SAND2015-9063C

The Effects of a Heat Sink on Self-Sustained Propagating Reactions in Sputter-Deposited Bimetallic Multilayers

D.P. Adams

R.V. Reeves, C. Sobczak, M. Hobbs

Sandia National Laboratories
Albuquerque NM

AVS San Jose

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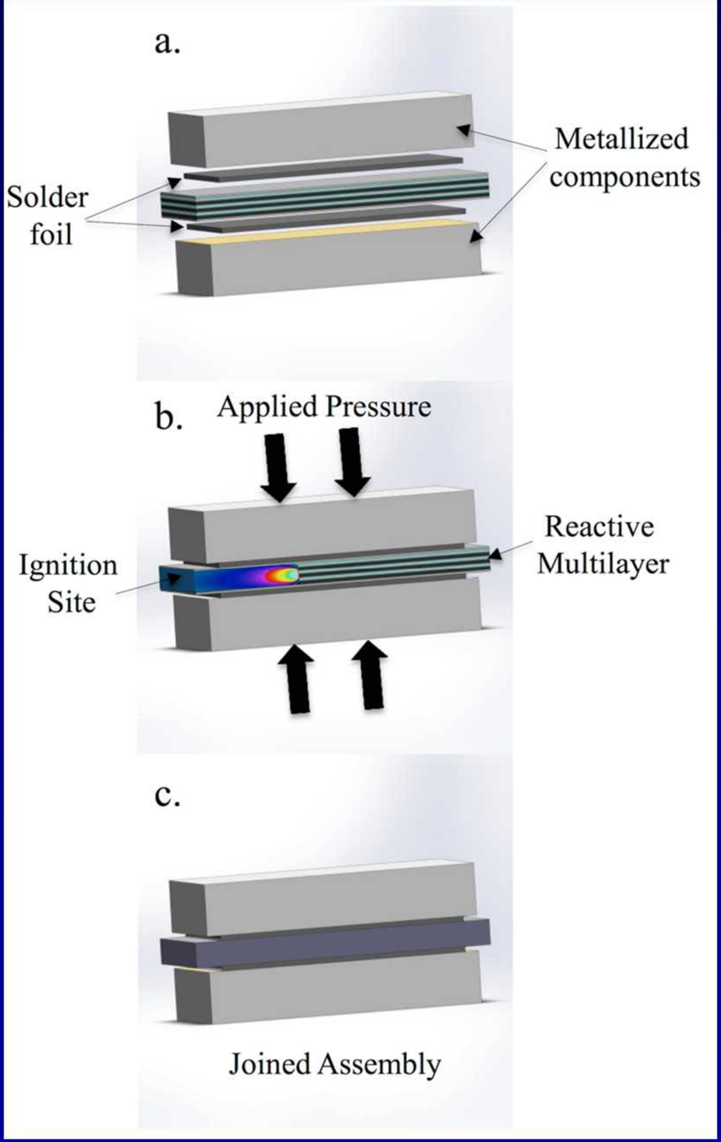
Reactive multilayers are used for local soldering, brazing and joining.

- 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.



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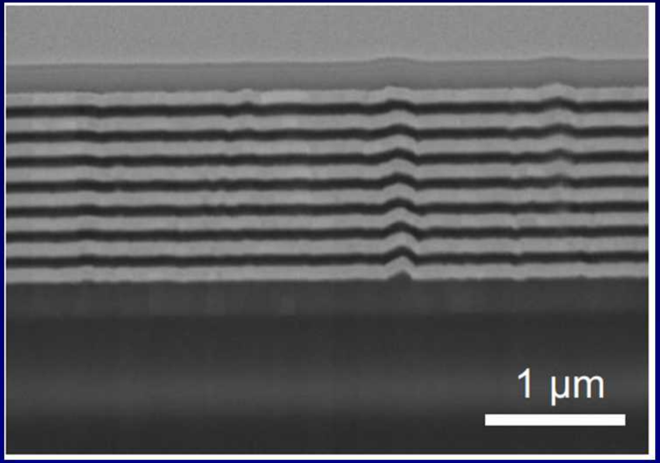
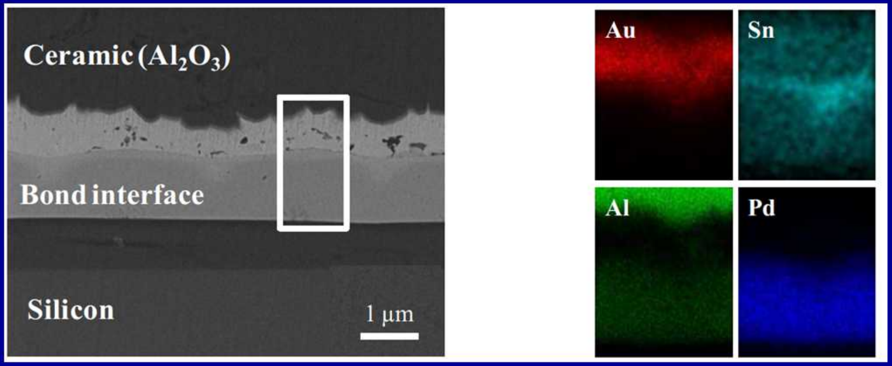


•Recent work by Braeuer with 1.6 µm thick sputtered films !!! (Ref. ECS Trans. 50 (2012))



Sputtering is used to produce reactive multilayers.

- Design includes two reactants

- Single, out-of-plane periodicity for each multilayer

- Heats of reaction, ΔH_o, for reactive pairs
  Ti/2B : - 102 kJ/mol at
  Al/Pt : - 100 kJ/mol at
  Al/Pd : - 95 kJ/mol at
  Ni/Al : - 60 kJ/mol at
  Co/Al : - 58 kJ/mol at
  Ni/Ti : - 34 kJ/mol at

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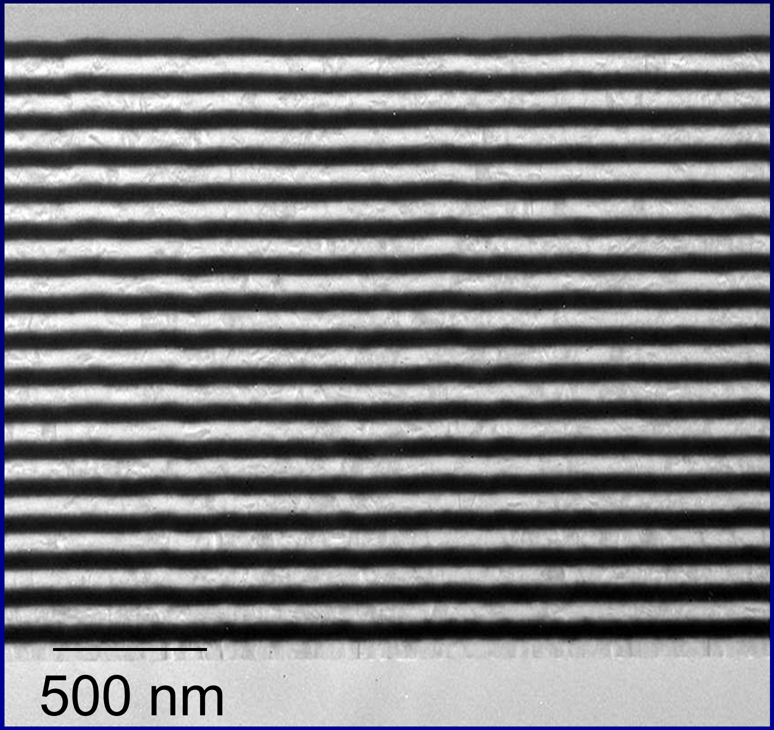

1 cm

Al/Pt multilayer in Cross Section by TEM

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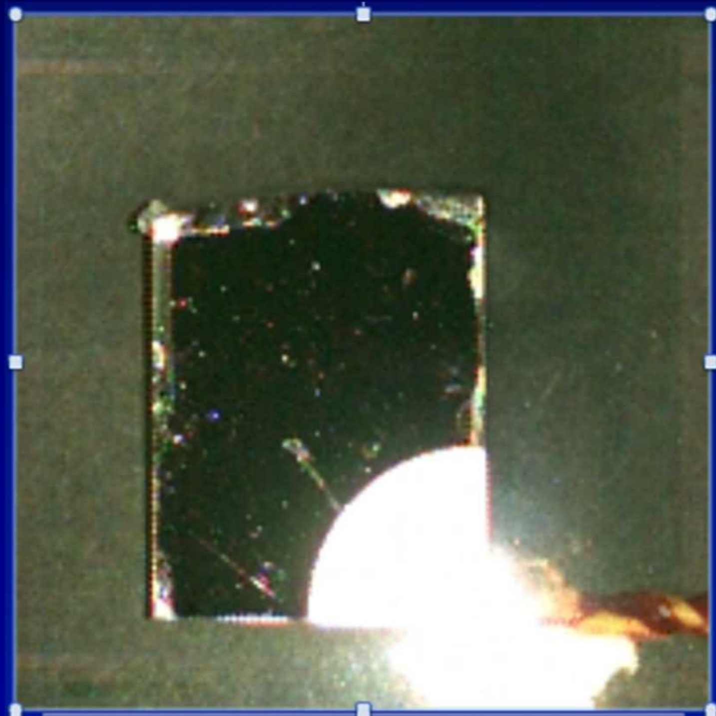


1 cm

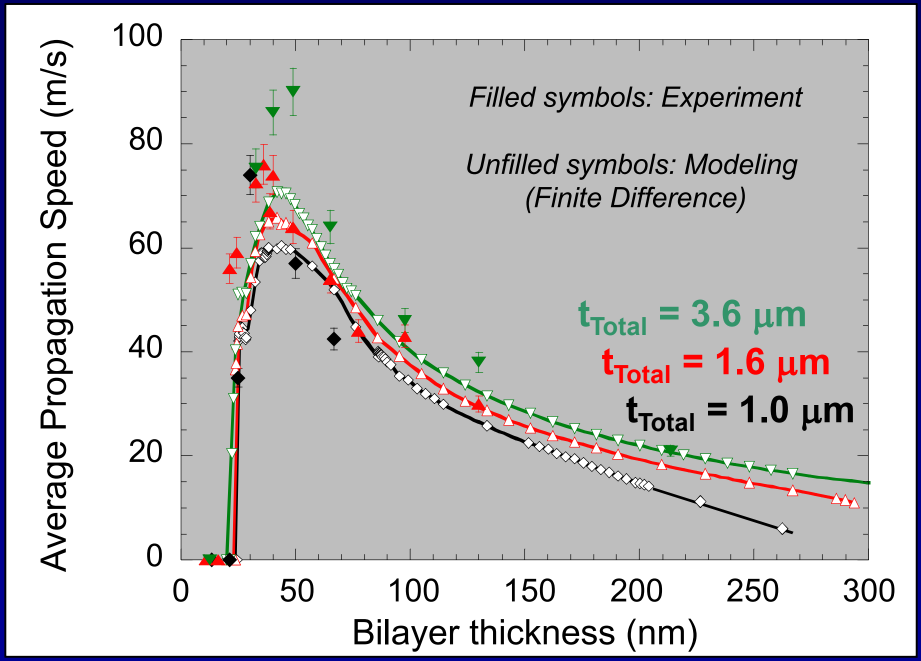
Equiatomic Al/Pt mulitlayers react at high rates; the rate of reaction varies with bilayer thickness.

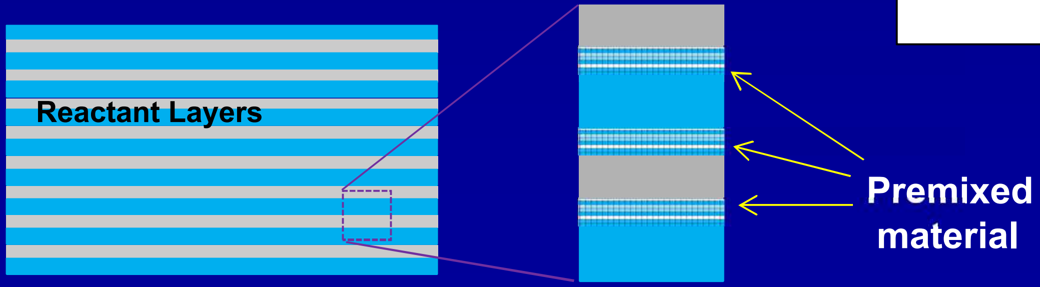
- Large range of bilayer thickness over which a decreased dimension gives rise to increased average speed.
- Peak speed at small bilayer thickness.
- Decreased speed for ultra-thin bilayers is due to the presence of relatively large amounts of premixed material.

first explanation: Wickersham, 1988

Equiatomic Aluminum/Platinum

Tested as Freestanding Foils





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

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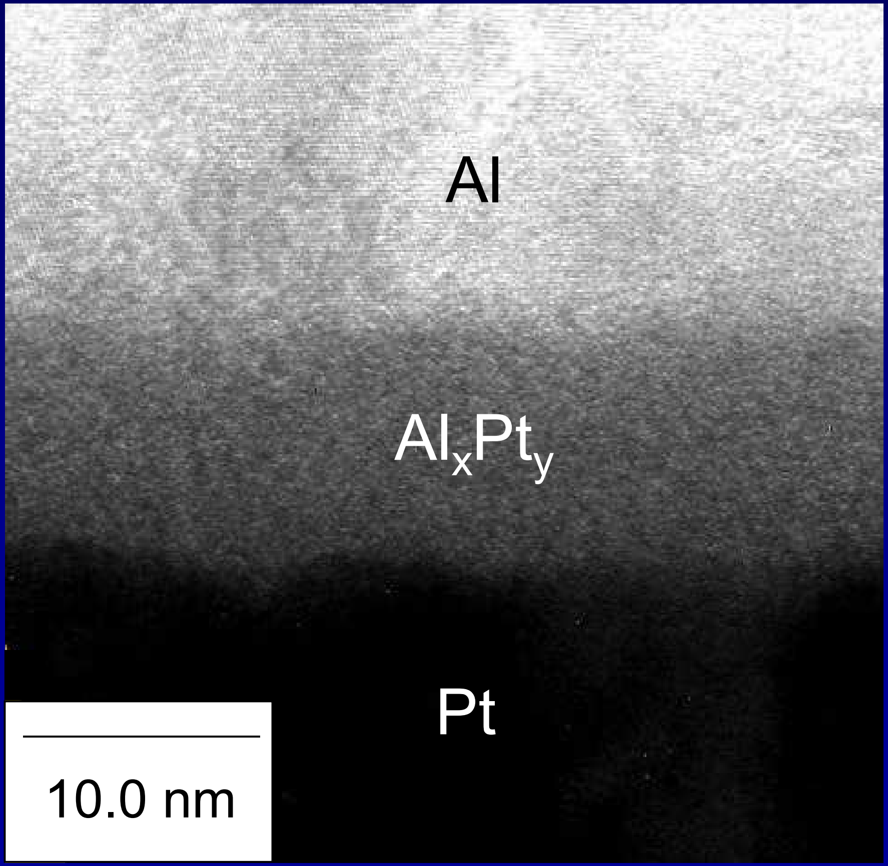

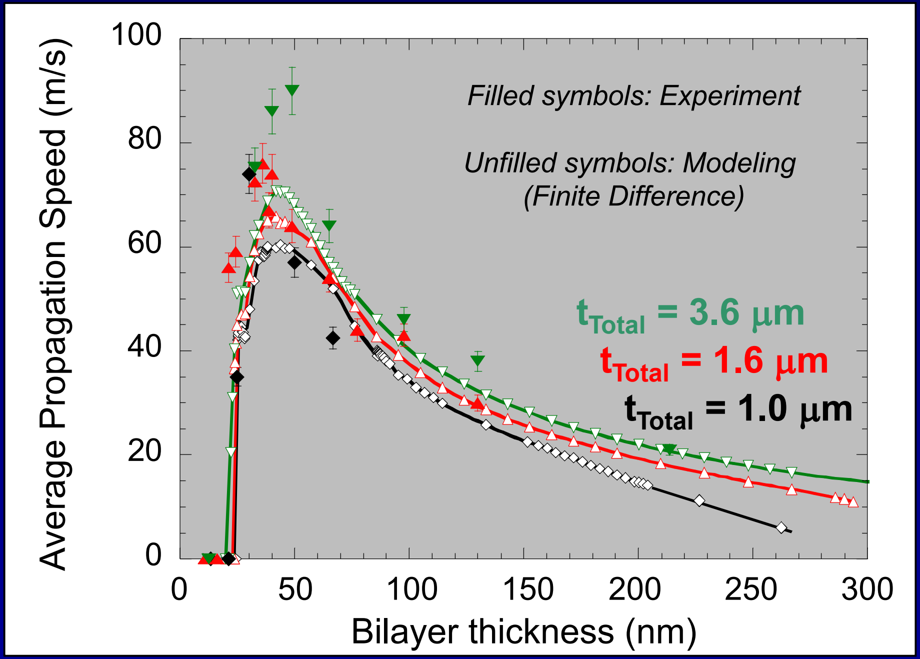

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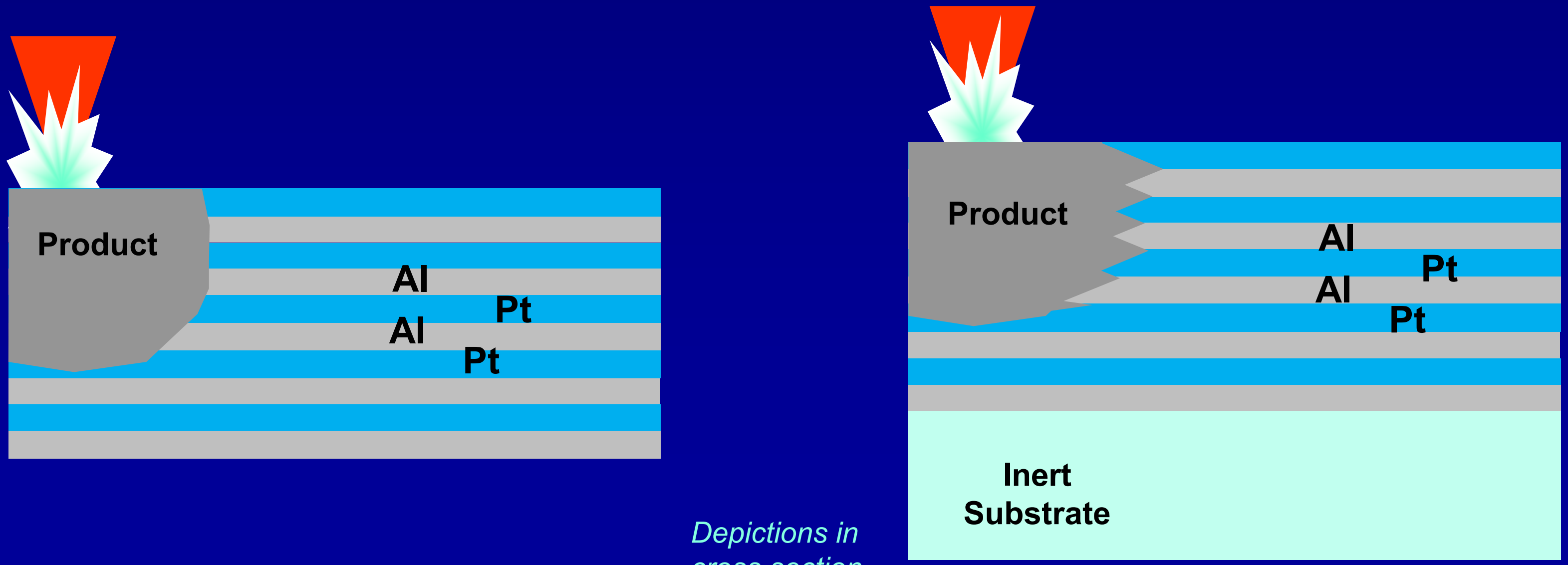
Goals and approach of current study

Determine

i) whether Al/Pt multilayers exhibit self-sustained, formation reactions when adhered to different substrates

i) the effects of different substrates on self-propagating reactions, and

ii) the range of multilayer designs that are reactive.



Depictions in cross section

Details of Experiments

Compositions investigated:

AlPt, Al_2Pt, Al_3Pt, Al_4Pt, $AlPt_2$, $AlPt_3$, $AlPt_4$

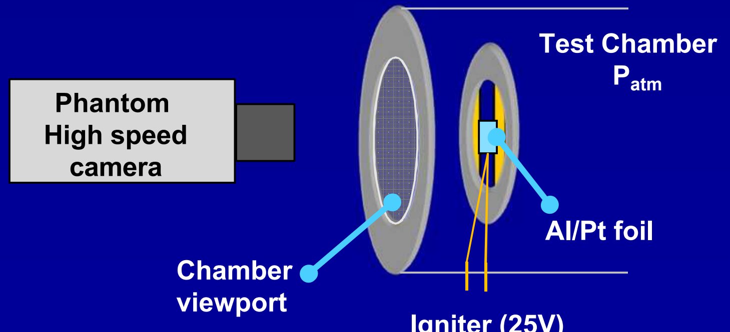
Point ignition in air

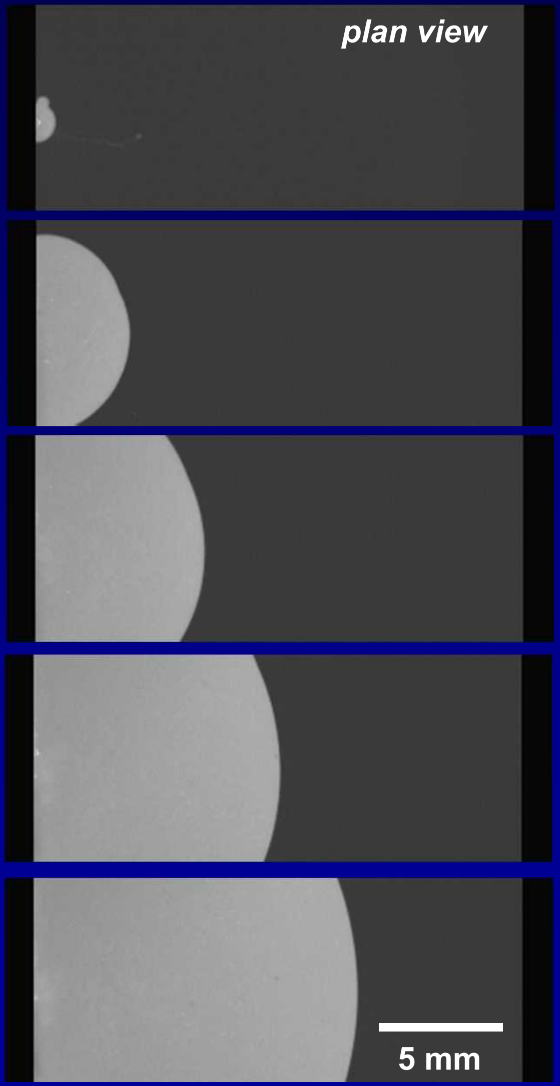
Tested as freestanding foils and as adhered films

No preheat above room temperature

High speed photo: Go/no go; steady-state speed

Phase analysis: X-ray diffraction

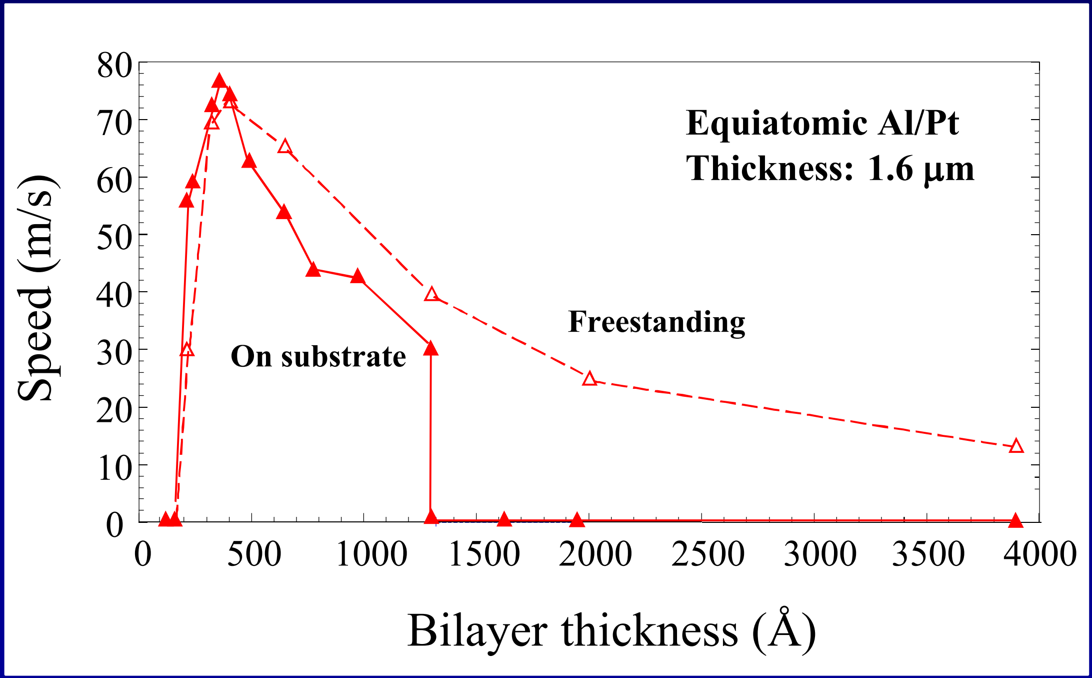




Equiatomic Al/Pt, bilayer thickness: 50 nm

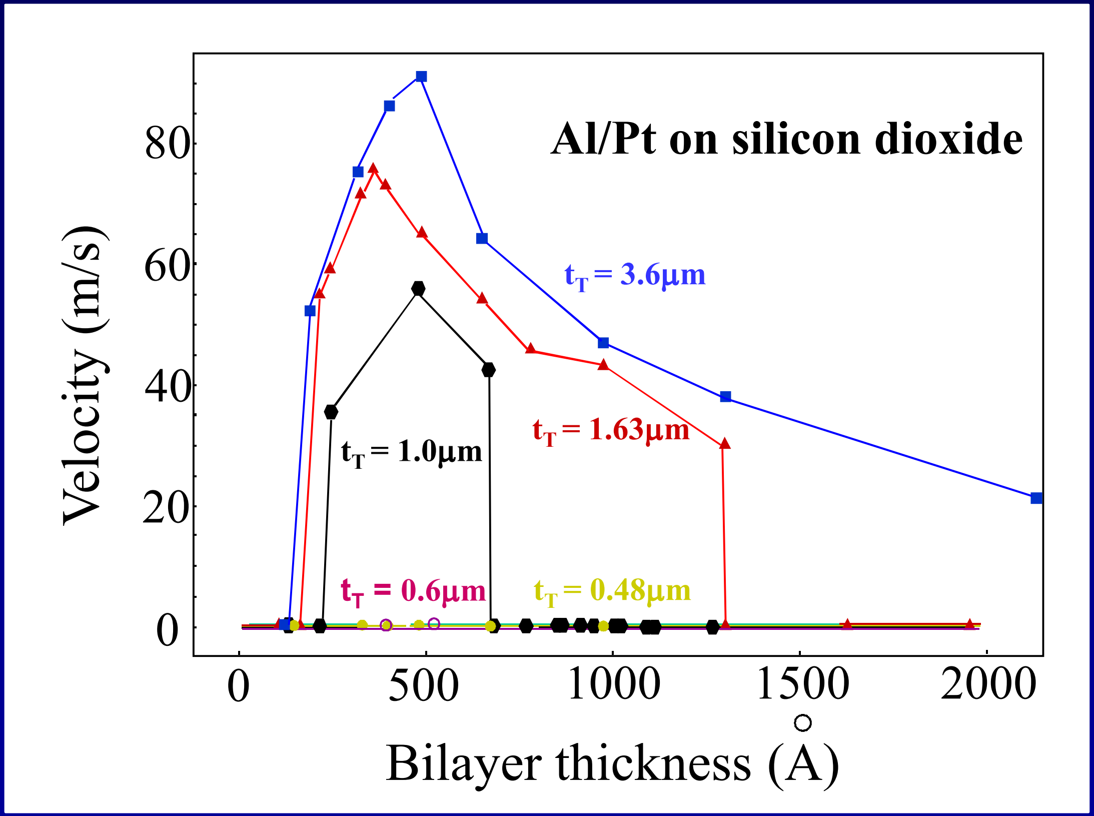
Equiatomic Al/Pt multilayers exhibit self-sustained formation reactions when tested as freestanding foils and as adhered films.

- Trend with bilayer thickness same for films and foils, at least for a range of bilayer thicknesses.
- Reduced range of reactive designs when reacted on glass.
- Evidence for discontinuity for bilayer ~ 1300 Å.



Equiatomic Al/Pt multilayers react as freestanding foils and as adhered films.

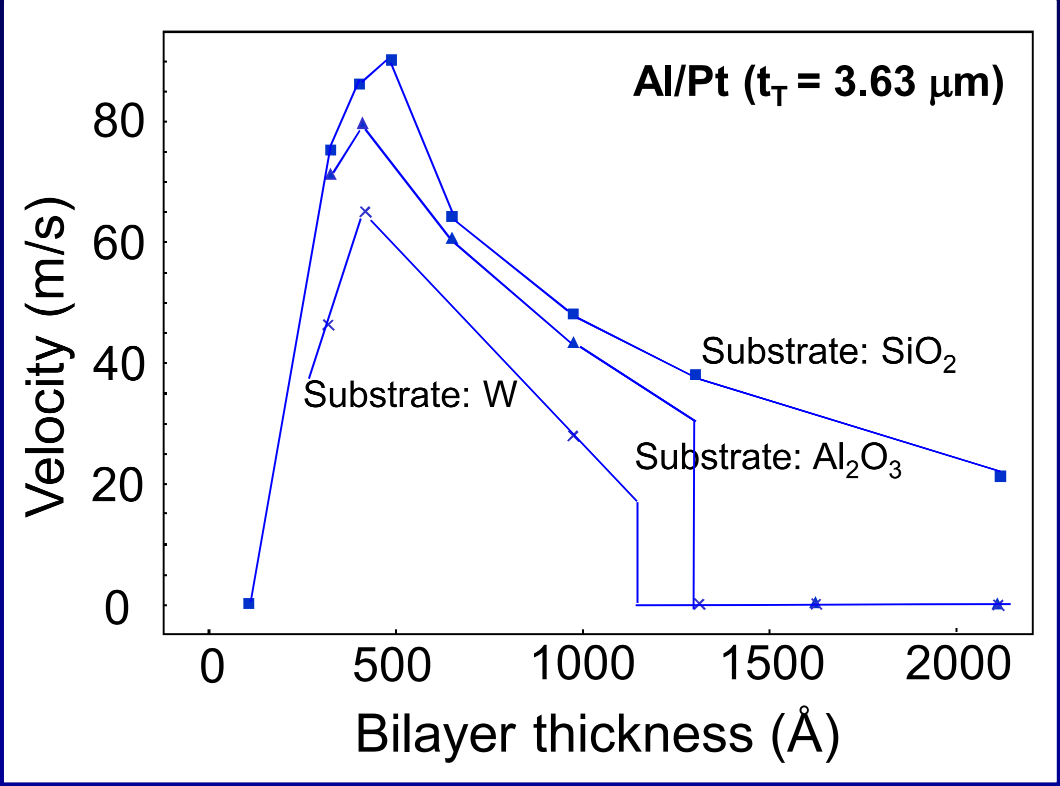
- Reduced range of reactive designs when film thickness is made smaller.
- Evidence for a critical bilayer thickness, above which reaction does not occur.
- Evidence for reduced critical bilayer thickness when total thickness is decreased.



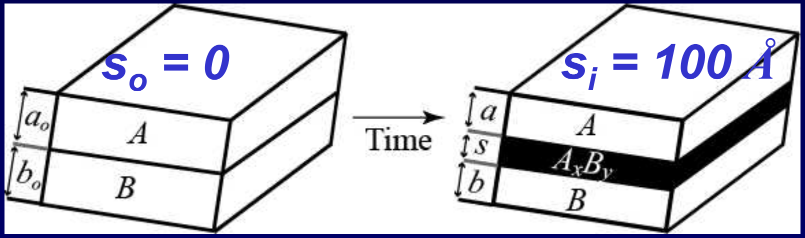
Reduced propagation speeds are discovered when utilizing more thermally conductive substrates.

- Speeds (for a given bilayer thickness design) decrease when attached to a more thermally-conductive substrate.

- Decreased range of reactive designs when tested on thermally-conductive substrates.



Approach to modeling propagation speeds



$$\xi_A A + \xi_B B \rightarrow A_{\xi_A} B_{\xi_B} + Q$$

Reacted Fraction is

$$1 - F = \frac{s}{a_o + b_o}$$

ODEs

$$\frac{da}{dt} = -\frac{D}{s}$$

$$\frac{db}{dt} = -\frac{b_o}{a_o}\frac{D}{s}$$

$$\frac{ds}{dt} = -\frac{D}{s}\left(1 + \frac{b_o}{a_o}\right)$$

$$\frac{dF}{dt} = -\frac{D}{a_o\, s}$$

Auxiliary Eqns.

$$D = D_o \exp\left(-\frac{E}{RT}\right)$$

$$a = \frac{a_o + b_o - s}{1 - \frac{\rho_A}{\rho_B}\frac{M_B}{M_A}\frac{\xi_B}{\xi_A}}$$

$$b = a\,\frac{\rho_A}{\rho_B}\frac{M_B}{M_A}\frac{\xi_B}{\xi_A}$$

$$\rho_{AB} = \frac{a_o\rho_A + b_o\rho_B}{a_o + b_o}$$

Algorithm

Choose a_o, calculate b_o

Choose s_i, calculate a_i, b_i, and F_i

Solve ODEs for s and F

Energy Equation

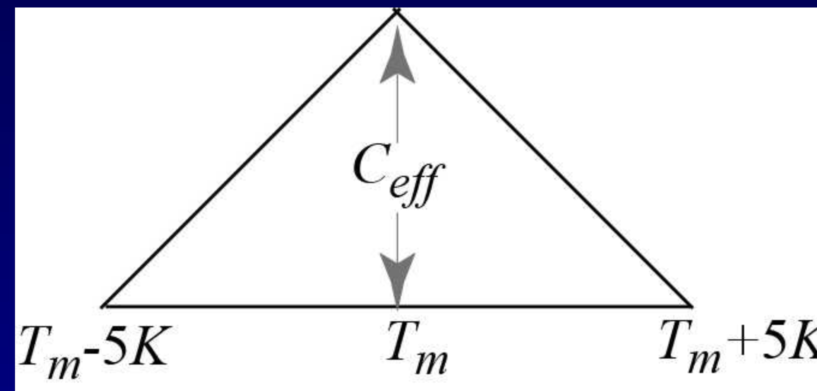
$$\rho c\,\frac{dT}{dt}\nabla(k\nabla T) = -Q\,\rho\,\frac{dF}{dt}$$

***Hardt AP and Phung PV, "Propagation of gasless reactions in solids—I. Analytical study of exothermic intermetallic reaction rates," *Combustion and Flame*, 21, pp. 77-89, 1973.**

Parameters for model simulation

Thermophysical Properties

Property	Description	Al	Pt	AlPt
c, J/kgK	Specific Heat	894-900	133	226
c_{eff}, J/kgK	Effective c at T_m	$h_{fus}/\Delta T$	$h_{fus}/\Delta T$	$h_{fus}/\Delta T$
ΔT, K	half of mush zone	4-6	4-6	4-6
h_f, J/kg	Formation enthalpy	0	0	-901,000
h_{fus}, J/kg[b]	Latent enthalpy	397,000	114,000	48,300; 100,000
k, W/mK	Thermal conductivity	213-261	71.6	158
M_w, kg/kgmol	Molecular weight	27.0	195	222
ρ, kg/m^3	Density	2700	21500	11600
T_m, K	Melting point	934	2040	934, 2040



$$Area = \tfrac{1}{2}(Base \times Height)$$
$$h_{fus} = \tfrac{1}{2}(10\ \mathrm{K} \times C_{T_{mp}})$$
$$C_{T_{mp}} = 5 \times h_{fus}$$

Diffusion model parameters

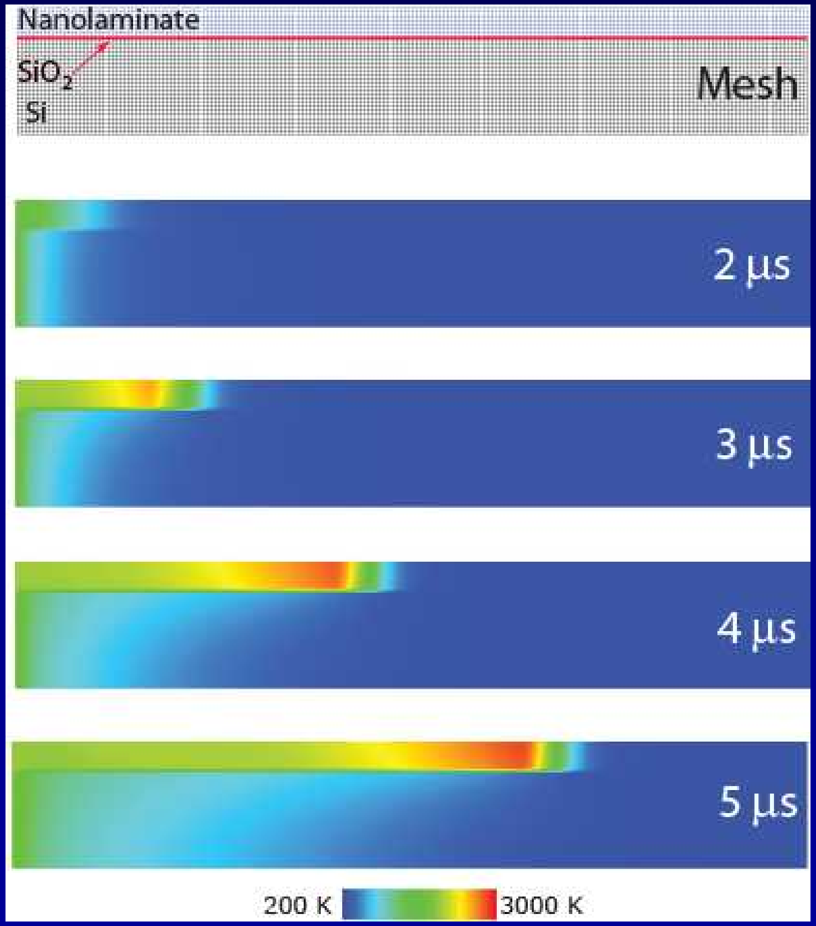
Property	Description	AlPt
s_o, m	Initial thickness of reacted layer	1×10^{-8}
D_o, m^2/s	Initial diffusion coefficient	1×10^{-7}
E, J/kgmol	Activation energy	4.1868×10^{7}

Two Phase Changes (Al, Pt)*

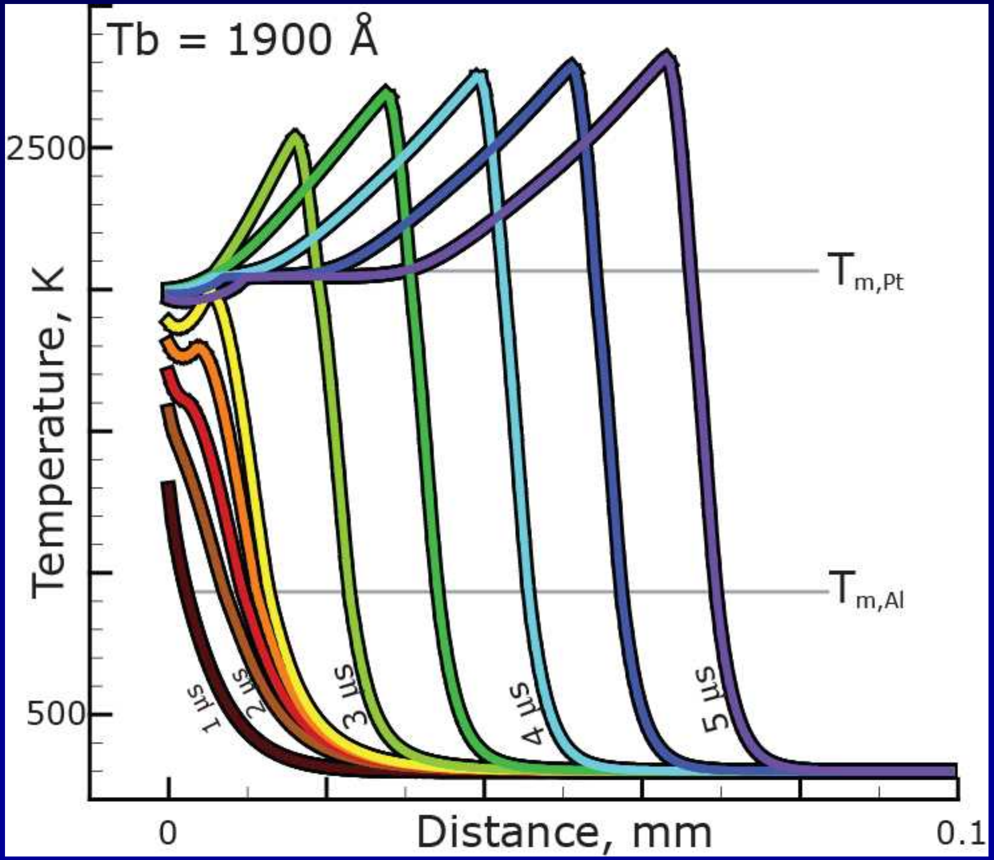
***Effective capacitance method: Yao, L.S. and Prusa, J., Melting and freezing, *Advances in Heat Transfer*, 5th Edition, John Wiley & Sons, New York, 2002.**

Temperature profiles leading to ignition

2D Axisymmetric Temperature



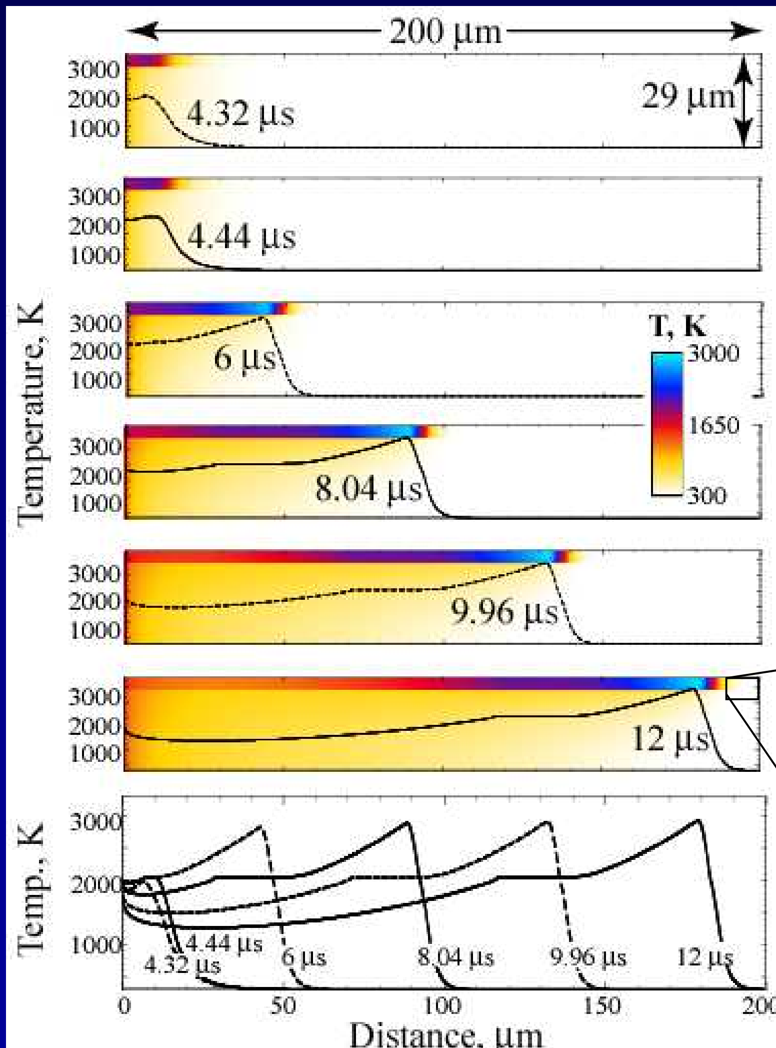
Temperature on top of nanolaminate*



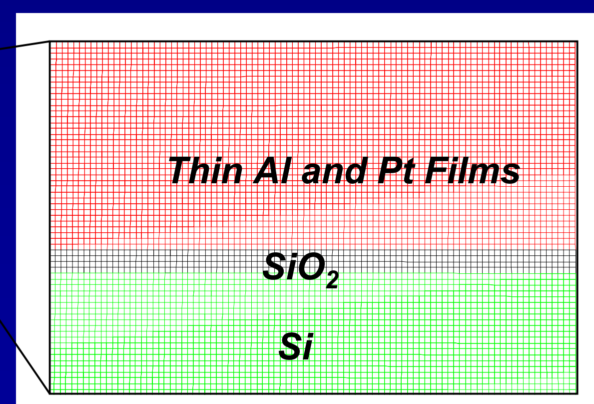
*each time is a different color

Reaction energy is sufficient to melt both layers

Propagating Reactions investigated with a 2D axisymmetric mesh (580,000 elements)

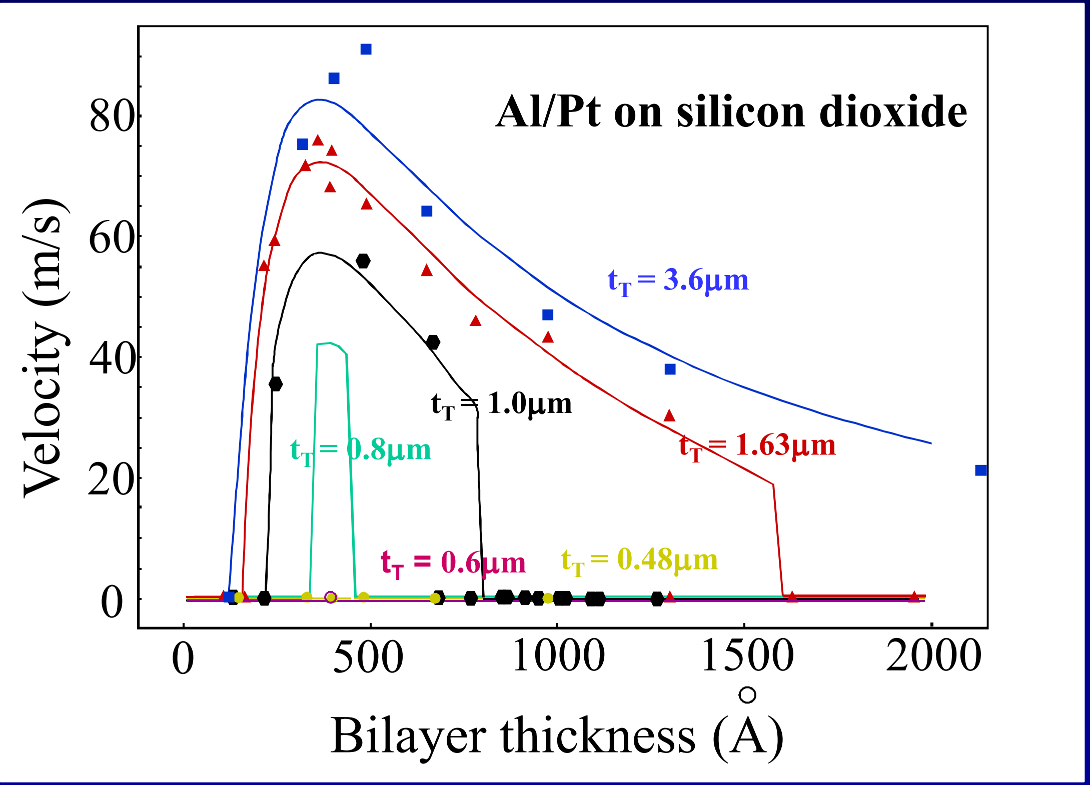


- Elements are 0.1×0.1 μm
- Fixed time step, 4×10^{-10} s
- Ignition occurs ~10μm from electric match
- Al melt in front of wave
- Solidification of AlPt should occur at 1830 K



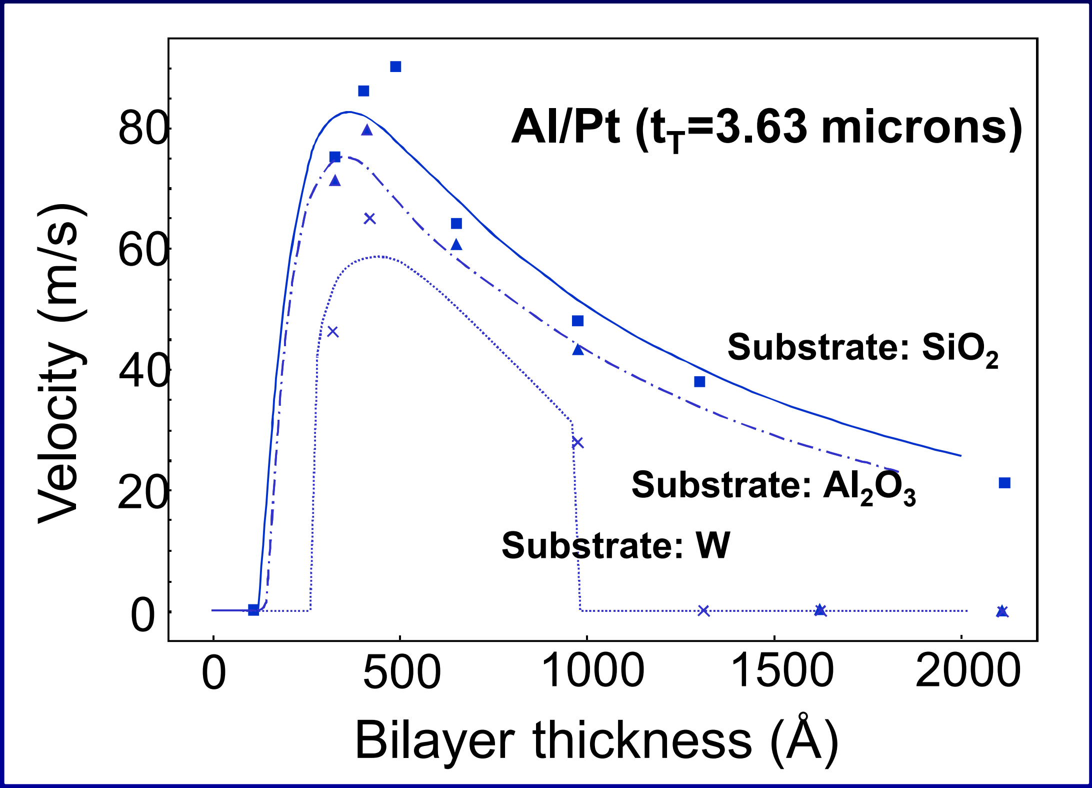
Model predictions of steady state propagation speeds in Al/Pt films (shown with lines in plot)

- Finite difference models predict the speed vs. bilayer thickness dependence.
- Models predict a critical thickness above which no reaction occurs.
- Improved models needed to precisely identify this critical thickness.



Model predictions of steady state propagation speeds in Al/Pt films

- Equiatomic AlPt exhibits largest reaction rate.
- Al-rich multilayers exhibit decreased propagation speeds as %Al increased
- Most designs of 4Al/Pt do not exhibit self-sustained reactions.



Summary

- Equiatomic Al/Pt multilayer foils exhibit rapid reactions (for a large range of bilayer thicknesses.

- Equiatomic Al/Pt multilayer films exhibit rapid reactions (for a reduced range of bilayer thicknesses).

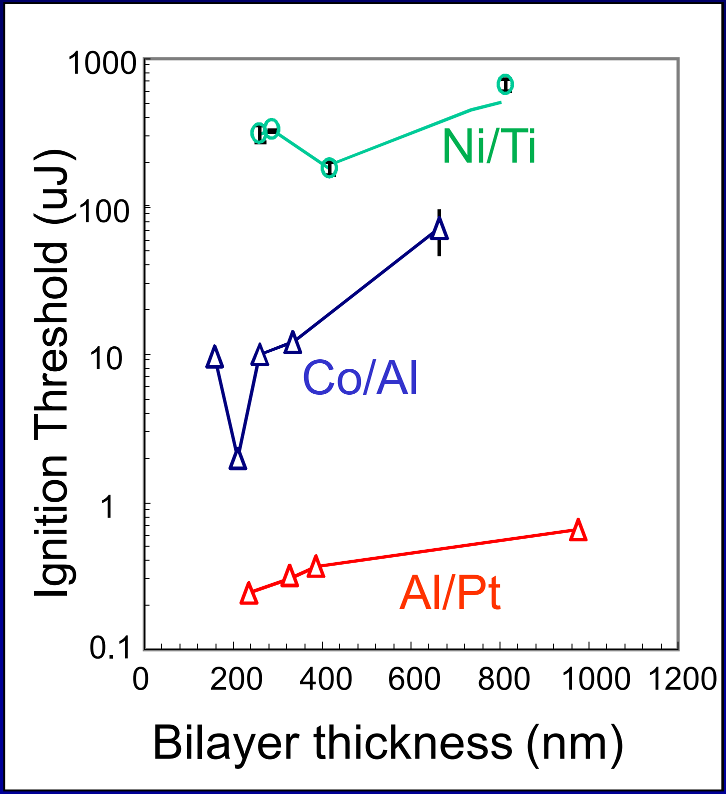
- The reduced propagation speed of a given multilayer design *and* reduced range of reactive multilayer designs owes to heat loss in to thermally conductive substrates.

- Thermal model (finite element simulation) predicts general trends of reduced speeds and reduced range of reactive designs with increasing substrate thermal conductivity.

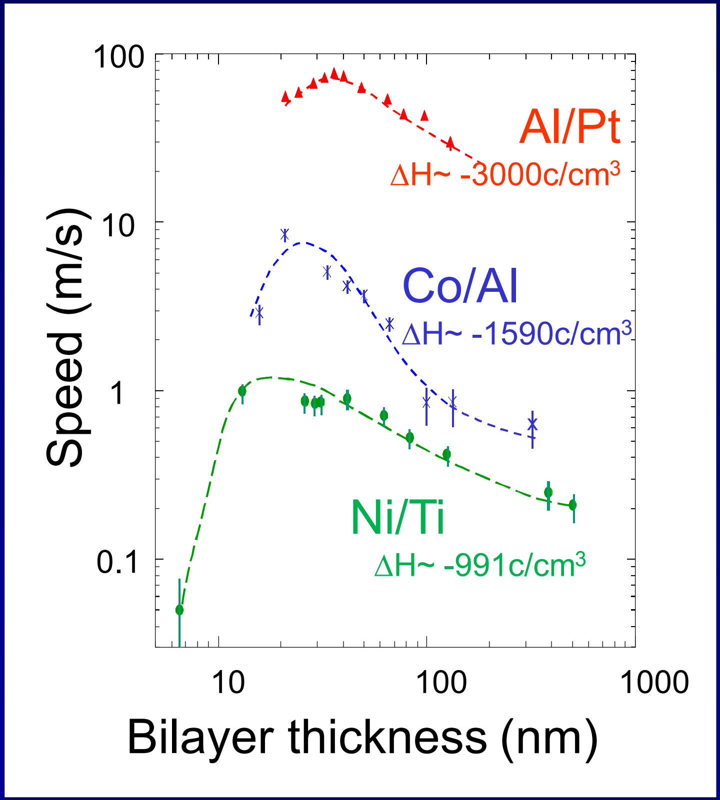
EXTRA SLIDES

Equiatomic Al/Pt multilayer foils are readily ignited and exhibit rapid propagating reactions.

Single 30 nsec laser pulse ignition thresholds (in air)



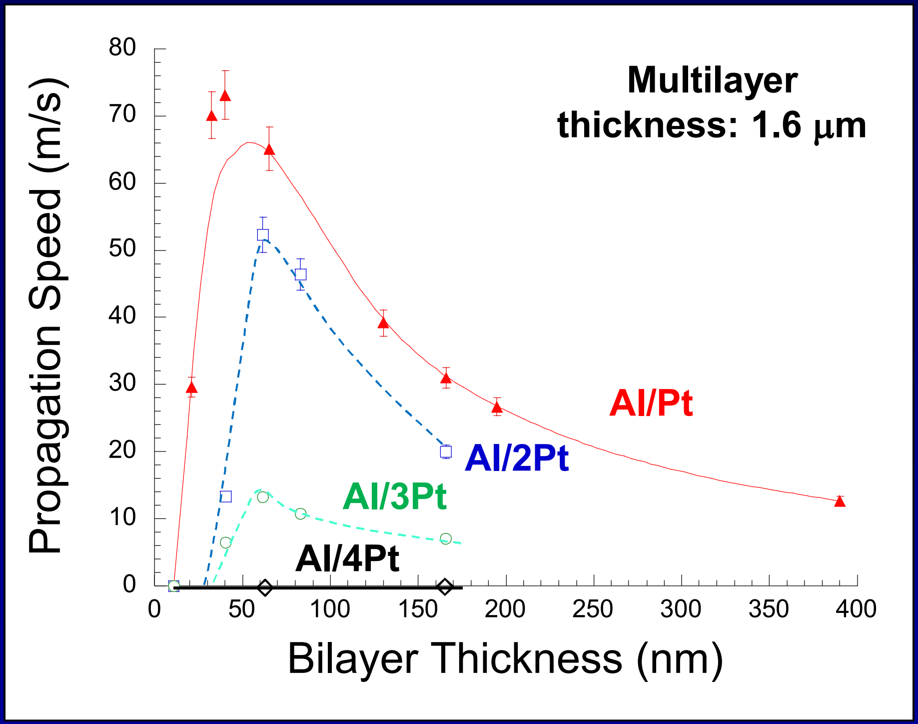
Average self-sustained speeds (in air)



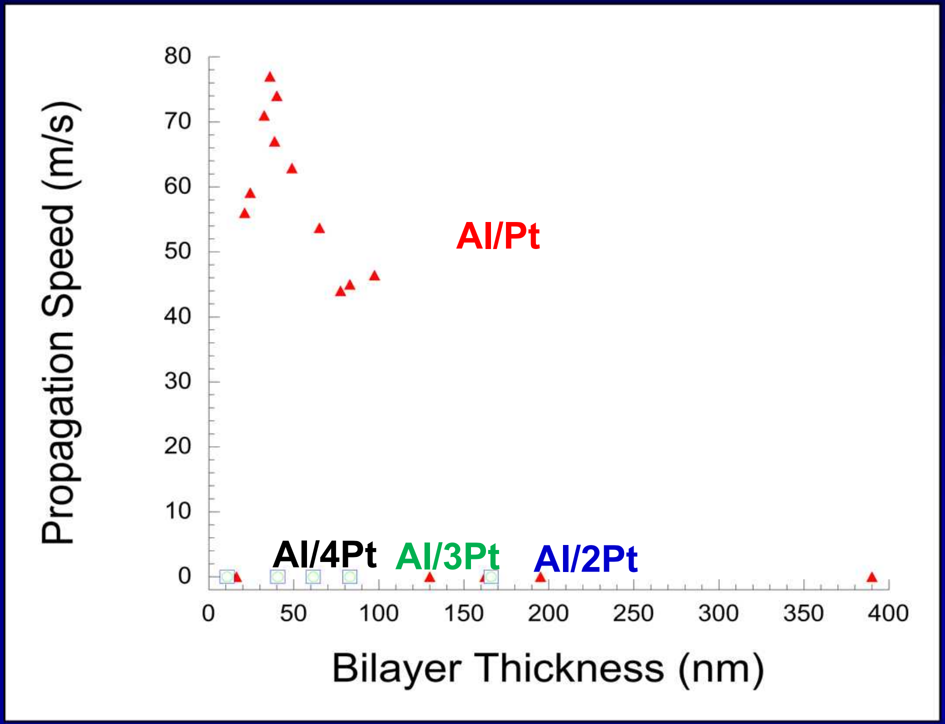
Y. Picard, J. P. McDonald, D.P. Adams, S. Yalisove Appl. Phys. Lett. 93 (2008).

Effects of substrate on self-propagating reactions: Al/Pt multilayers (includes Pt - rich compositions)

Freestanding Foils



Films on Silica Substrate



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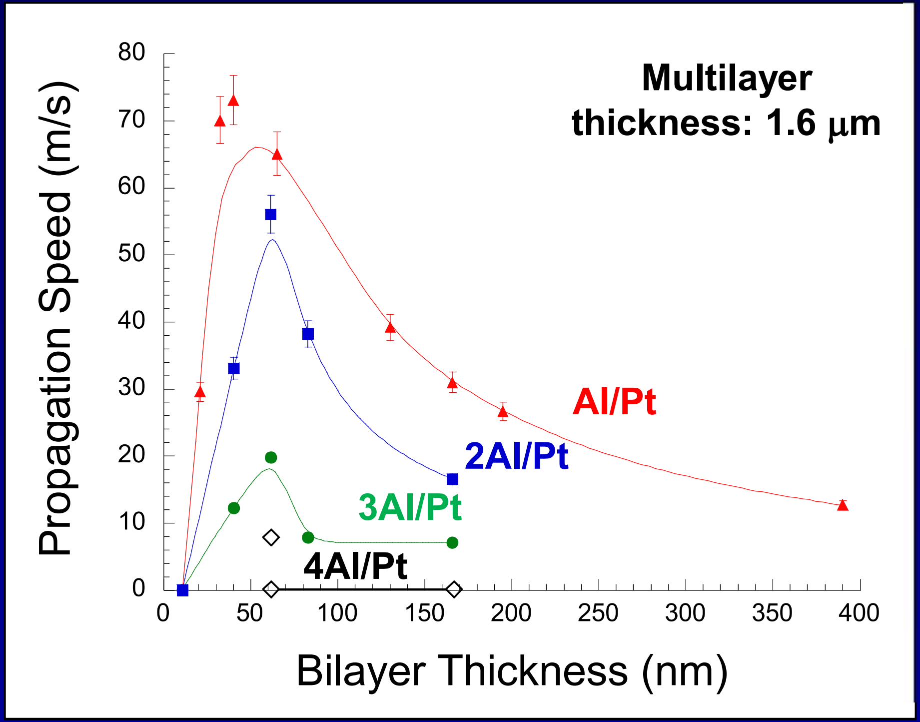

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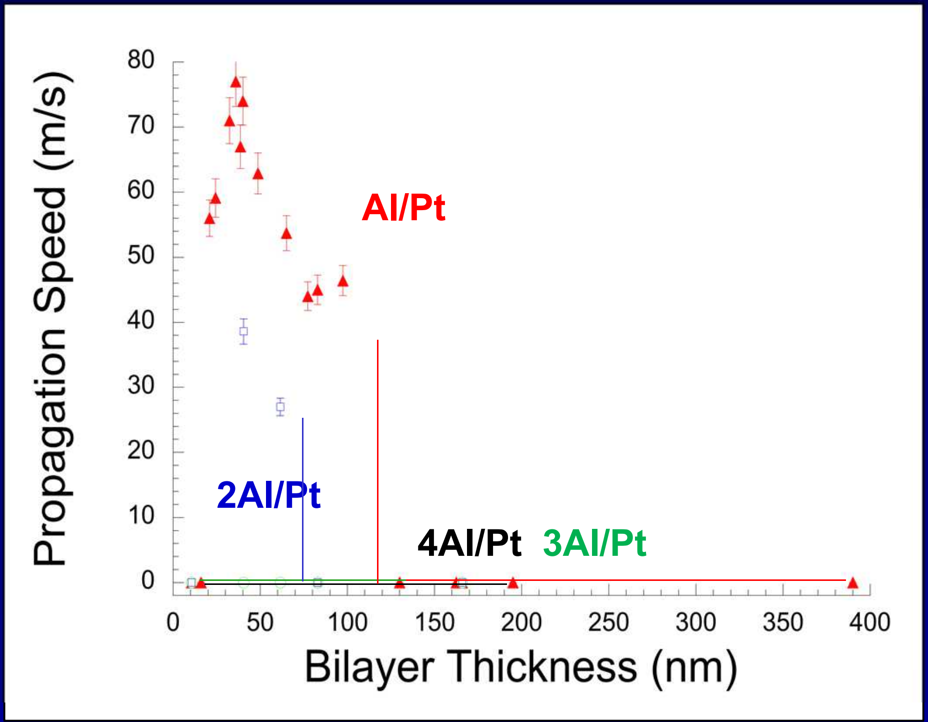
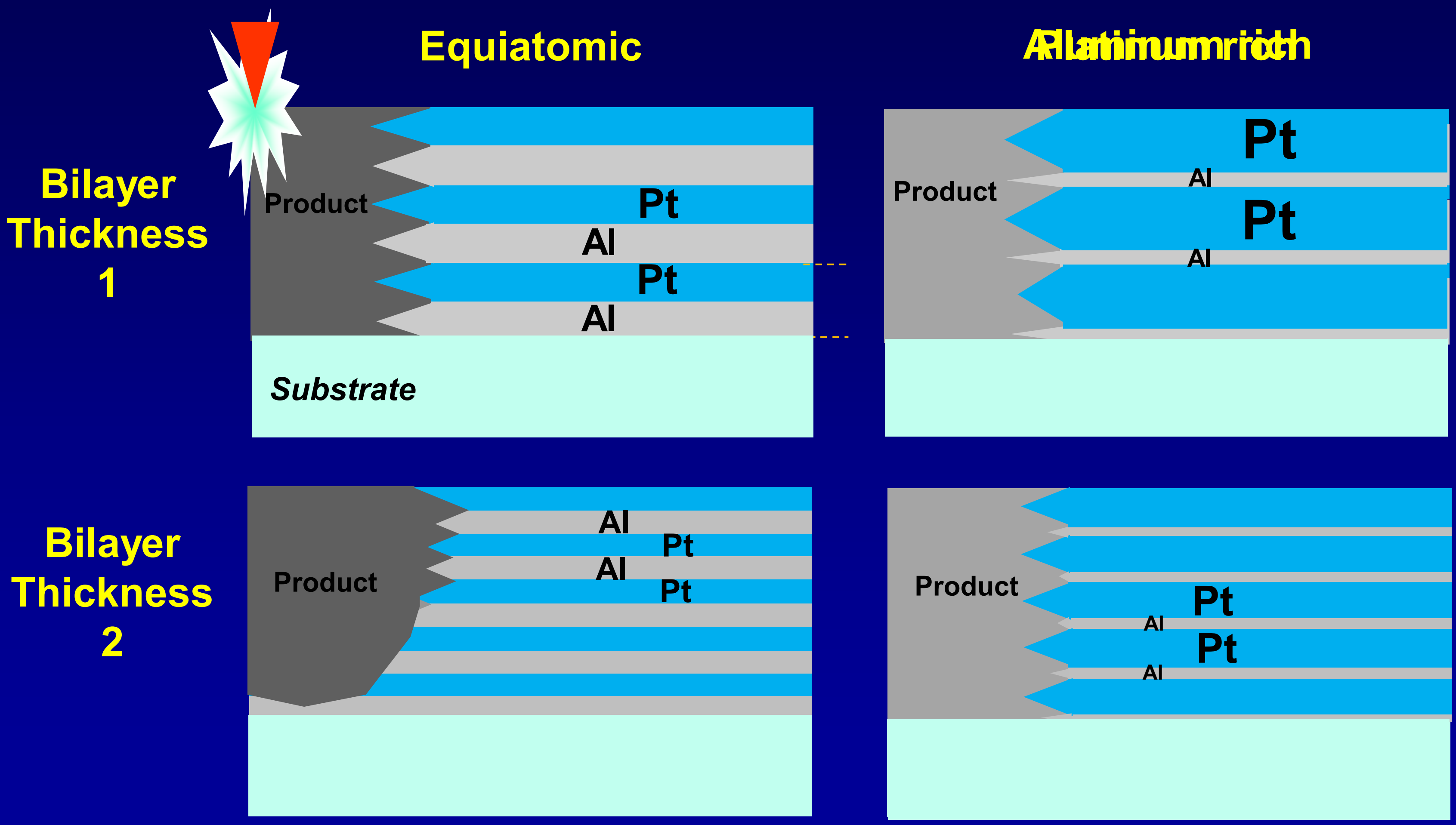


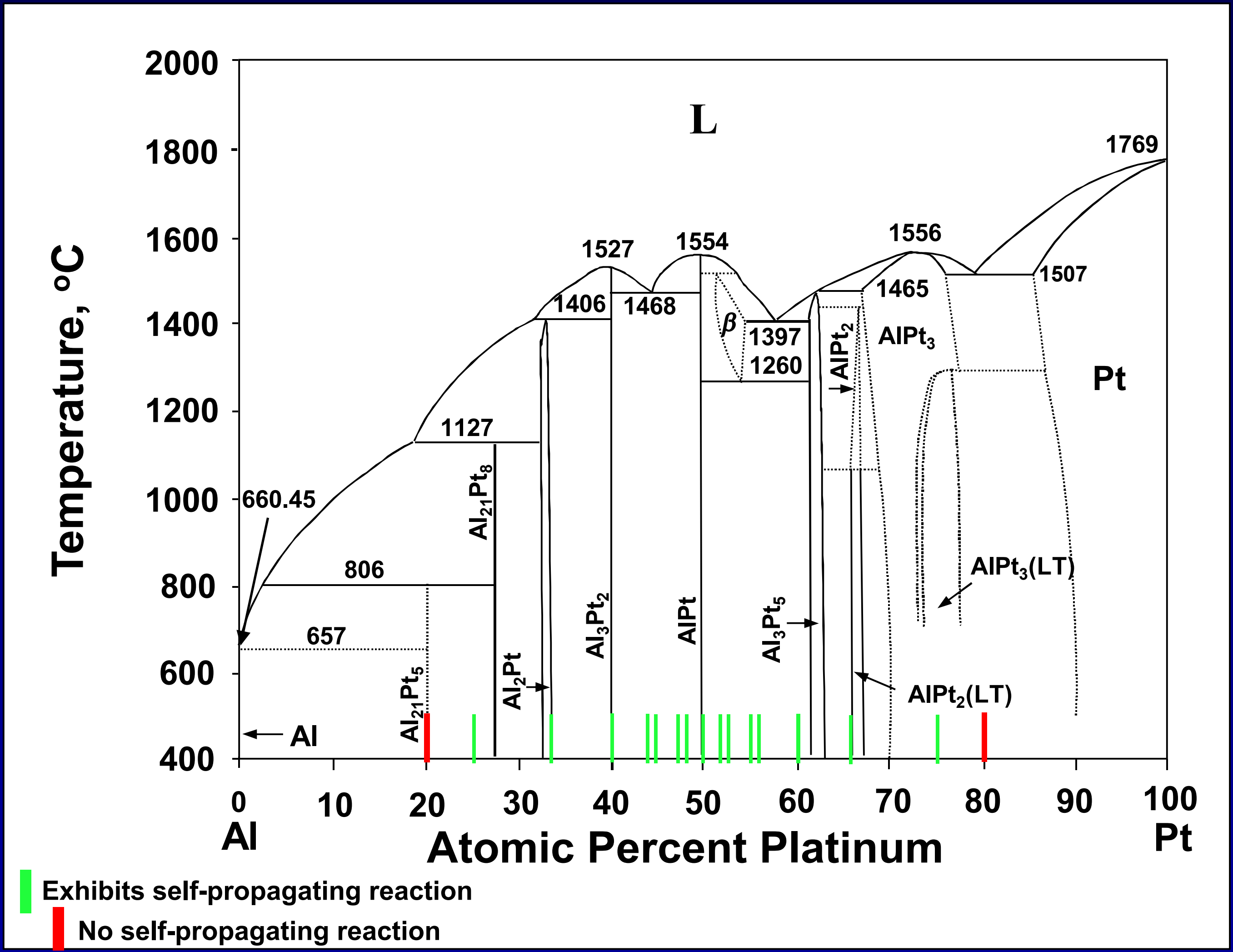
Self–propagating when 0.2 < x < 0.8.

