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Propagating Exothermic Reactions in in Al/Pt Multilayers of Varied Composition

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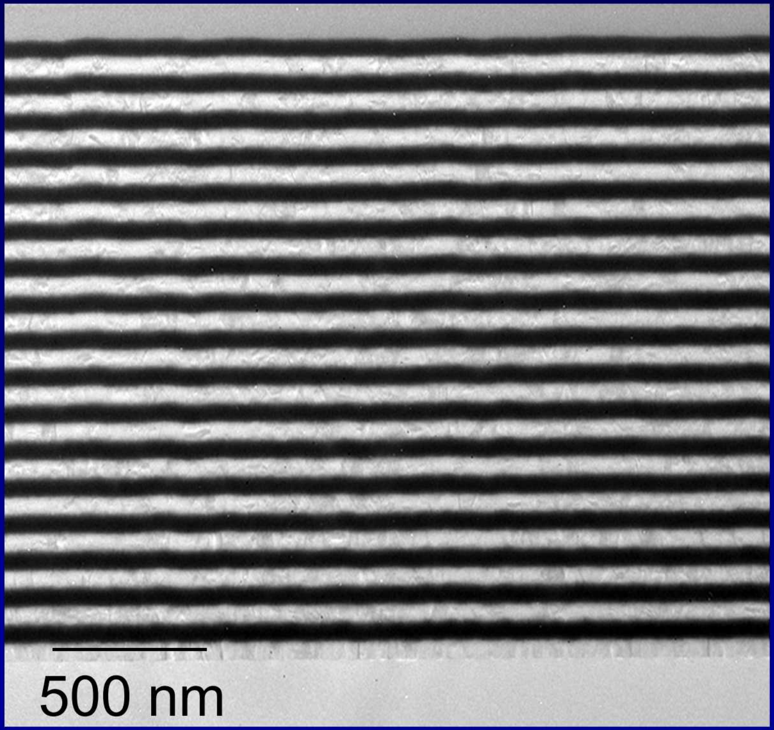
Sputter-deposited reactive multilayers.

- