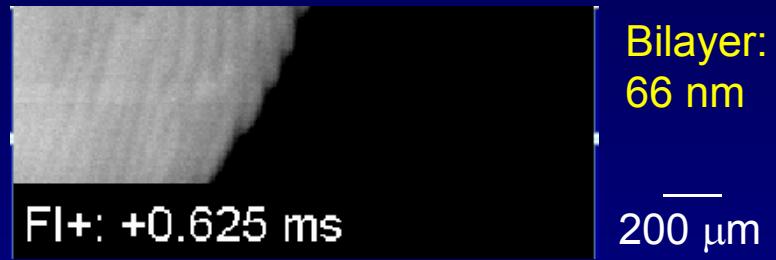


Large bilayer thickness Co/Al multilayers are characterized by 2-D (spin-like) instabilities.

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

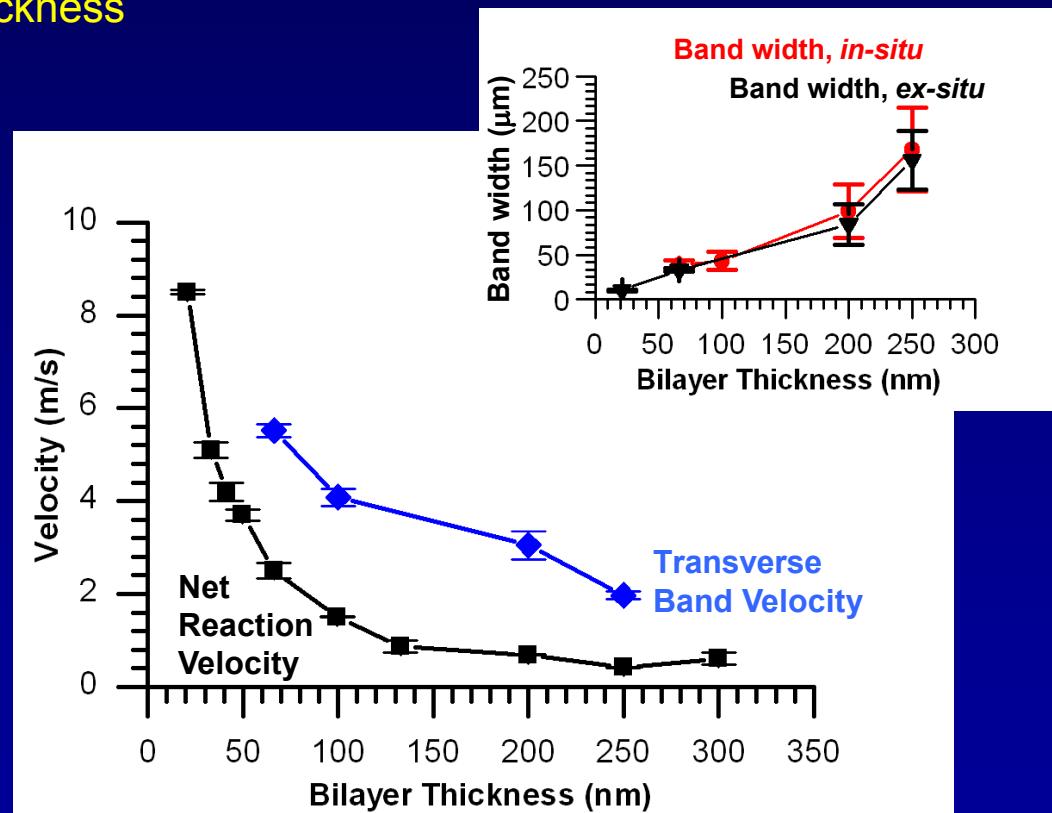
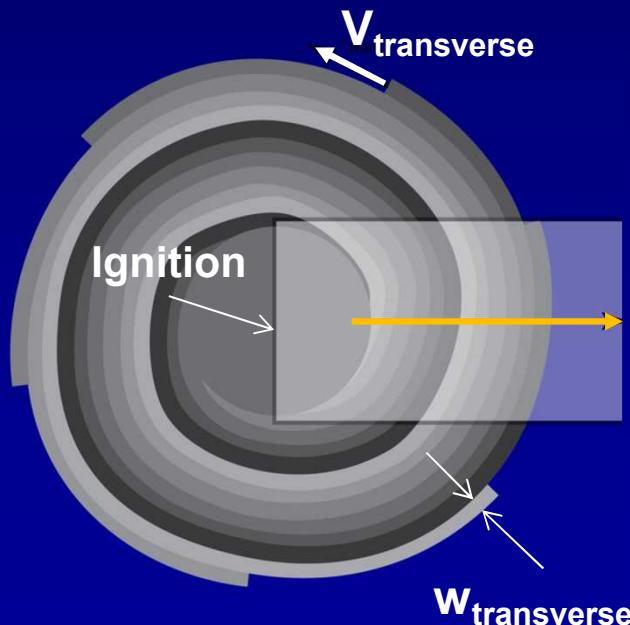


*Cobalt/Aluminum
(in plan view)*



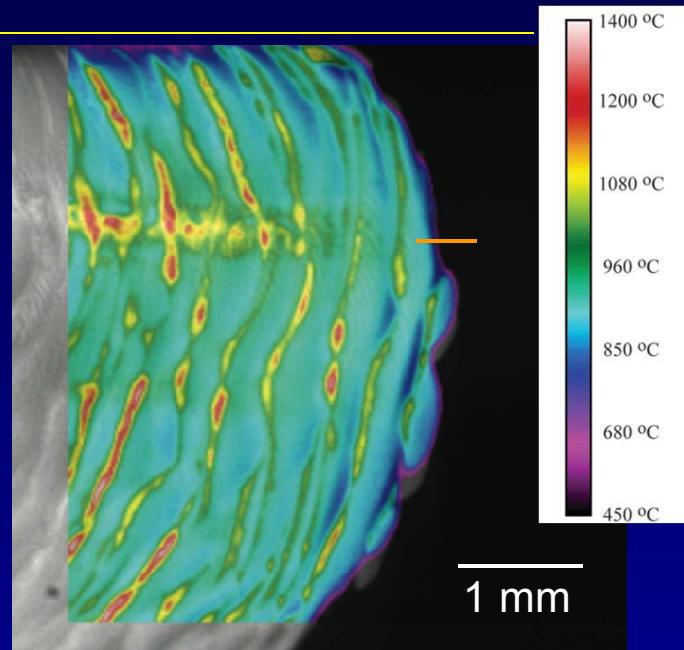
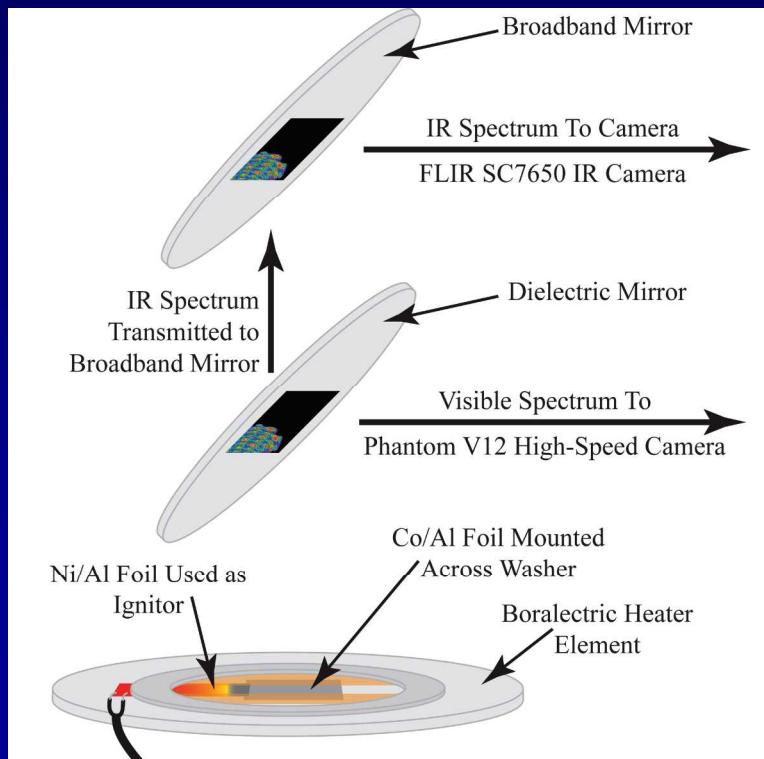
Large bilayer thickness Co/Al multilayers are characterized by 2-D (spin-like) instabilities.

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

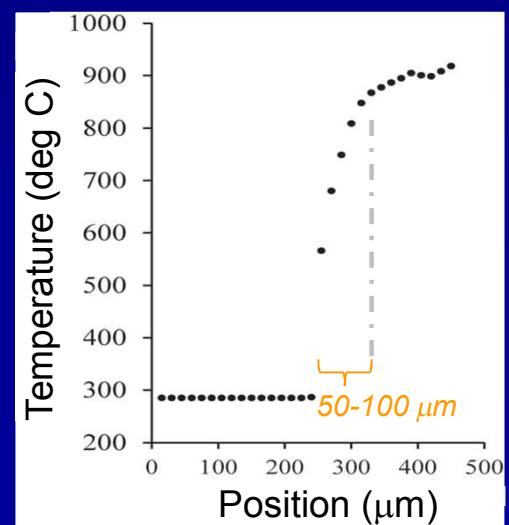


Spin mode is characterized by large temperature variations and chemical kinetics that vary over micron scales.

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



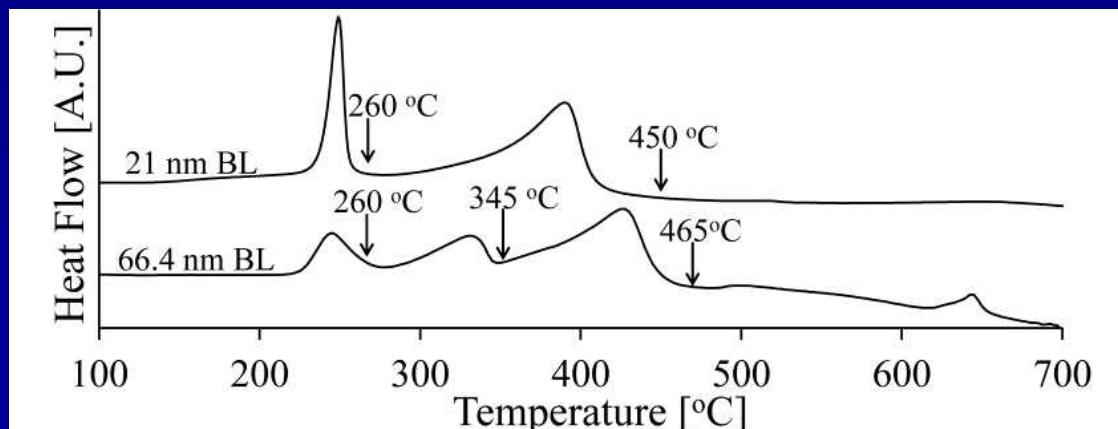
Temperature profile across line drawn above



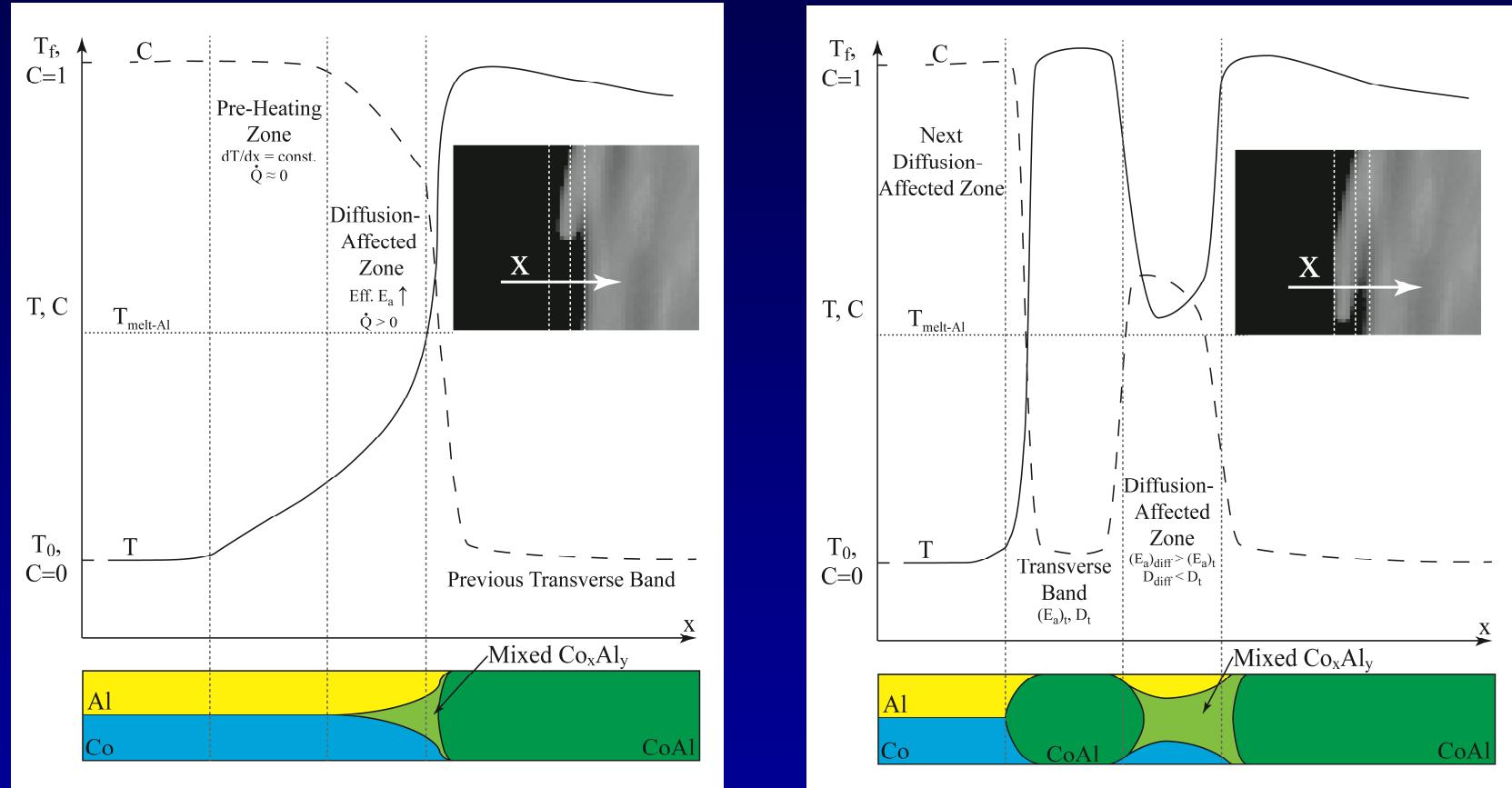
Quenched Samples Phase ID (after slow heating)

	Co	Al	Co_2Al_9	$\text{Co}_4\text{Al}_{13}$	Co_2Al_5	CoAl
BL \leq 33.2 nm	Initial	x	x			
	Exotherm 1	x		x	o	o
	Exotherm 2					x
BL \geq 66.4 nm	Initial	x	x			
	Exotherm 1	x	x	x	o	o
	Exotherm 2	x		o	o	o
						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.

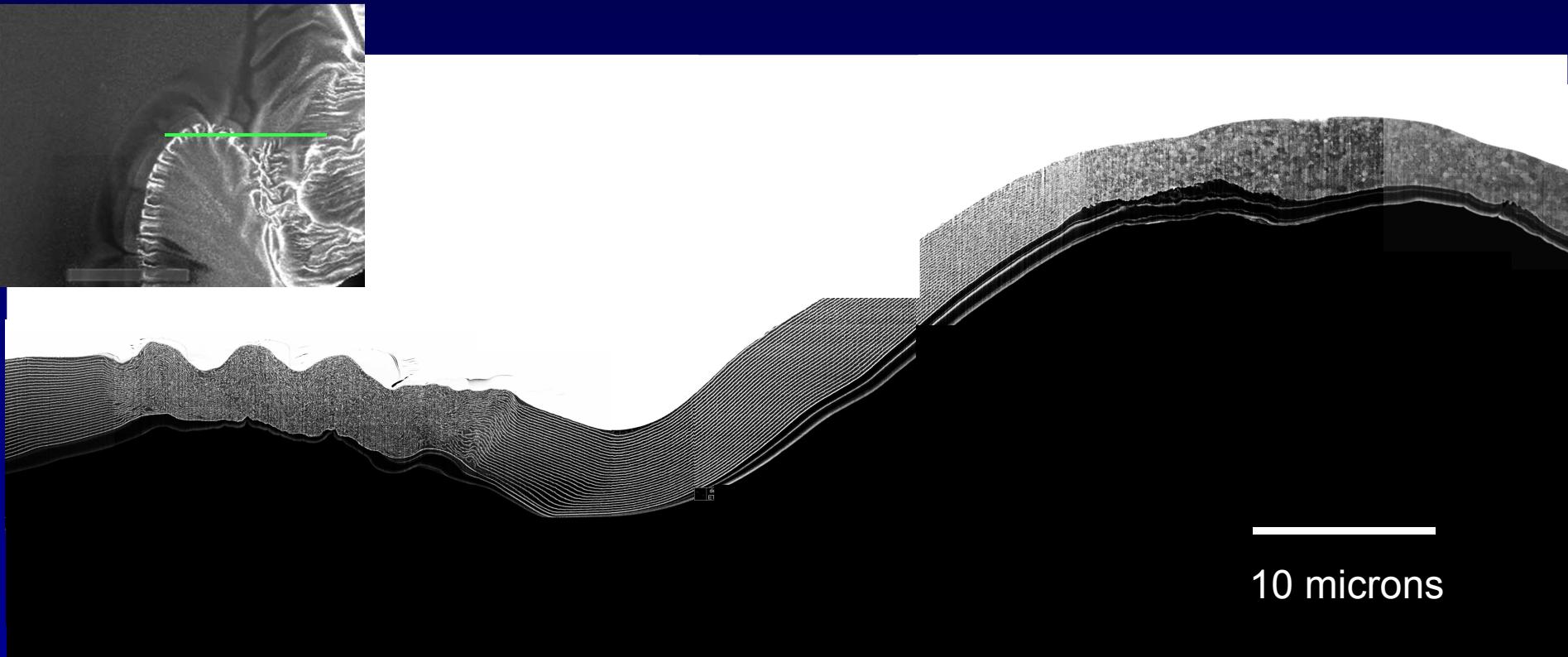


Proposed mechanism for unsteady propagation



- 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

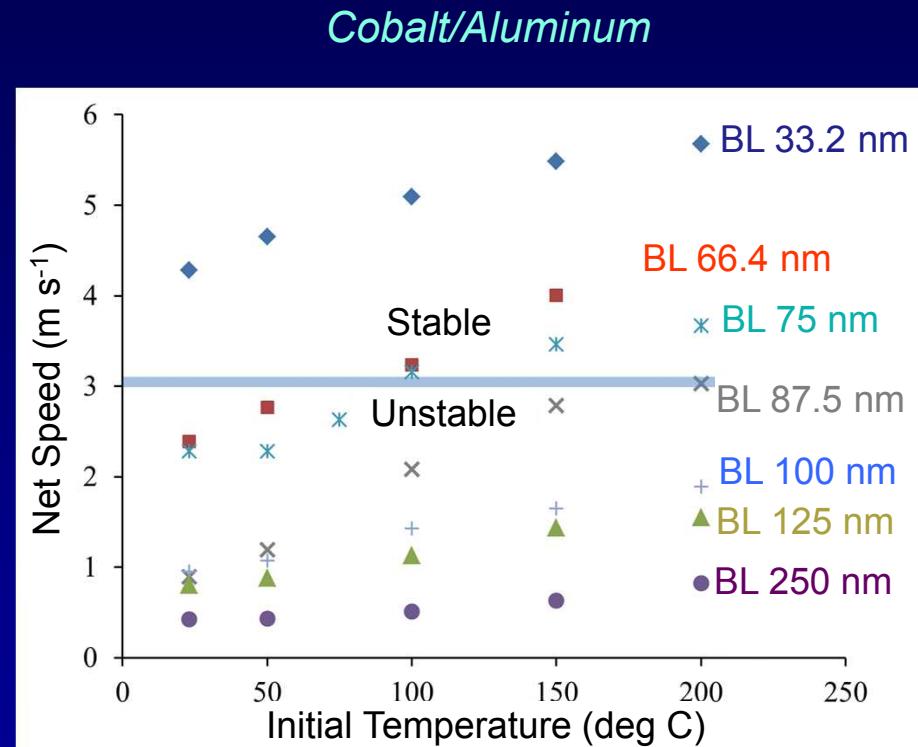
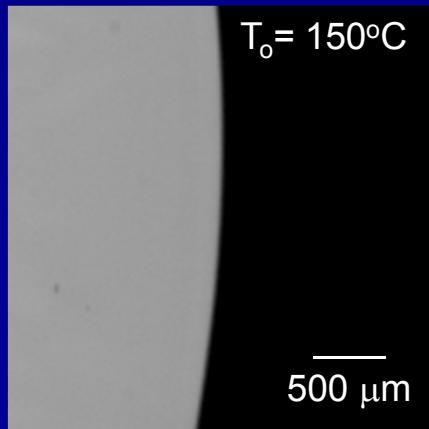
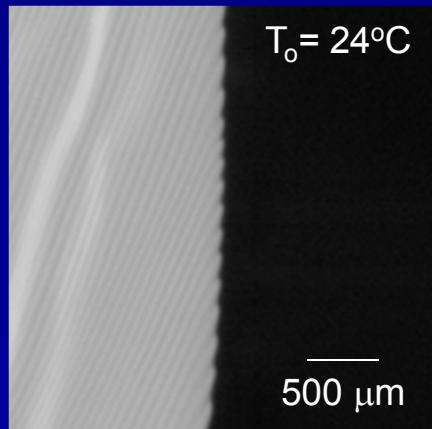
Evidence for diffusion affected zones is suggested by quenched samples.



- Intermediate area in quenched sample is characterized by a mixture of reactants (Co, Al) and Co_2Al_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.



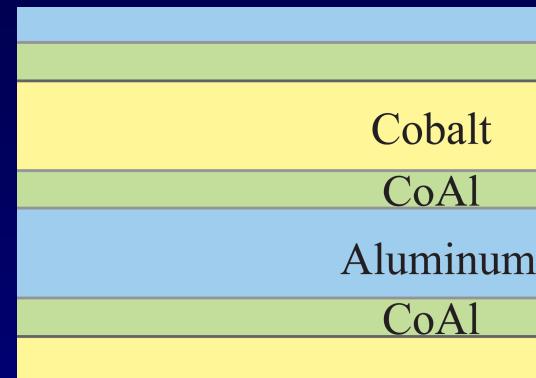
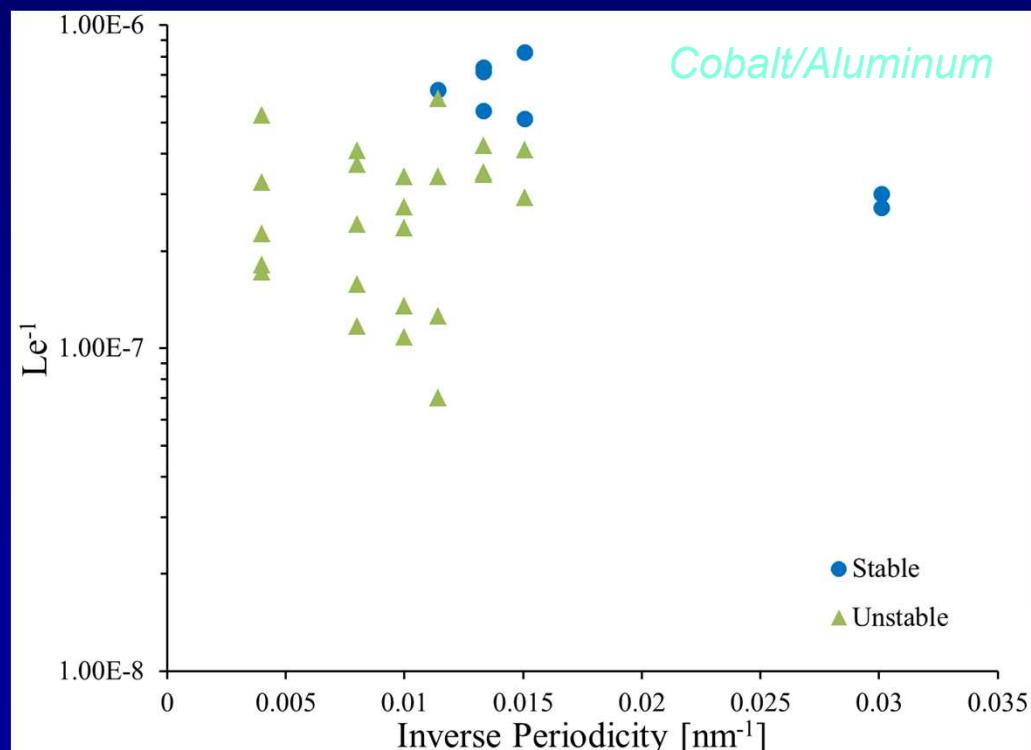
Bilayer thickness: 75 nm
Total thickness: 7.5 μm

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

Le^{-1} at Transition to Stability

Using Armstrong's relationship*,

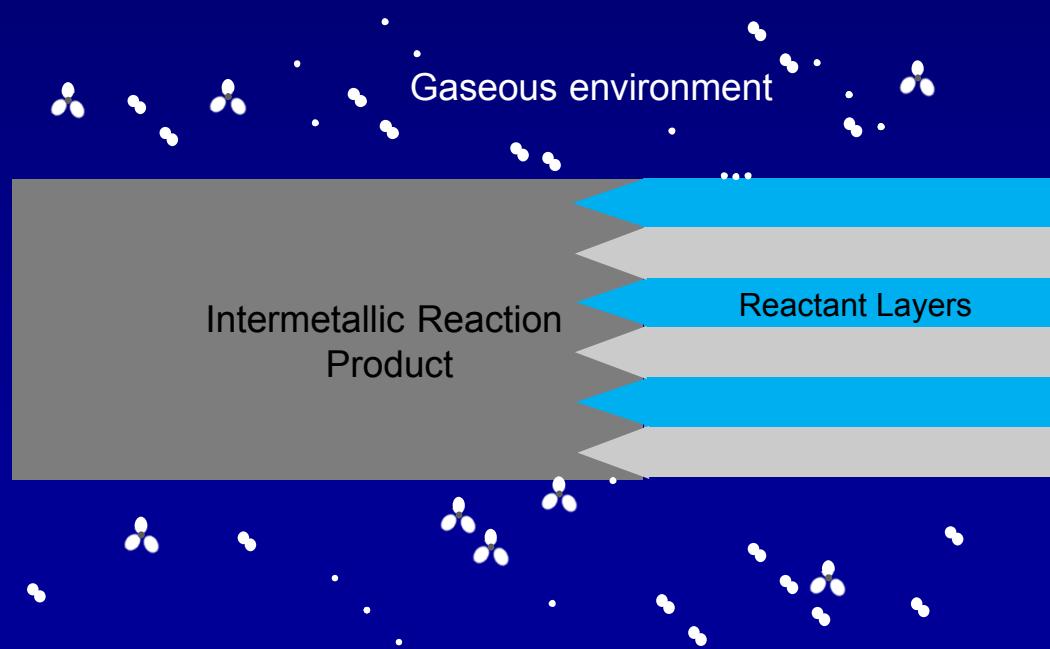
$$Le^{-1} = D/\lambda = \frac{u^2 \delta^2 E_a (T_{max} - T_o)}{3\lambda^2 T_{max}^2 R} = A \exp(-E_a/RT_{max})$$



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

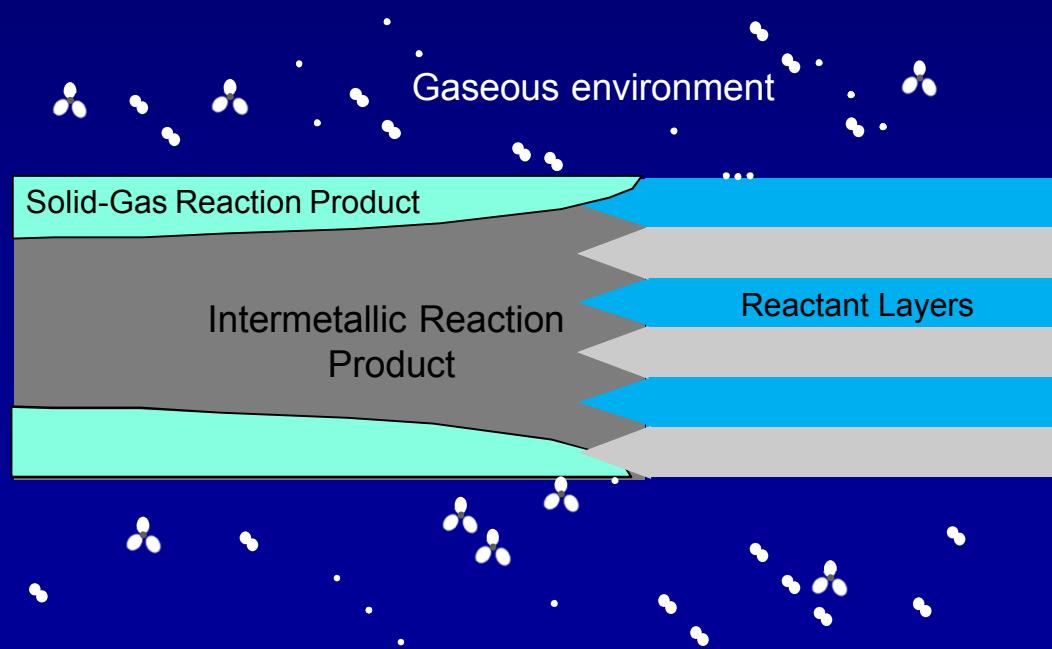
Are self-propagating reactions in reactive multilayers affected by the surrounding gaseous environment?

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.

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

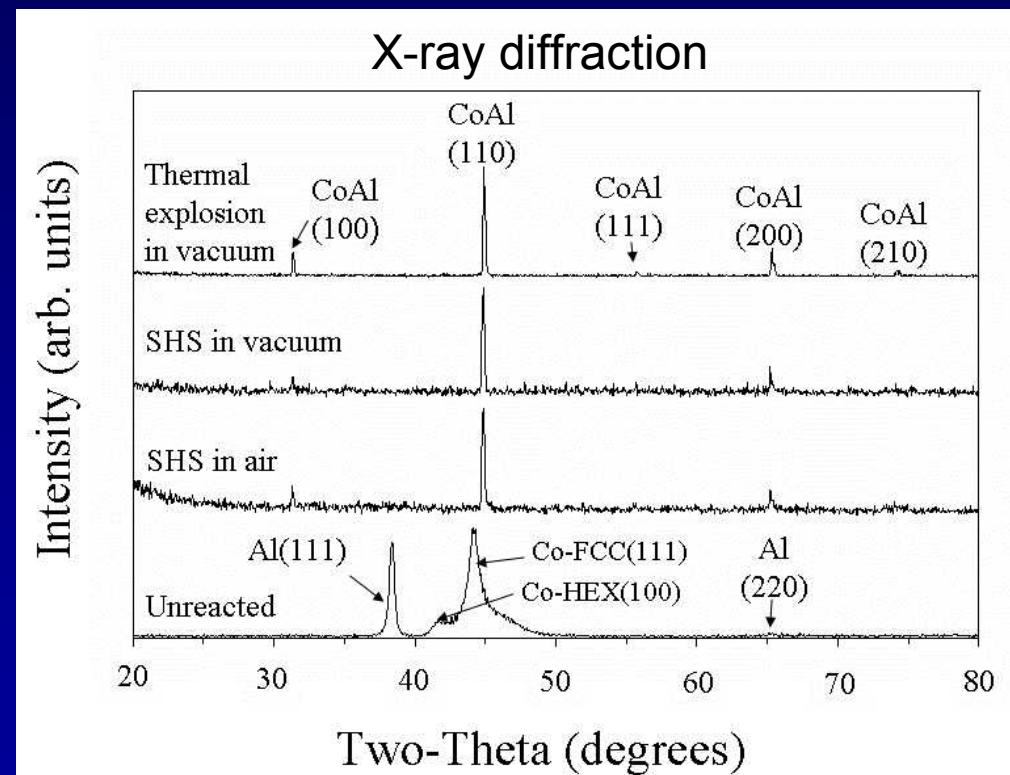
- Compare Gibbs free energies

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

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

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

Cobalt / Aluminum



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

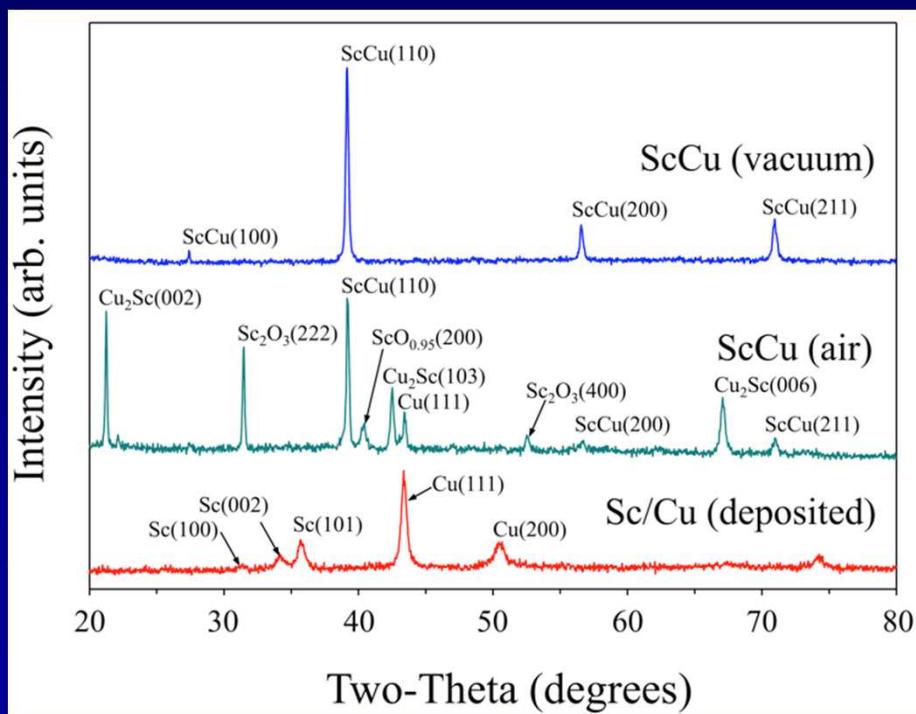
- B2 Structure (CsCl type) is the single phase formed when reacted in vacuum.
- A mixture of metal oxides and intermetallic compounds is formed when reacted in air.
- Compare heats of formation

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

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

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

Scandium/Copper

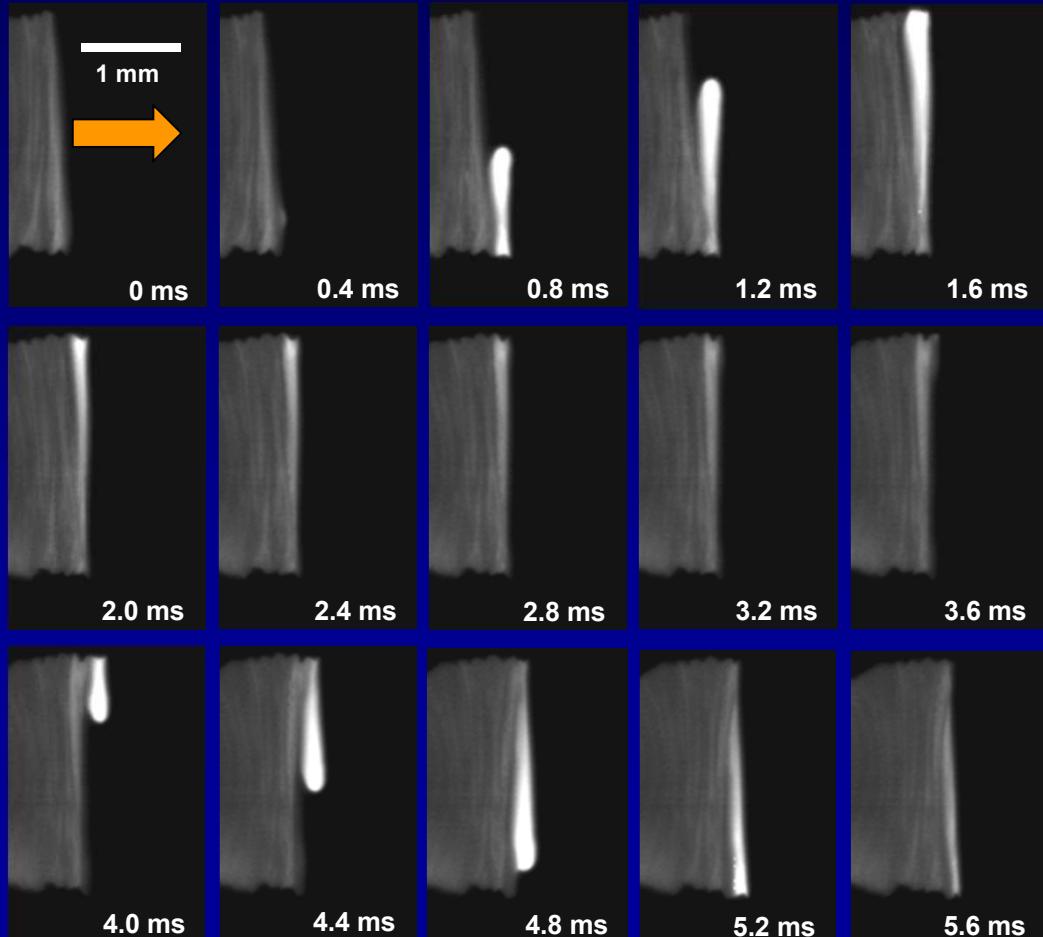


Ni/Ti exhibits a 2-D reaction front instability when reacted in vacuum.

Nickel / Titanium

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

- 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

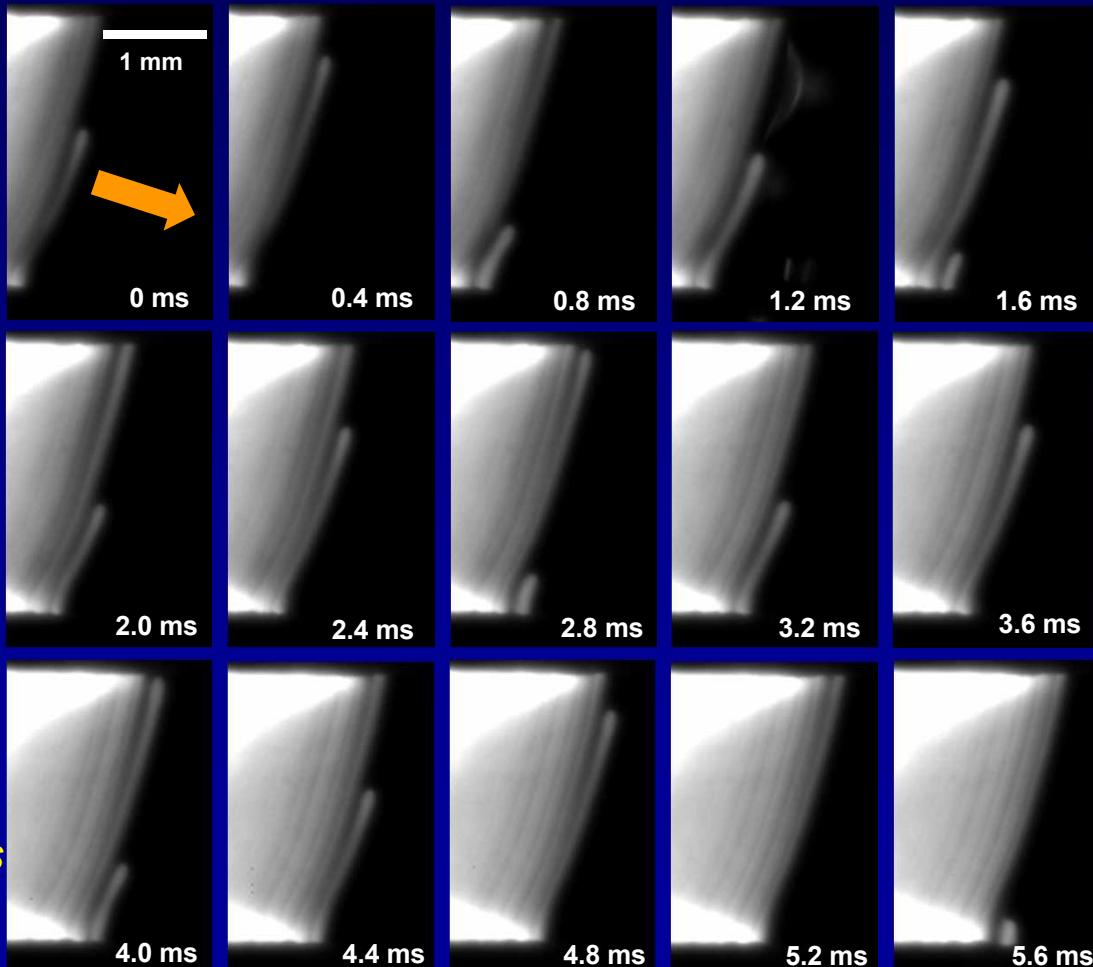


Ni/Ti exhibits a 2-D reaction front instability and undergoes secondary combustion when reacted in air.

Nickel / Titanium

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

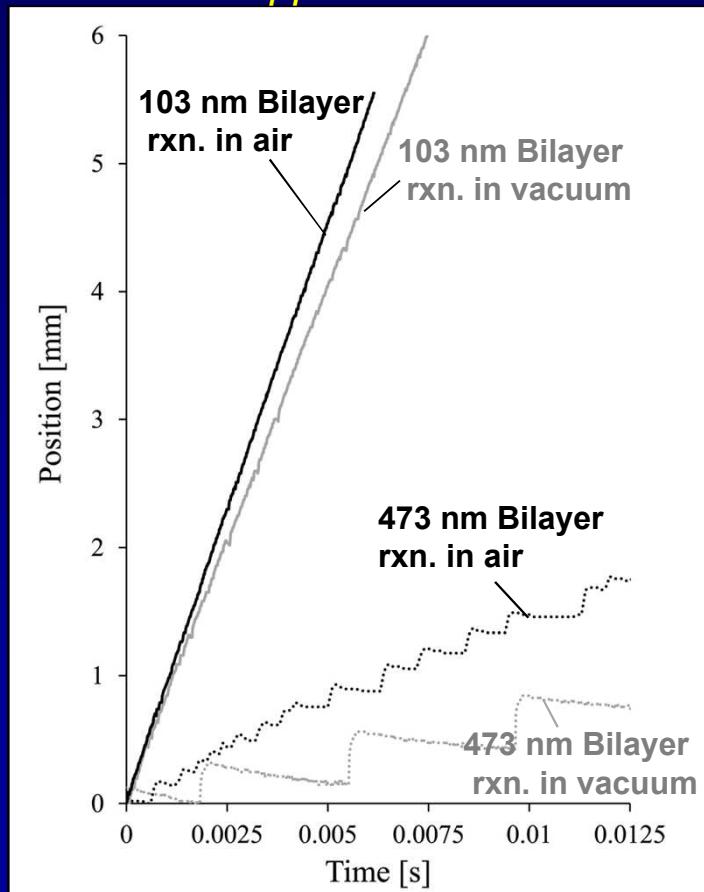
- Similar to reactions in vacuum, reaction bands propagate transversely.
- A second reaction 'wave' appears behind the intermetallic reaction front.
- Second reaction front is faster along the edges of foils.



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

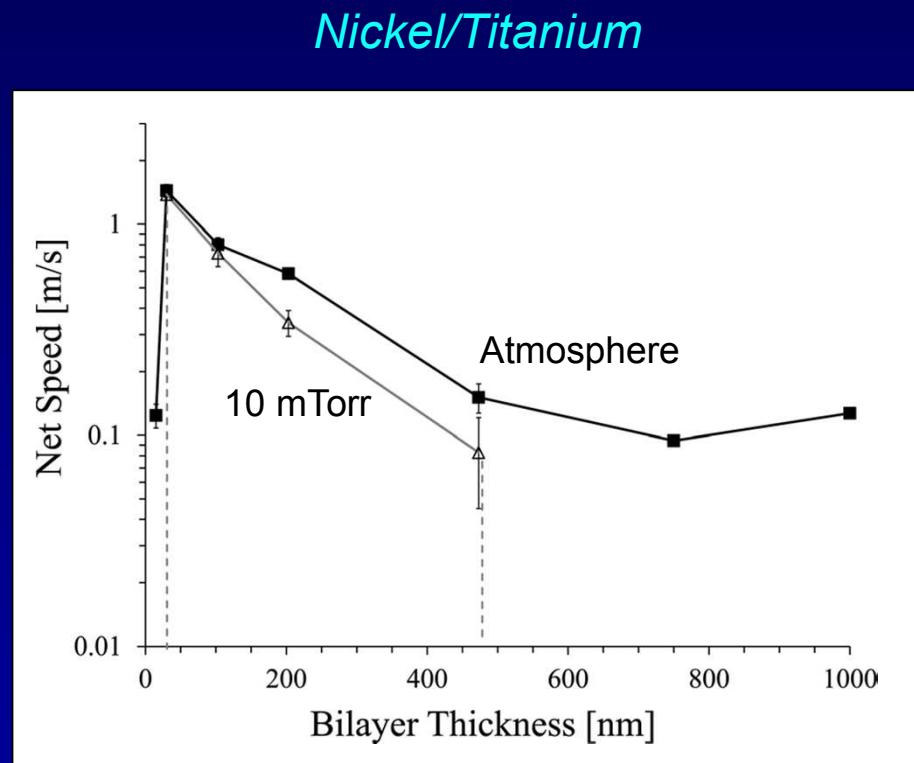
- Frequency of transverse bands is increased when air is present.
- Air does not change the transverse band speed in Ni/Ti.
- Conclude that the nucleation rate of transverse reaction bands at foil edges is increased when oxygen is present and is responsible for increased net speed (in forward direction).

Nickel/Titanium
Total thickness = 5.0 μm
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.



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.

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

Scandium/Copper

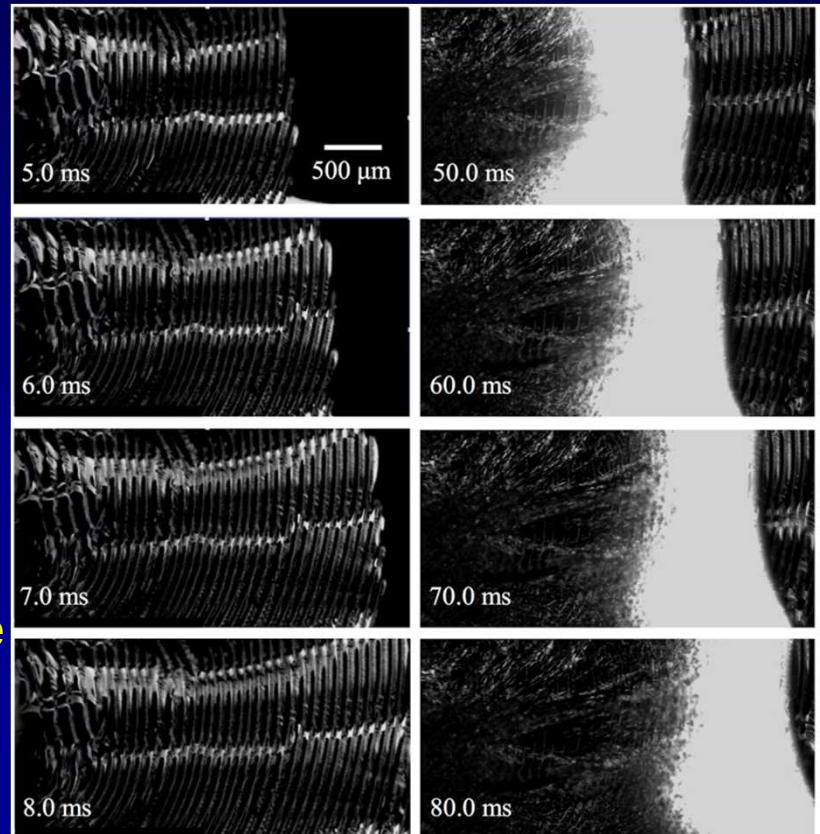


Bilayer thickness: 41 nm
Total thickness = 2.5 μm .

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

- 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

- 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

I sincerely thank all of these folks:

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Carter Hodges

David Ingersoll

Mark Rodriguez

Joe Michael

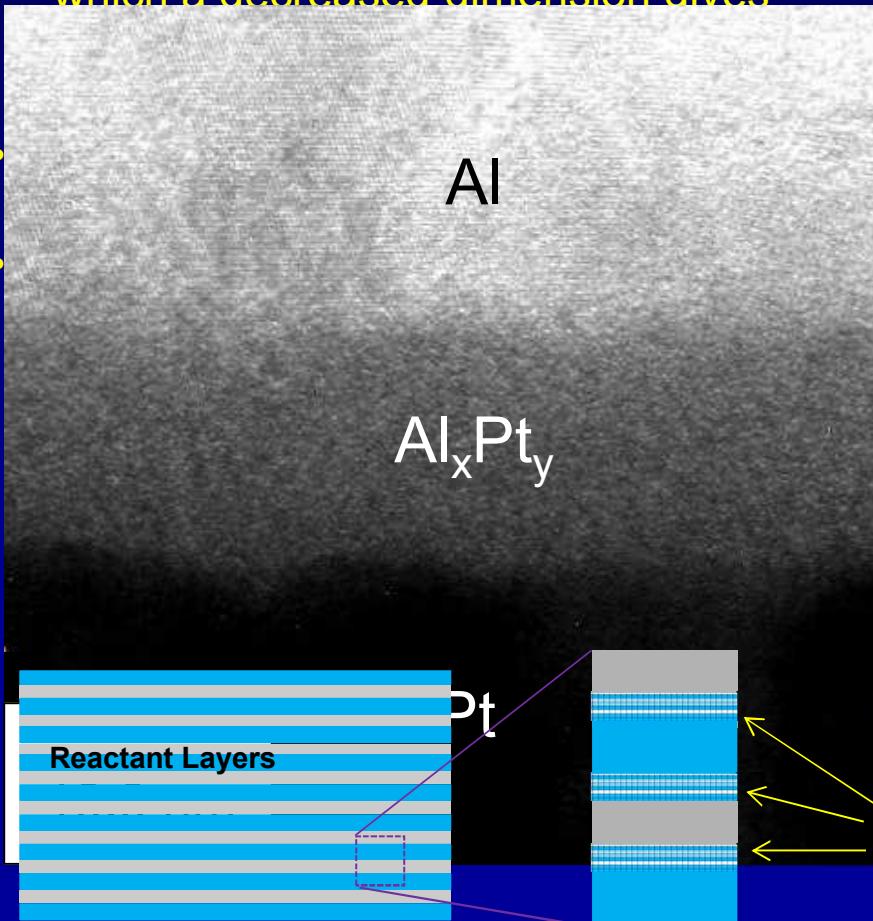
Paul Kotula



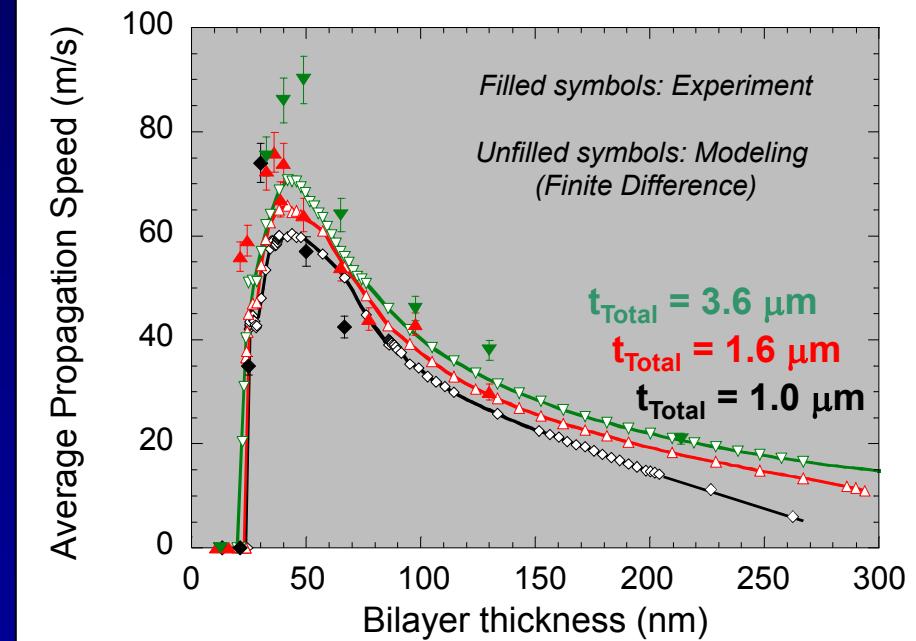
EXTRA SLIDES

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



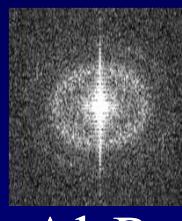
*Ex. Equiatomic
Aluminum/Platinum on SiO_2*



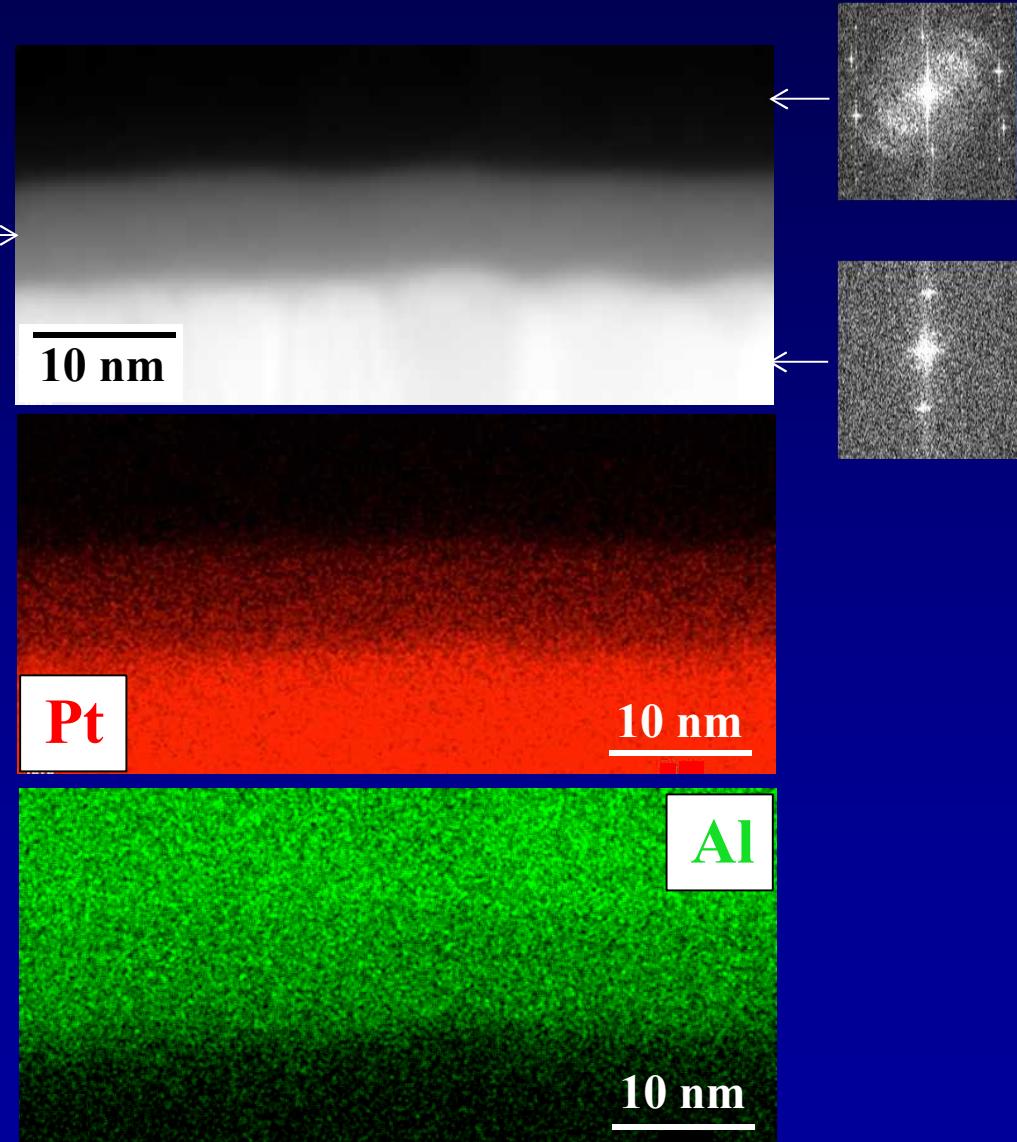
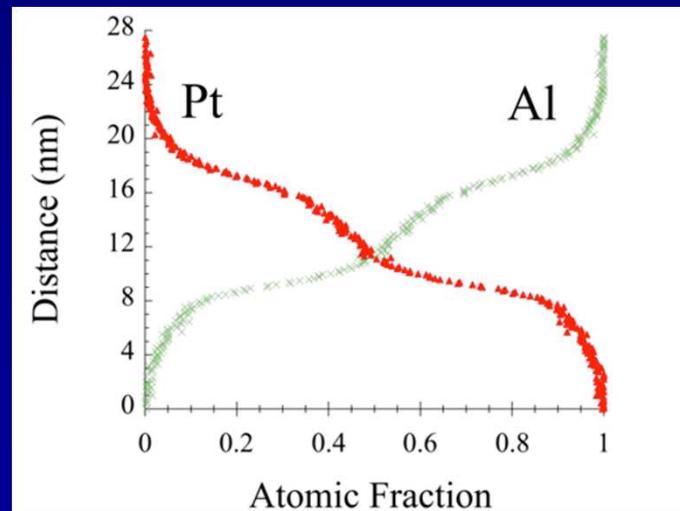
M. Hobbs, D.P. Adams
et al. 8th World Congress
Comp. Mech. 2008).

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

- Equiatomic AlPt.
- Evaluated prior to ignition.
- Premix thickness ~ 10 nm.