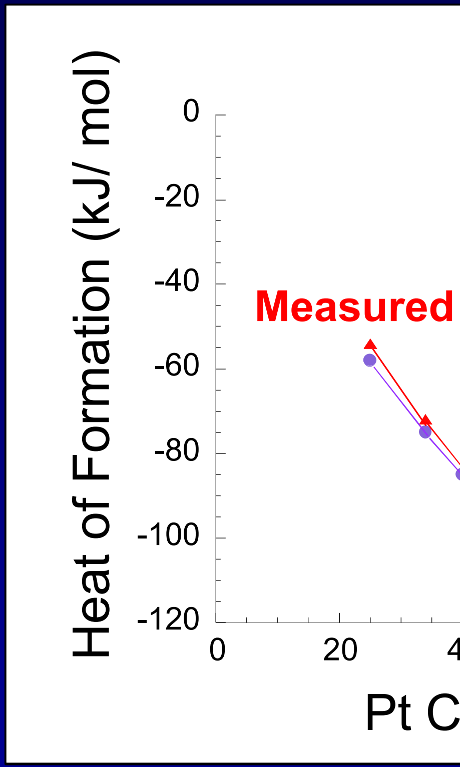
Design of experiments that vary net composition and bilayer thickness.



Investigate various Al-rich and Pt-rich compositions.

Summary of reactive compositions (tested as foils).





Phase Diagram redrawn from McAlister and Kahan, ASM 1986

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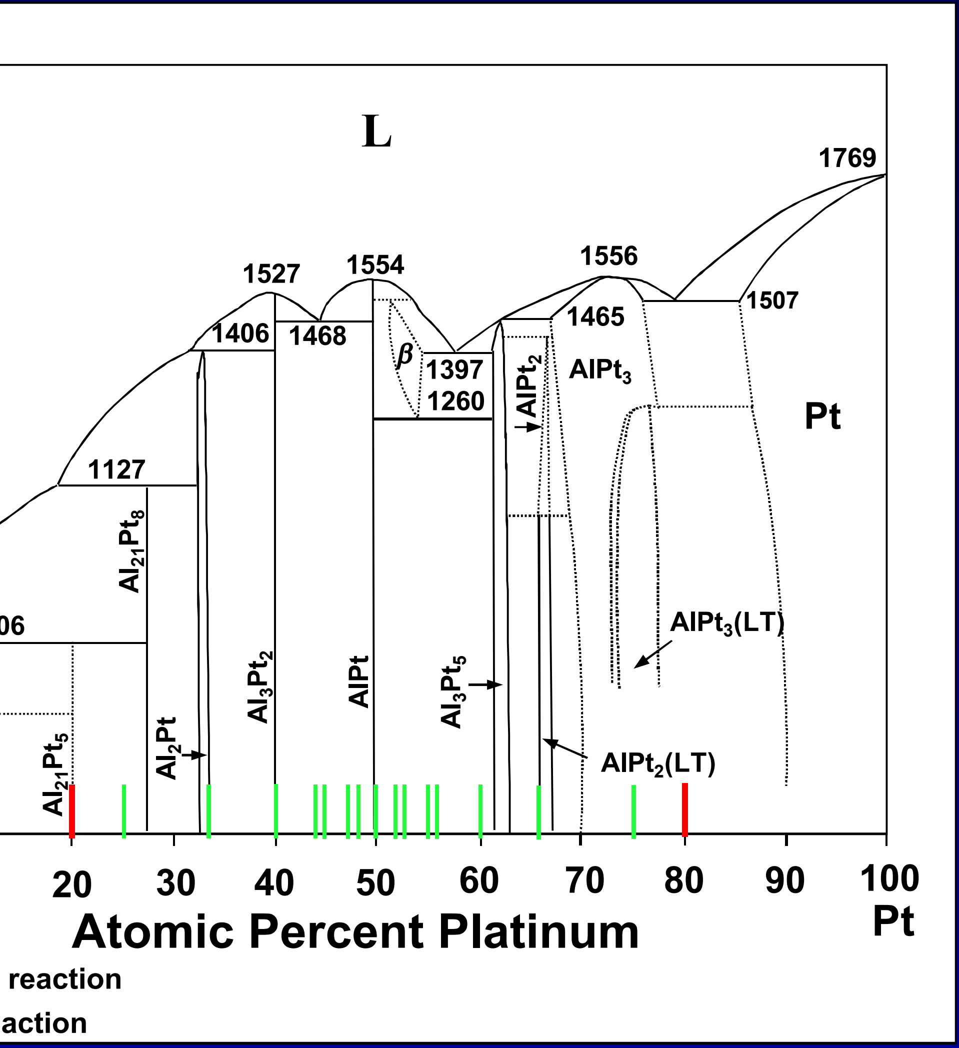

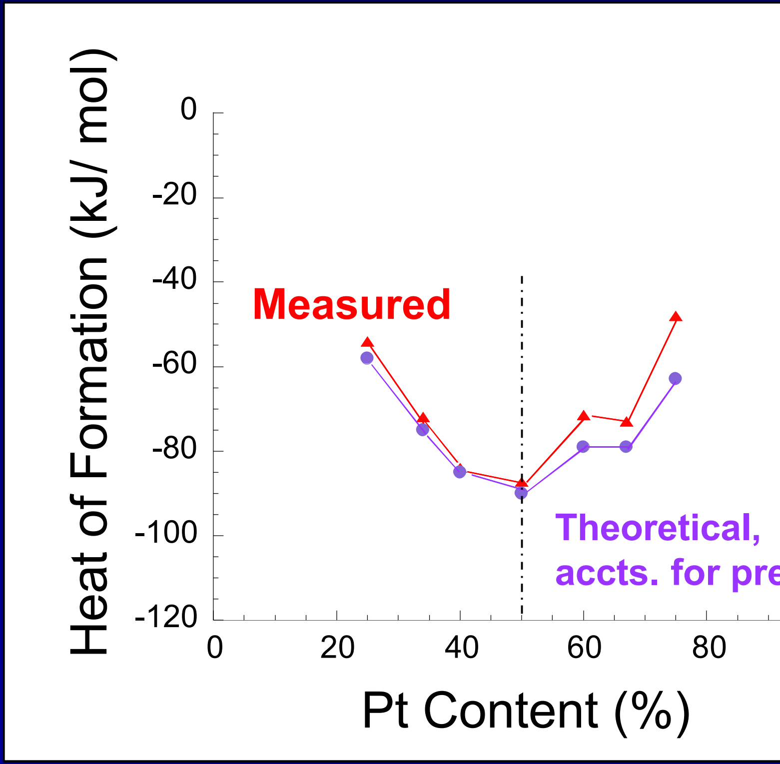

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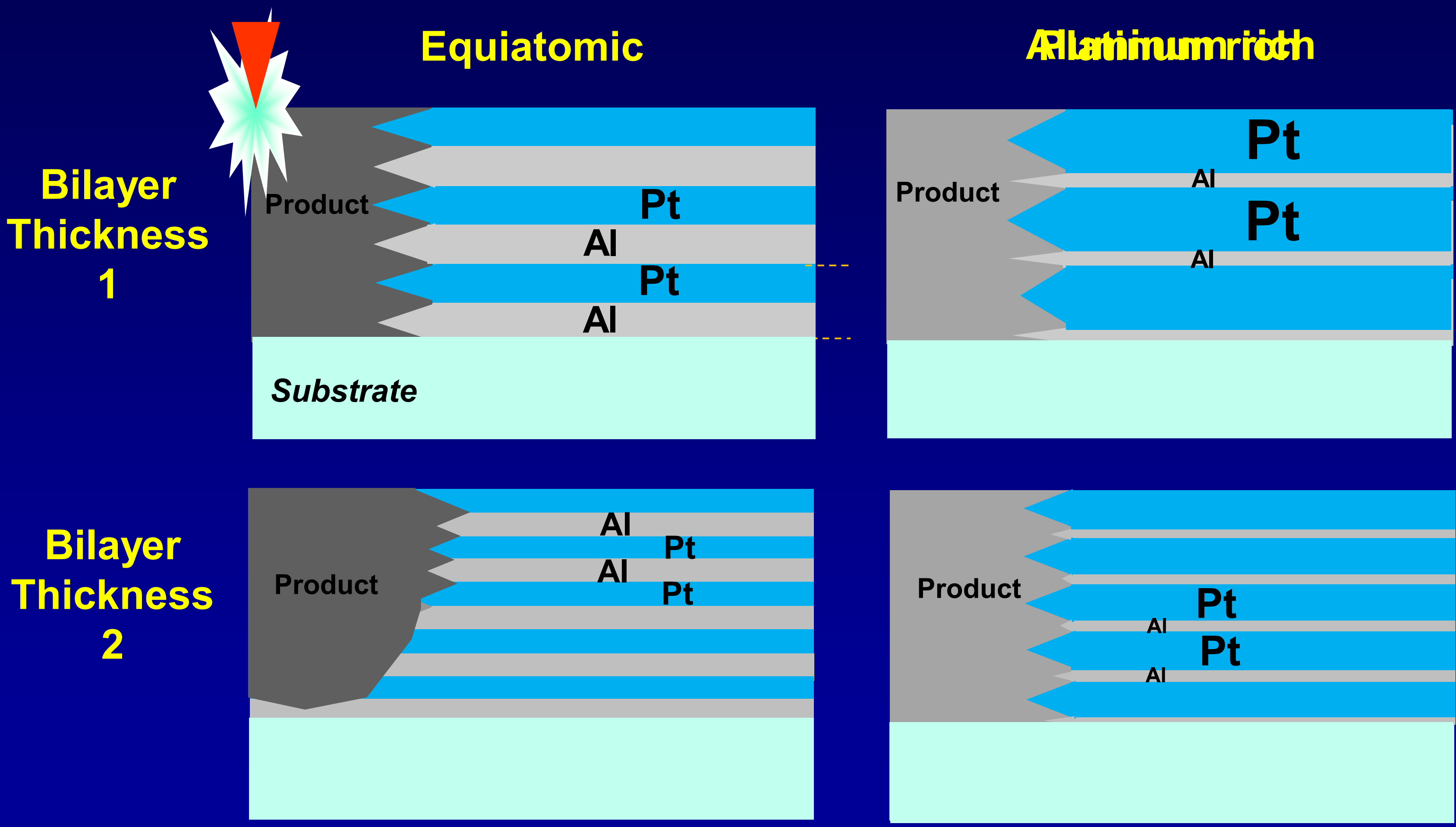
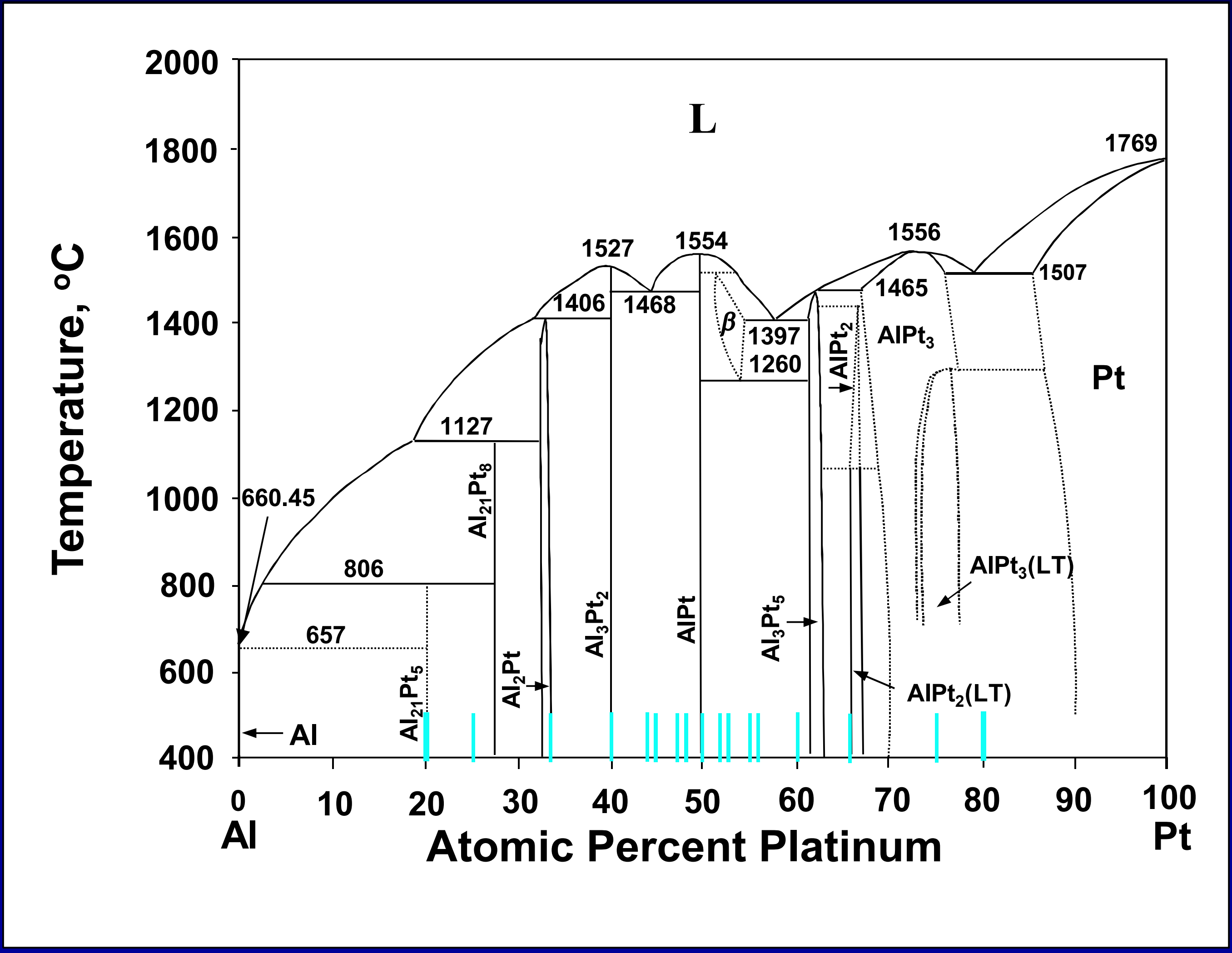


Investigate various Al-rich and Pt-rich compositions.

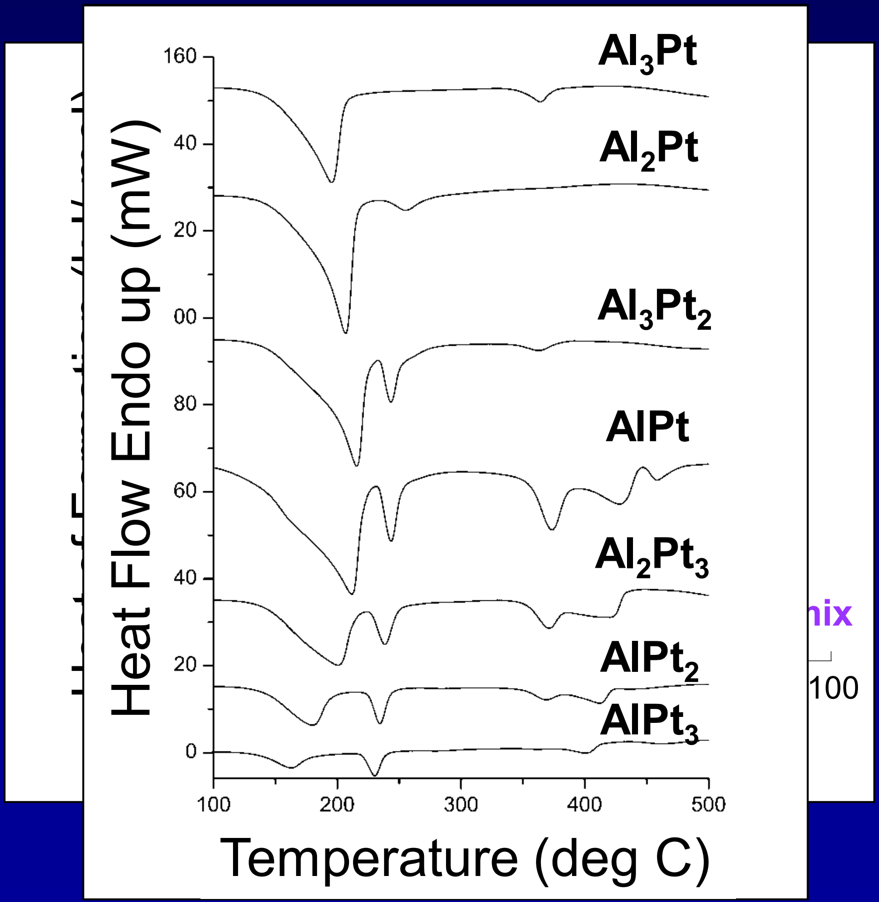
Summary of compositions tested.



Phase Diagram redrawn from McAlister and Kahan, ASM 1986

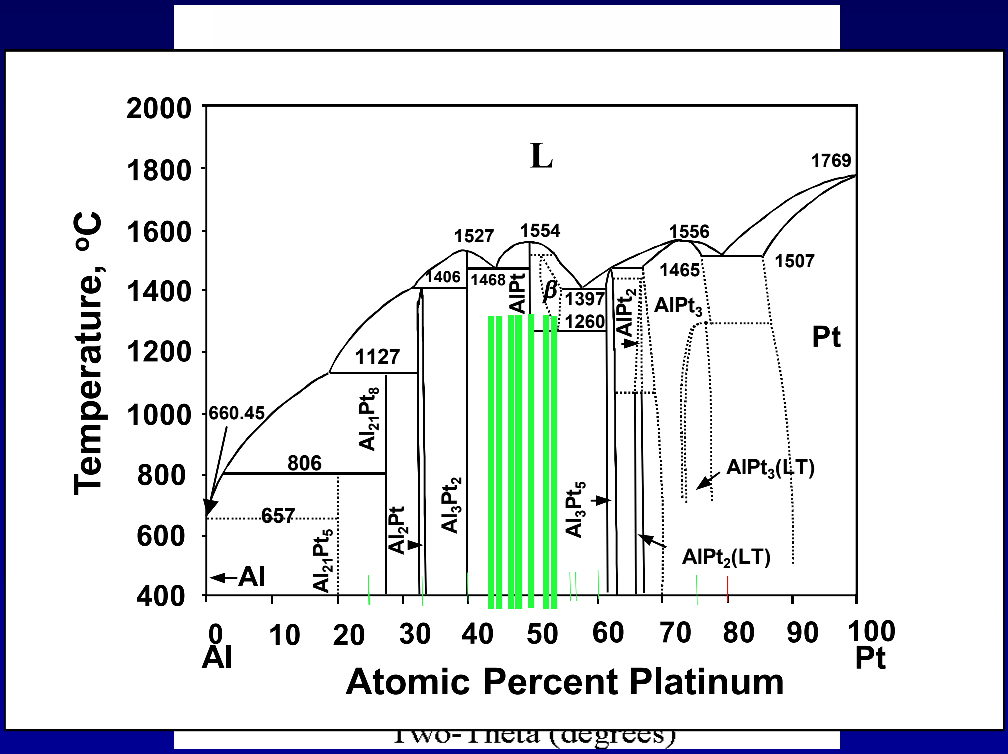
Differential Scanning Calorimetry is used to measure heat of formation for Al_xPt_y.

- All Al_xPt_y compositions studied here are characterized by exothermic rxns.
- Equiatomic AlPt exhibits maximum ΔH_o.
- Al- and Pt-rich multilayers have reduced stored chemical energy.
- Reasonable matching to ΔH_o (literature*) - E_{premix}

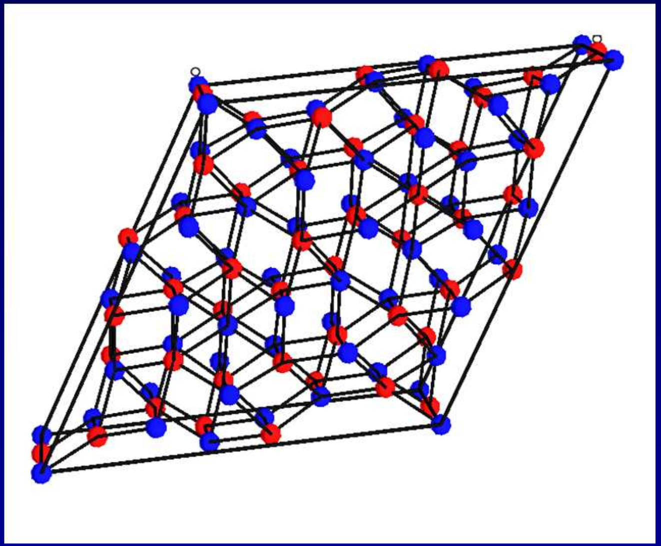


* deBoer, Cohesion of Solids

For other compositions, phase formation is not consistent with published equilibrium phase diagrams.



rhombohedral AlPt
(new metastable phase)



- 39 formula units per unit cell.
- composition range 44-53% Pt.
- previously reported for AlPd.

Suggest that rapid quench rates (est. -3.9×10^8 C/sec) influences phase

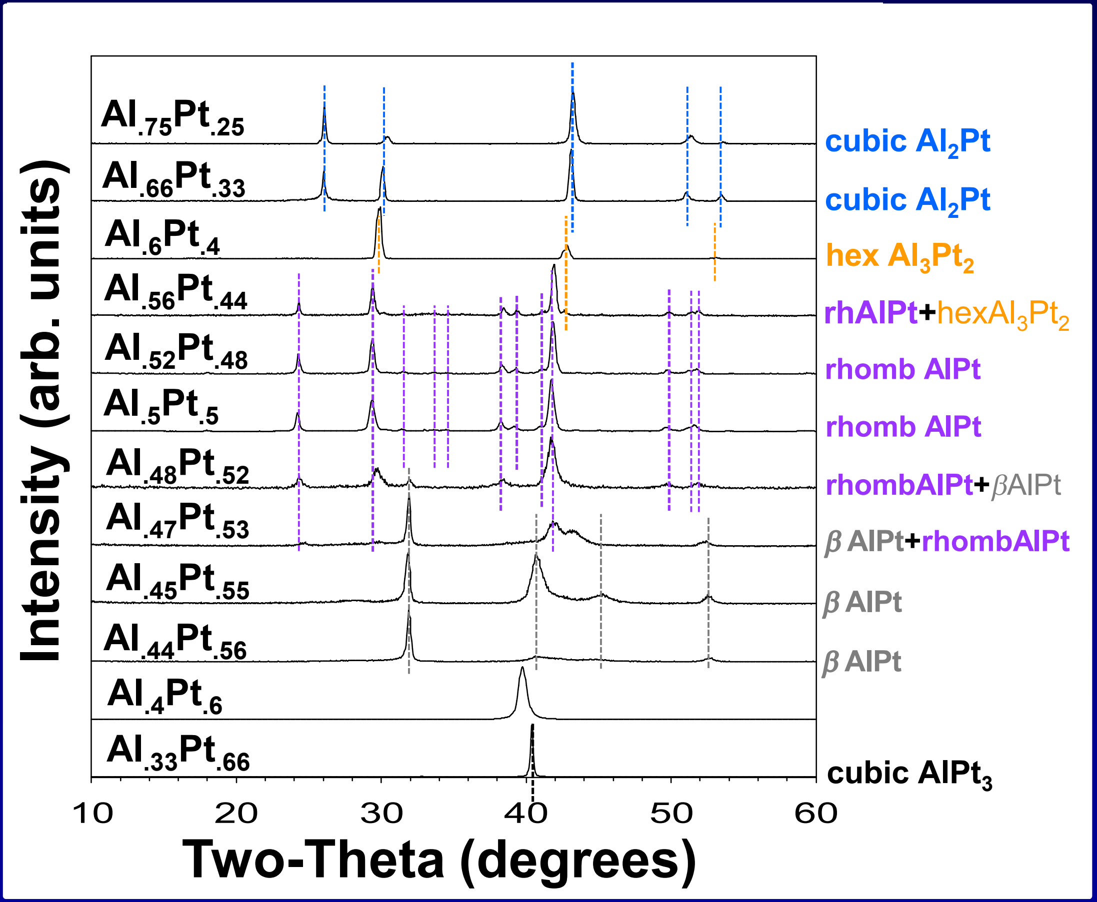
XRD determines phase(s).

- No evidence of unreacted Al or Pt after self-sustained high temperature synthesis
  - all foils listed

- A variety of different phases form depending on the net composition of the reacted foil.

  - in some cases, single product

  - in other cases, dual product



WDS determines composition ±1% uncertainty, 95% confidence.

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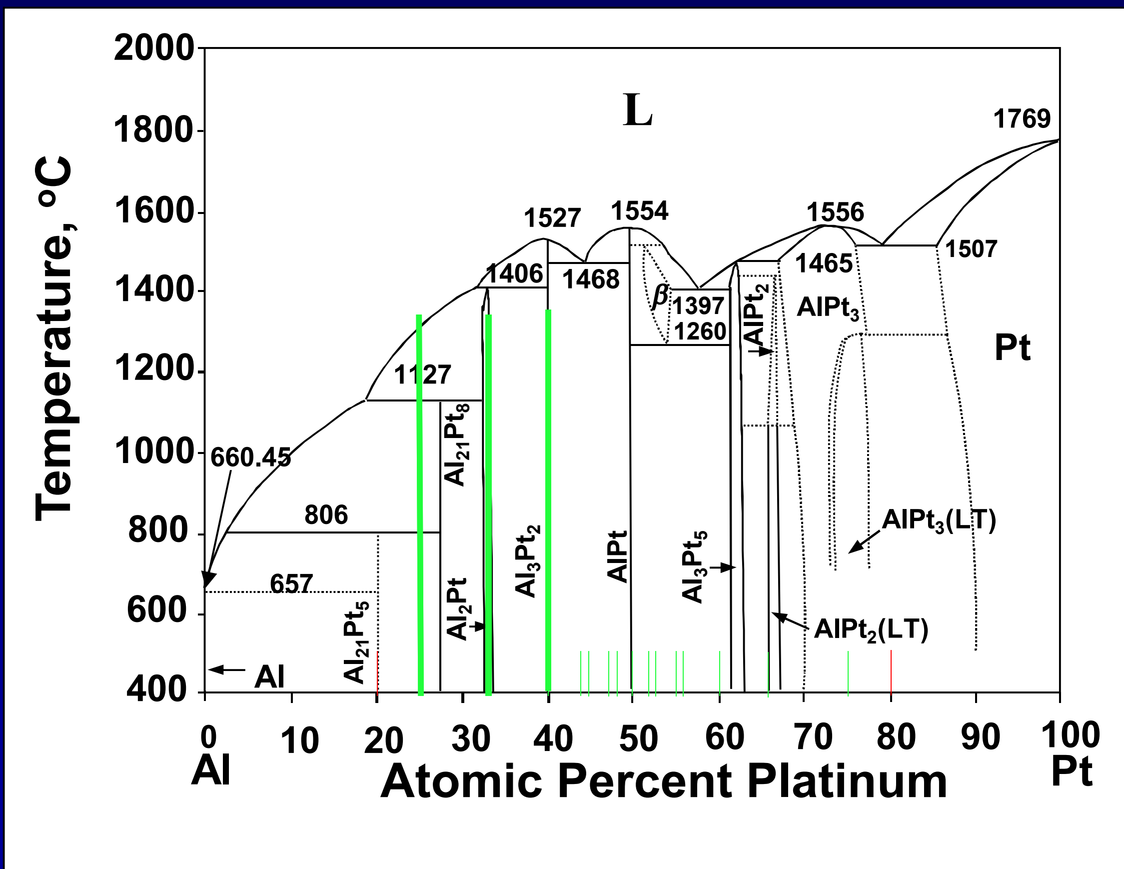
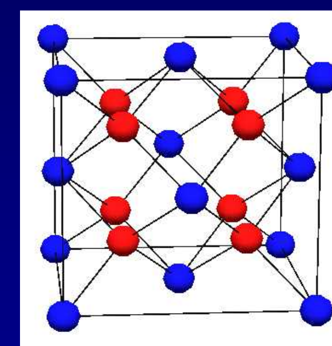


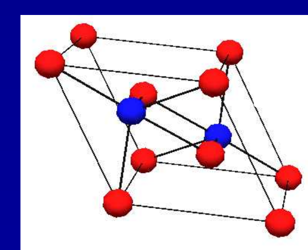
Exhibits self-propagating reaction

No self-propagating reaction

cubic Al_2Pt



hexagonal Al_3Pt_2



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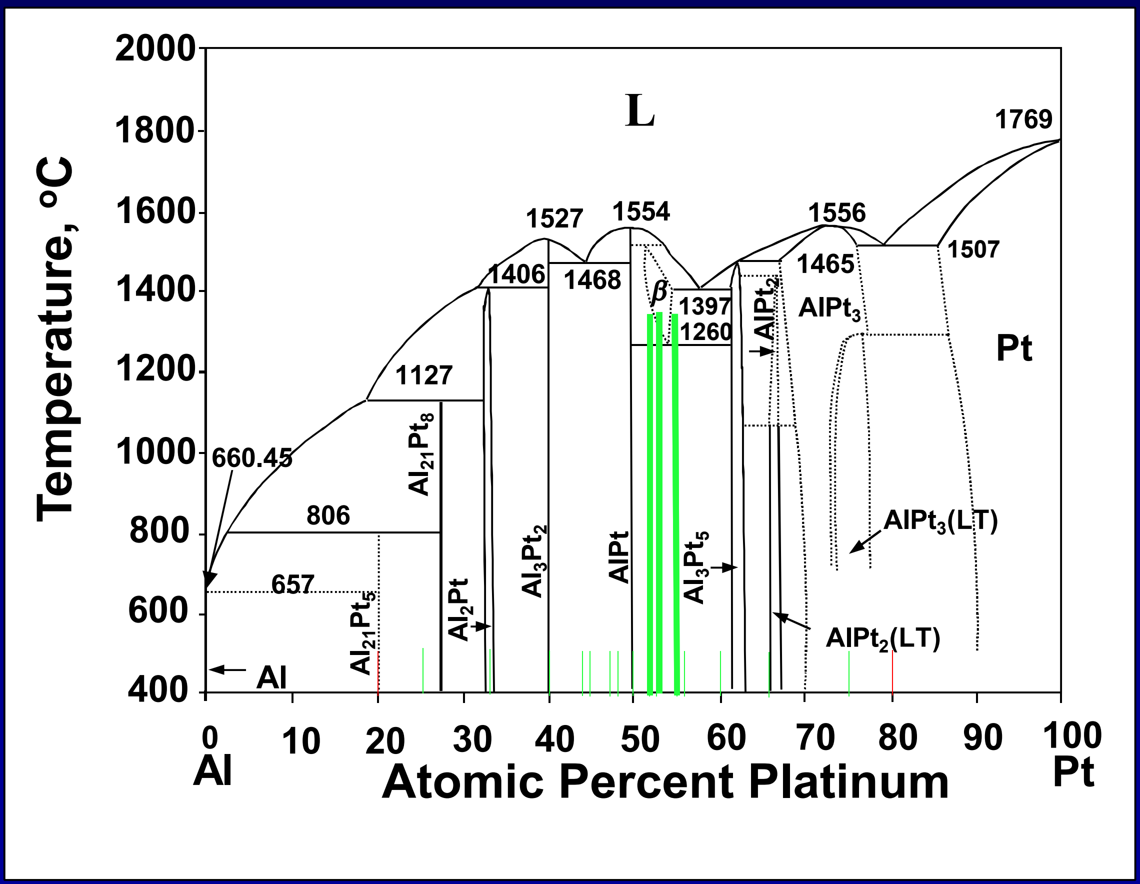
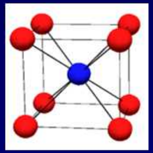