Al-Pt

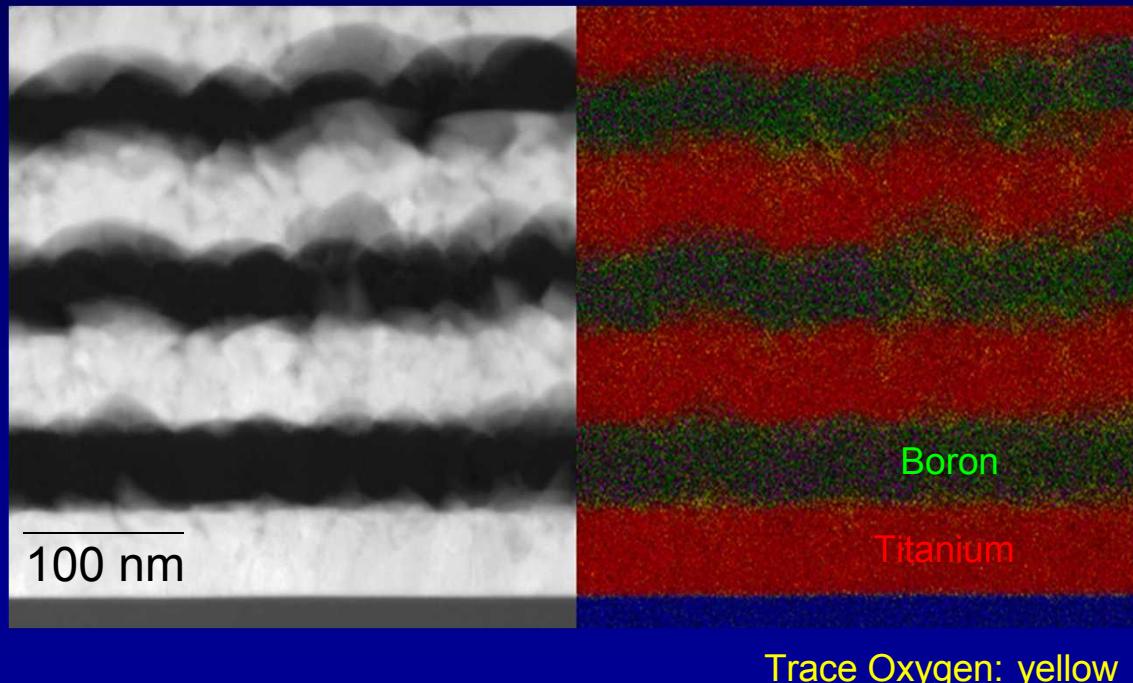


Vapor deposition plays a vital role in fabricating multilayers for research and application.

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

Sputter multilayers include

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

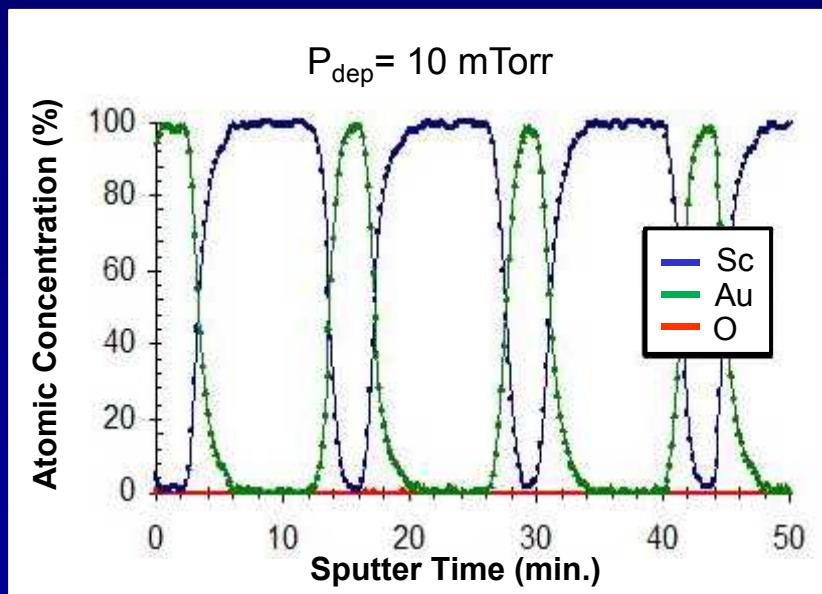


Well-defined structure enables reliable ignition and tailorabile heat release rates.

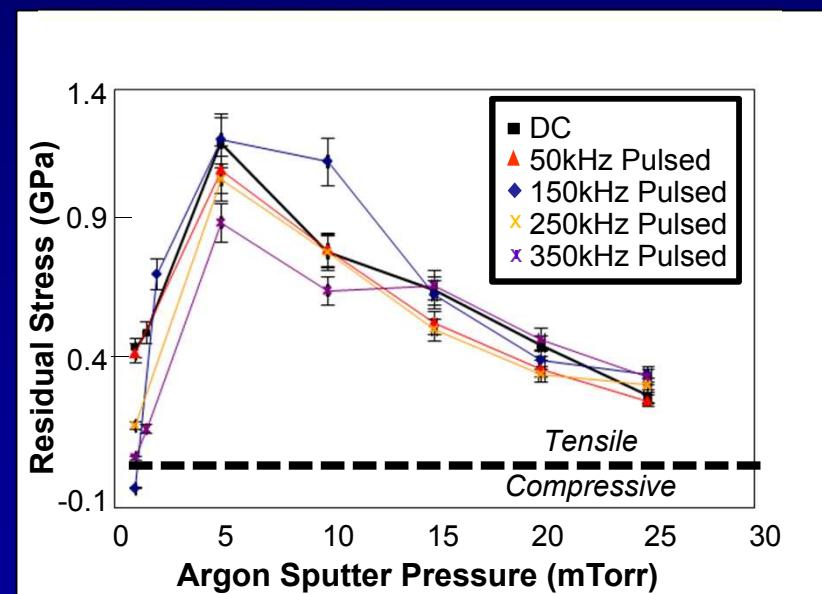
Nanometric multilayers can be ignited with no preheating above T_{room} .

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

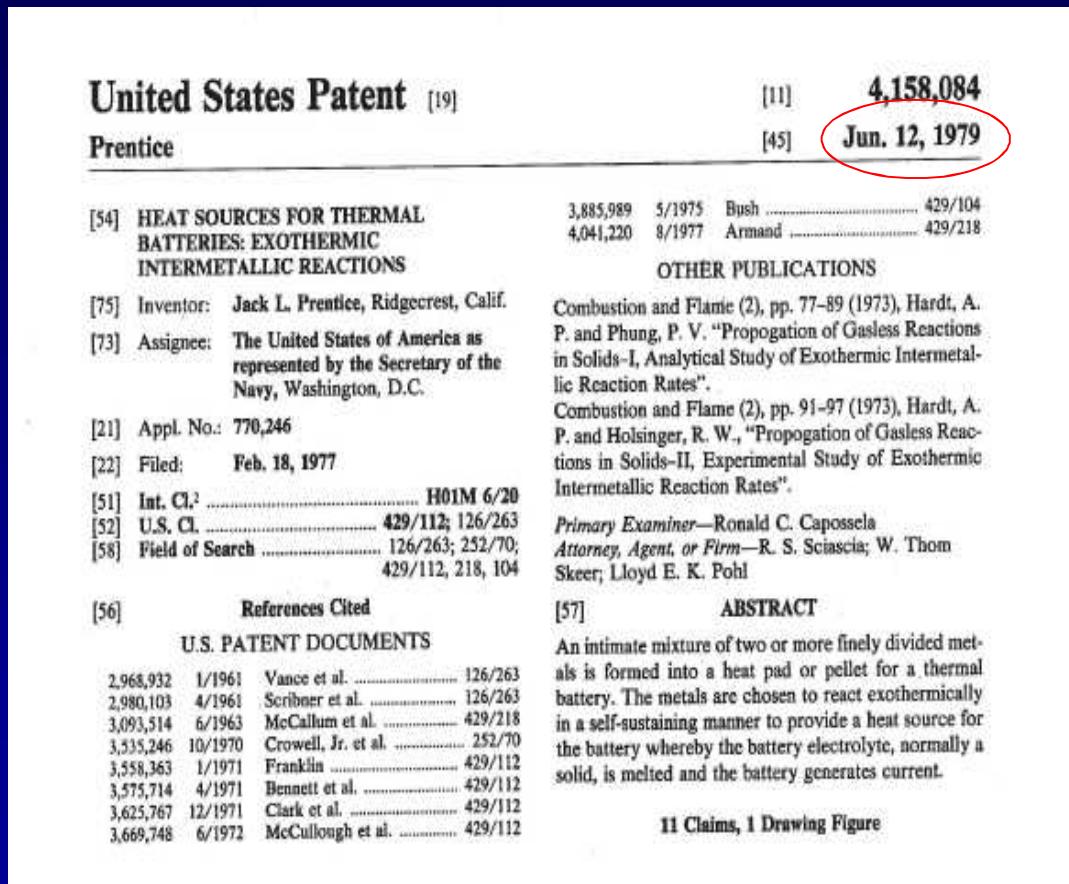
Purity evaluated by Auger electron spectroscopy



Residual Stress evaluated by wafer curvature techniques



This idea was conceived several decades prior to our research.



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 55

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 60 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 de- 65 sired 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 ₂	-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 _{.43} Ti _{.48} B _{.09}	-38	0.5 - 4.5	340 - 500
Ni/Ti/C	Ni _{.43} Ti _{.48} C _{.09}	-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

ΔH_o (Al₂O₃) =
-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)	Compare with ΔH_o (Fe/KClO ₄) ~ -1560 J/g
Ti/B	TiB ₂	-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 _{.43} Ti _{.48} B _{.09}	-772	0.5 - 4.5	unknown	
Y/Au	YAu	-769	8 - 15	unknown	
Ni/Ti/C	Ni _{.43} Ti _{.48} C _{.09}	-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	YC _u	-419	0.2 – 0.4	unknown	