Exhibits self-propagating reaction

No self-propagating reaction

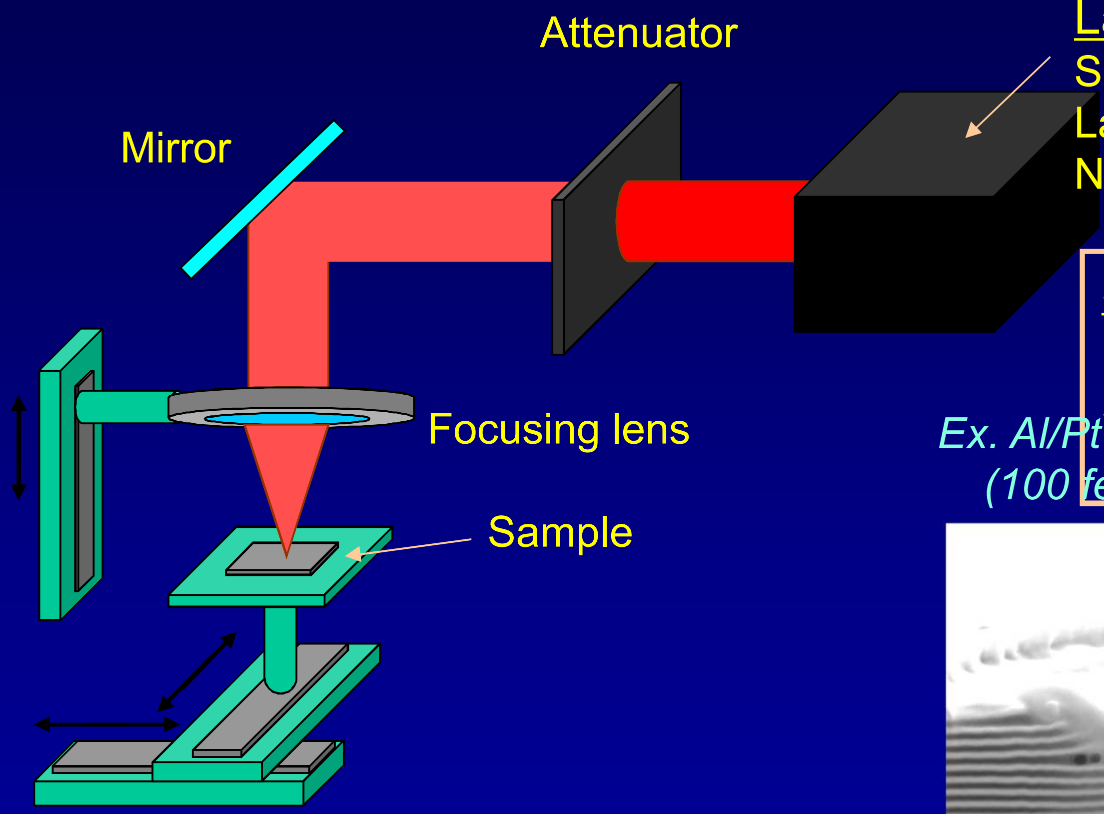
β AlPt



Cubic (CsCl unit cell type)
- two previous reports

- composition 52,53, 55 % Pt consistent with high temp portion of phase diagram

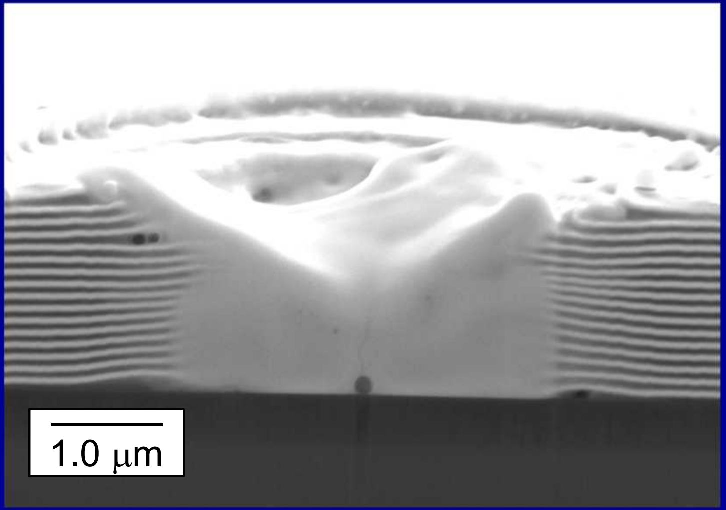
Experimental schematic: quantifying point ignition thresholds



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)



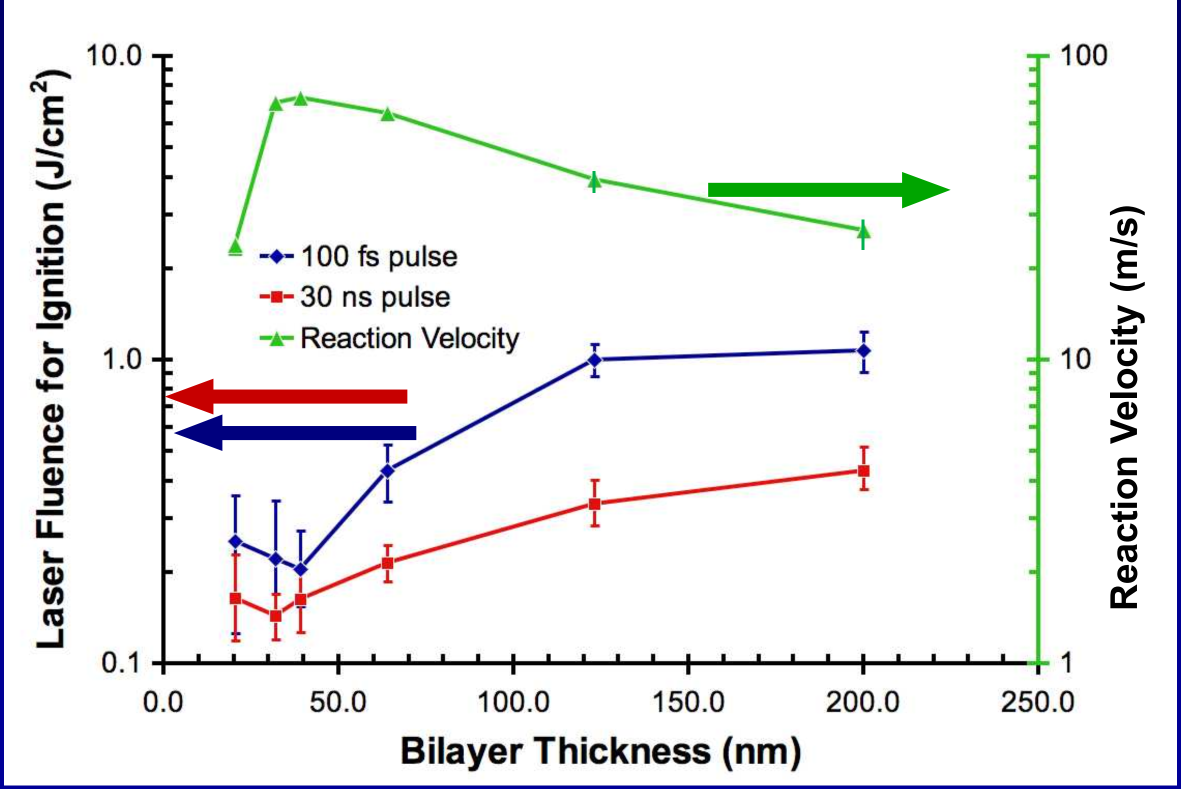
Cross section SEM (sectioned by focused ion beam)

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

Ex. 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).

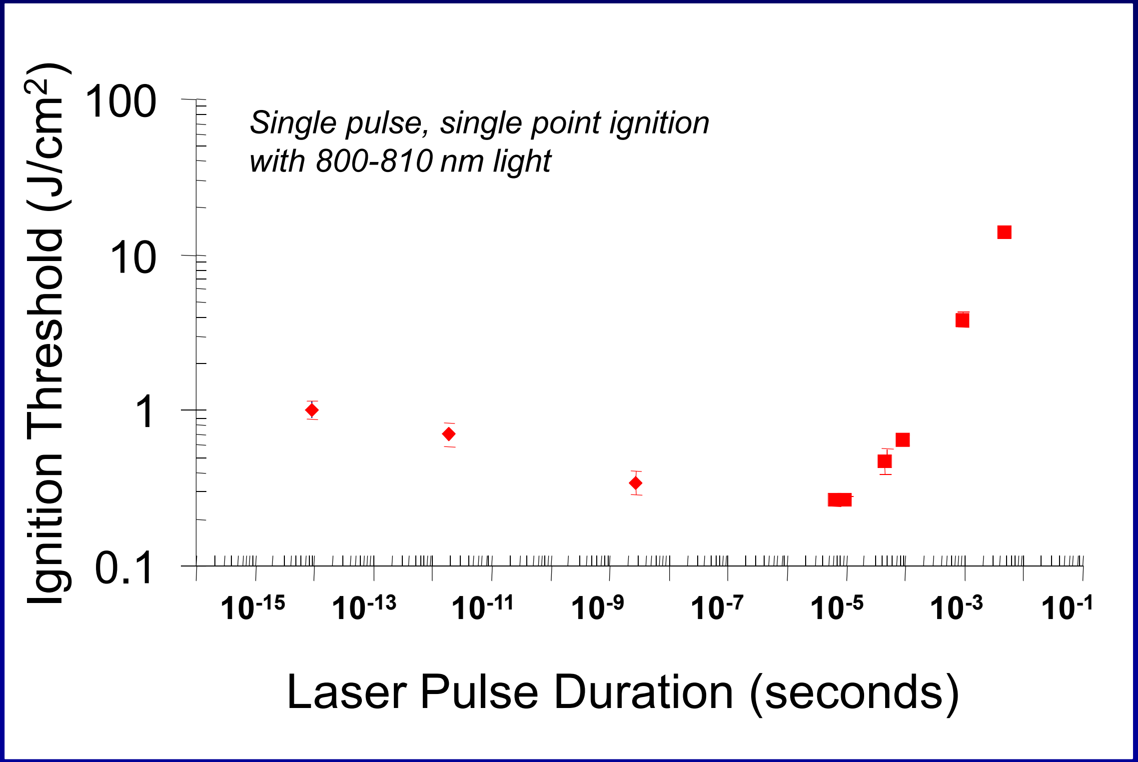


J. P. McDonald, D.P. Adams, Mat. Res. Soc. Symp. Proc. (2008).

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
Fixed spot size: $1/e^2$ = 28 μm



Reactive multilayers are useful for applications requiring localized heating (e.g., joining).

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).

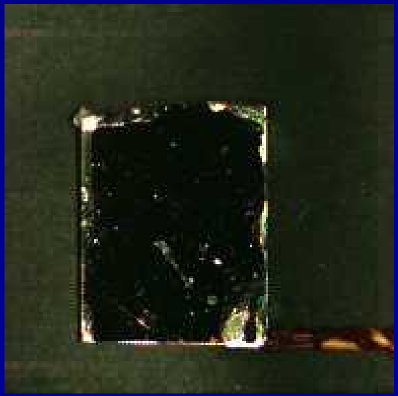
Applications:

Joining, Soldering,
Lid seal, MEMS.

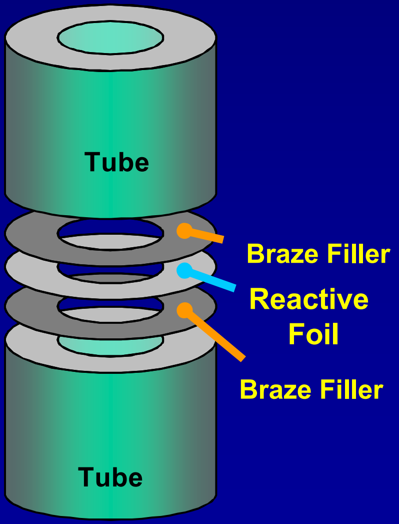
Key Properties:

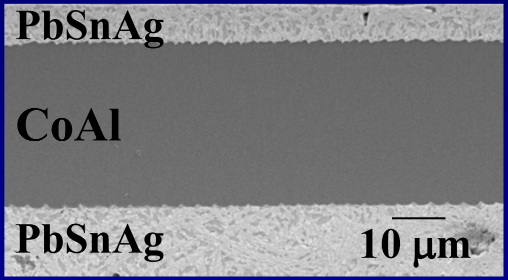
Stored chemical energy
Ignition at a point
Self-propagating Synthesis
Structure and Morphology

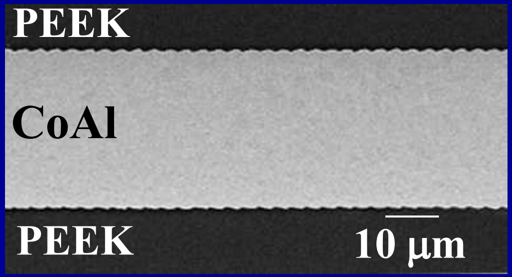
Movie in plan view
Aluminum /Platinum



1 cm







Joined assemblies using Cobalt/Aluminum

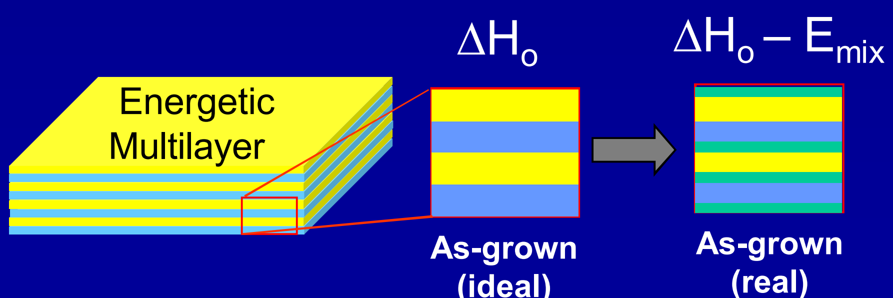
Nickel / titanium foils exhibit SHS in air.

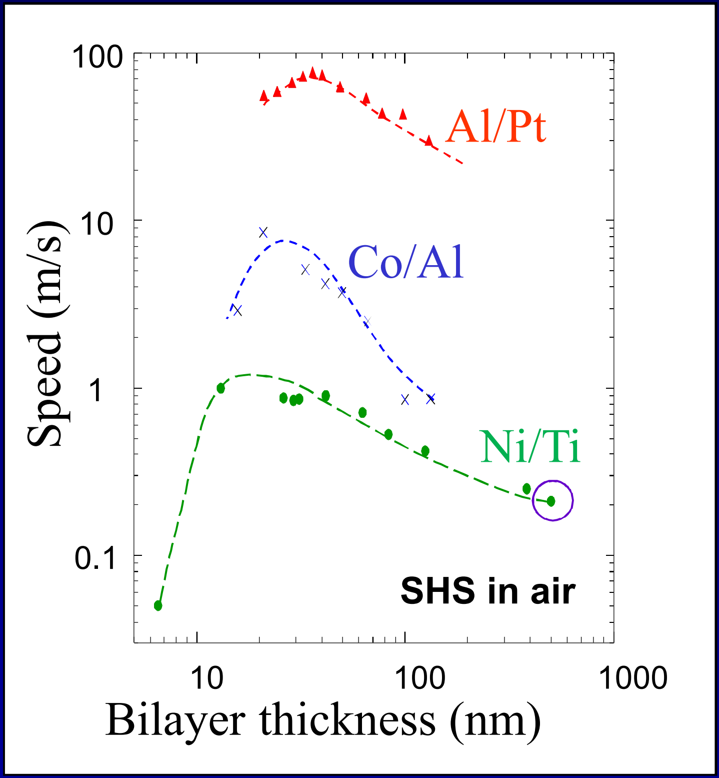
- Ni/Ti exhibits SHS in air without pre-heating.
  (ignition with 9 V battery, pulsed laser or other)

- Propagation speed increases with decreasing bilayer thickness for a large range of designs.

- Maximum propagation speed of ~ 1 m/s for 5 μm thick foils (equiatomic).

- Decreased speed at small bilayer thickness due to premixed reactants.



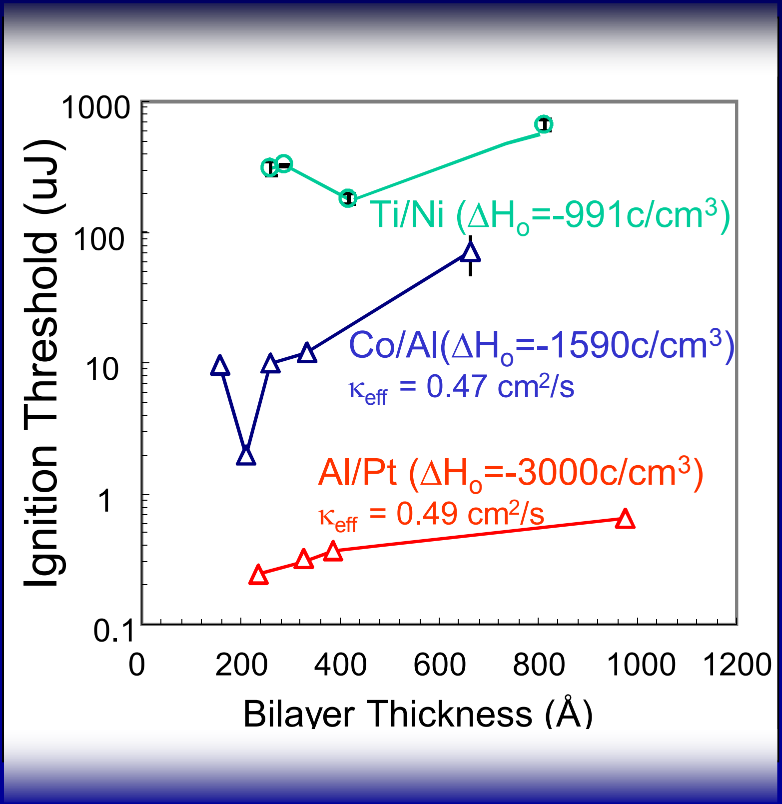


Y. Picard, J. Mcdonald, S.M. Yalisove, D.P. Adams, Appl. Phys. Lett. 93 (2008).

Laser-induced ignition studies of multiple reactive foil systems

Example: Single pulse, single point ignition with 30 nanosecond excimer laser, 248 nm

- Thresholds span a large range of energies from < 1 μJ to 500 μJ.
- Differences between metal pairs is attributed to enthalpy, and possibly mass transport kinetics.
- Data suggests an effect of multilayer design (i.e., bilayer thickness).



Results compensate for reflectivity differences between systems

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

General Technology

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 (^oC)
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	YCu	-419	0.2 – 0.4	unknown

Compare with

ΔH_o (Fe/KClO4) ~ -1560 J/g

Exothermic multilayers are deposited at Sandia using magnetron DC sputter methods.

Multiple deposition systems

10^{-9} - 10^{-8} Torr base pressure
Ar sputter gas
In-situ quartz crystal monitors

Capabilities:

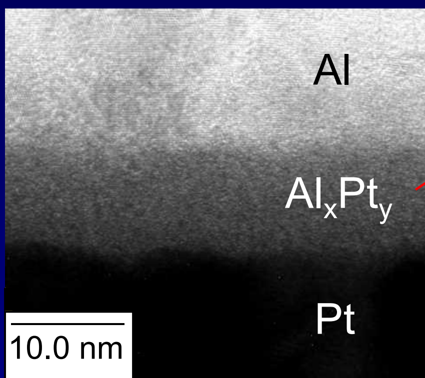
> 99 % uniformity across 8" area
Sample at 45^{o}C during deposition
Precision of layer thickness:10-15 Å

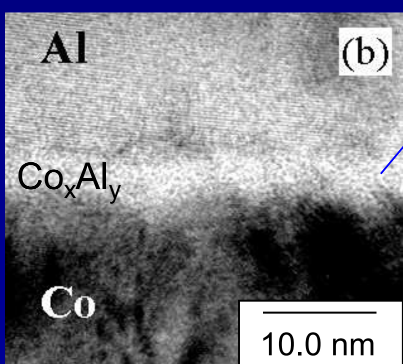
Other:

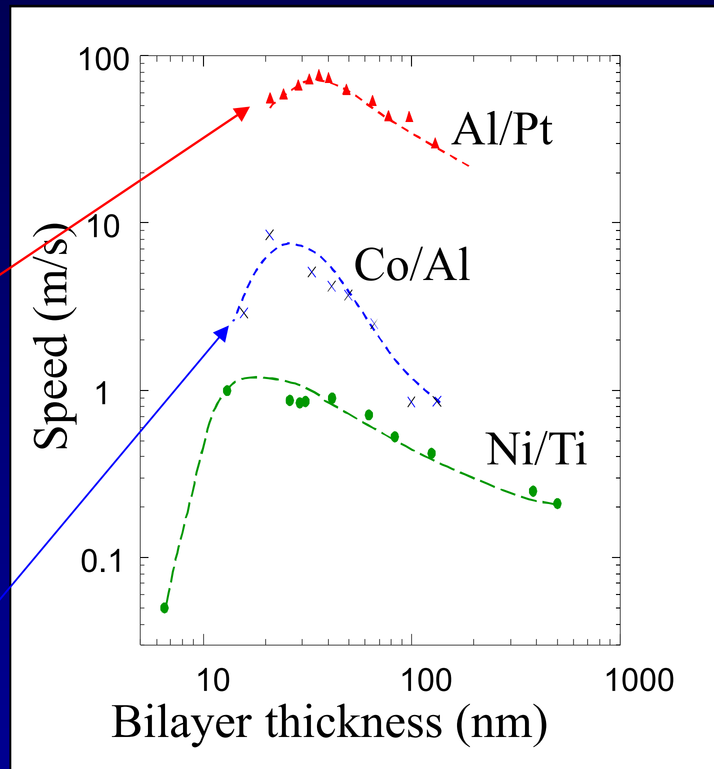
Adjust film thicknesses to
compensate for densities

Generally, multilayer is peeled off to 'create' a foil for testing.

Propagation rate is affected by multilayer design



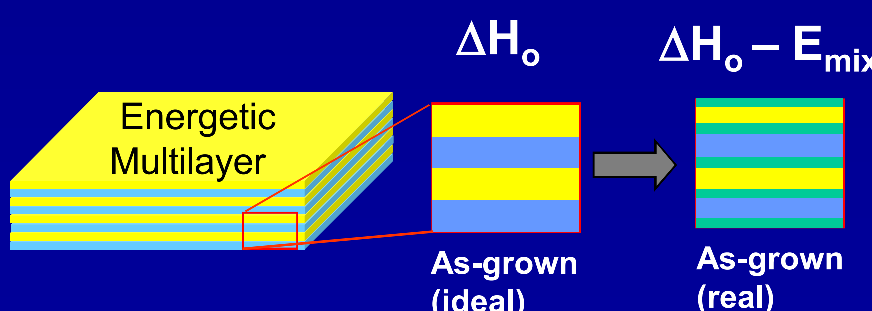




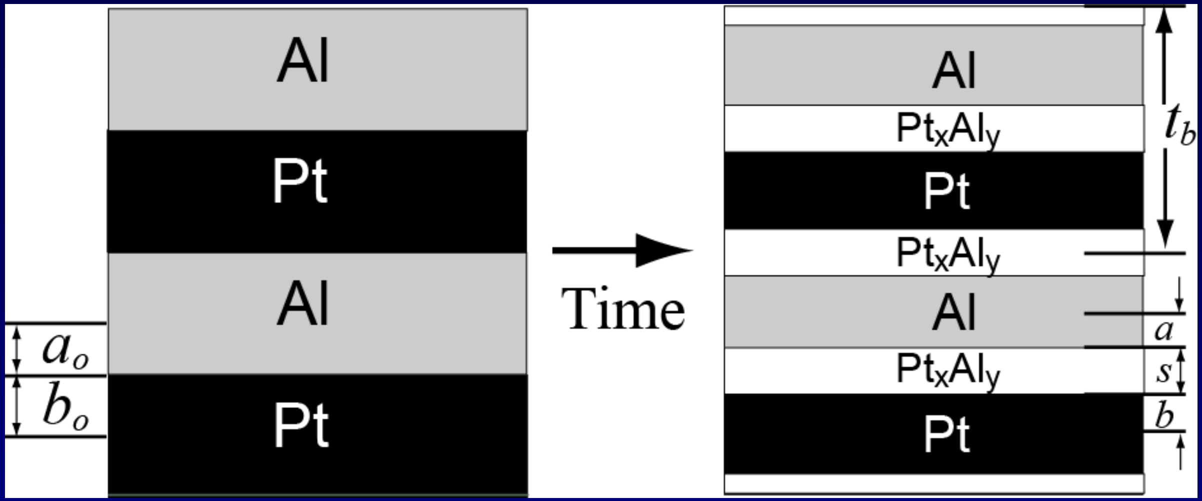
- Propagation speed increases with decreasing bilayer thickness for a large range of designs.

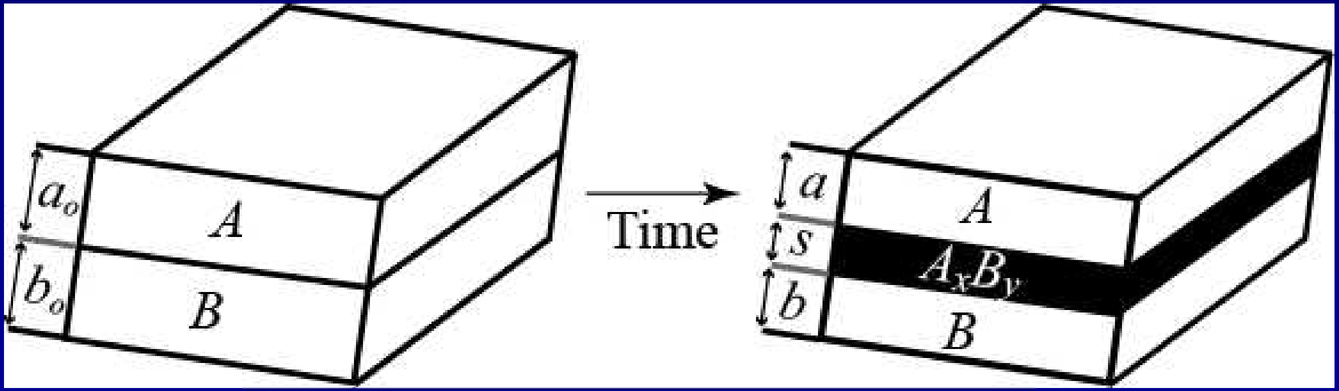
$$V^2 = \frac{3A\exp(-E/RT_c)RT_c^2\lambda^2}{(1/4t_{BL})^2E(T_c-T_o)}$$

- Differences in speeds (for diff. materials) owe to a larger ΔH_o and differences in mass/thermal transport.
- Propagation speeds affected by premixed reactants when periodicity is small.



Two bilayers of Al and Pt



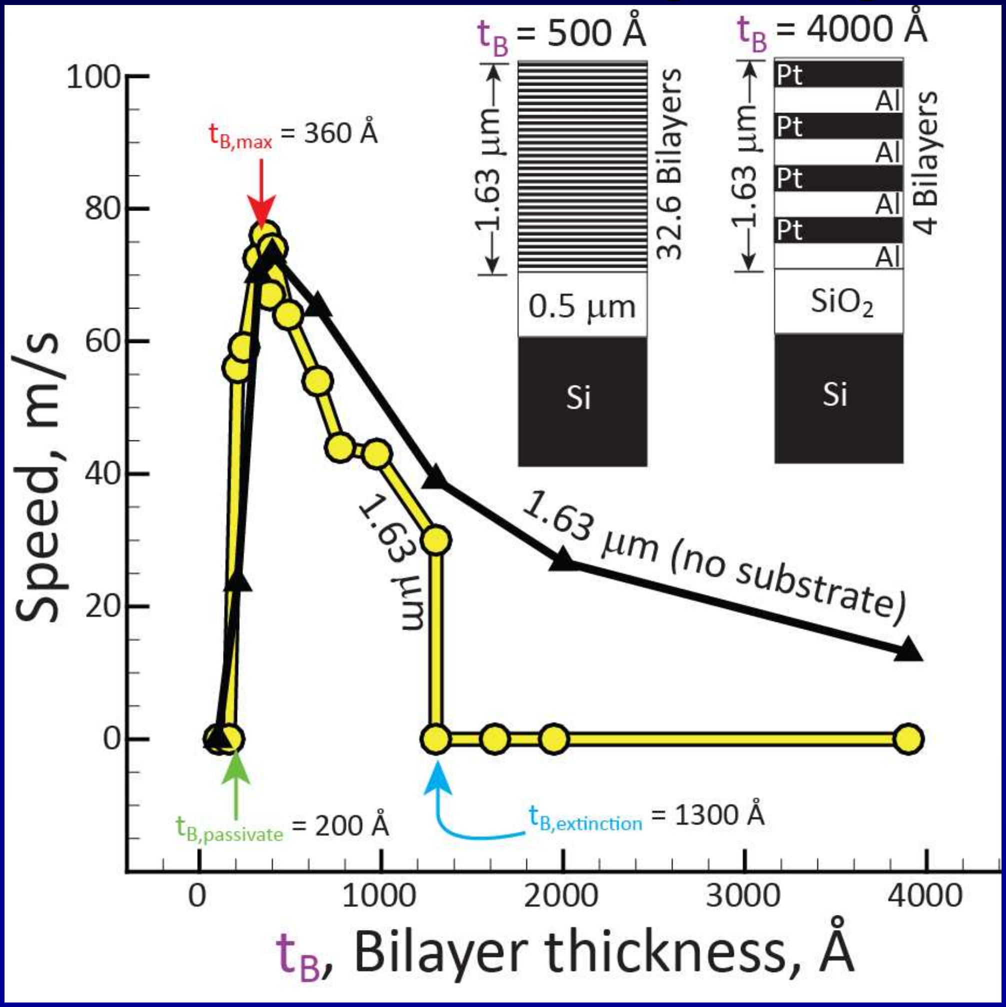


$$t_b = 2(a + b + s)$$

A bilayer is a single layer of Al plus a single layer of Pt.

Critical Bilayers Definitions

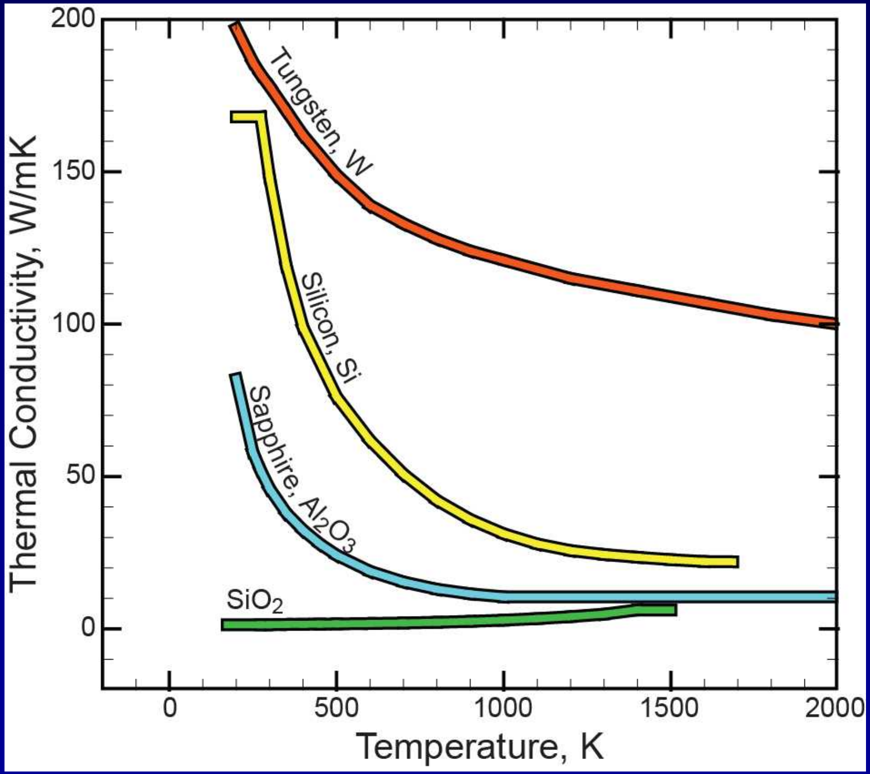
kindling **logs**



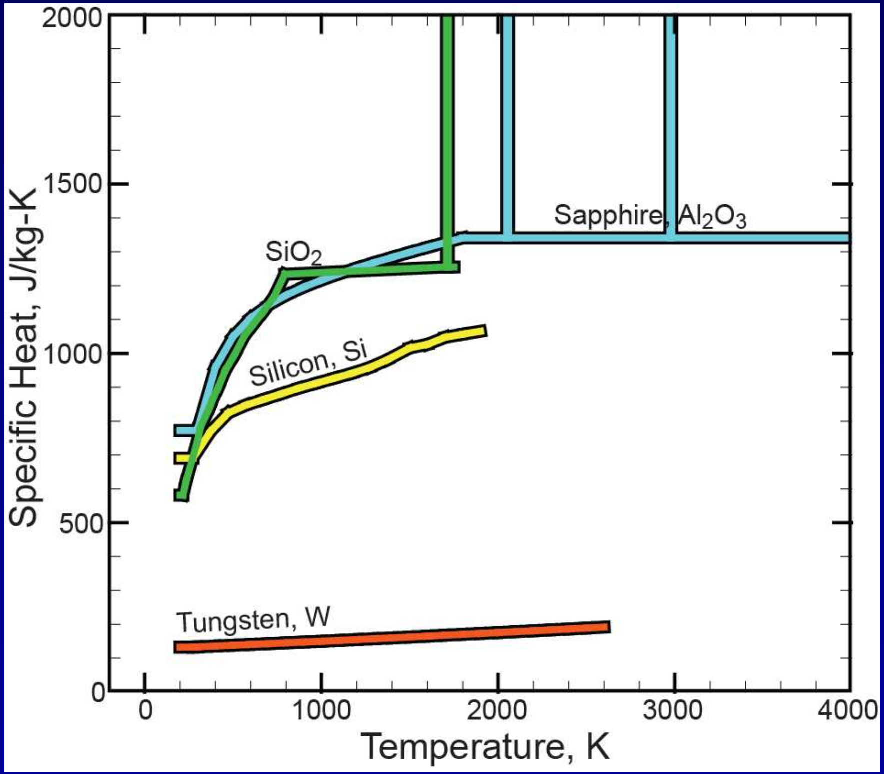
- **t_B = bilayer thickness**
- **$t_{B,passivate}$ = bilayer thickness where front fails to propagate due to relatively large passivation layers**
- **$t_{B,max}$ = bilayer thickness that produces maximum front speed**
- **$t_{B,extinction}$ = bilayer thickness where front fails to propagate due to large diffusion paths**

Thermophysical Properties

Thermal Conductivity



Specific Heat



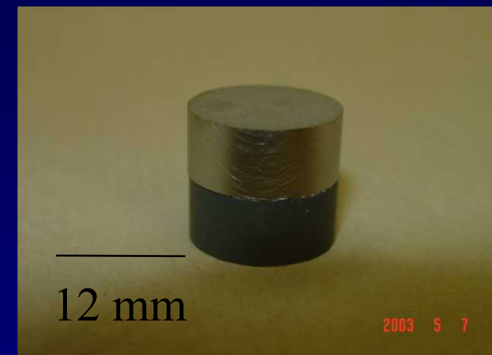
Temperature dependent properties

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

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

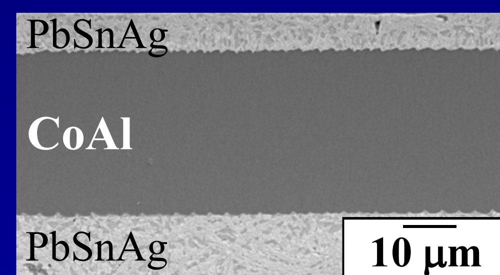
$$M_1+M_2 \Rightarrow M_1M_2$$
$$M_1+M_2O \Rightarrow M_1O+M_2$$

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



Brazed with heated Ni/Ti foil

Courtesy: J. Moore (CO School of Mines, R. Radtke, Technology International.



Soldered with Co/Al foil

Direct Attach to plastic with Co/Al foil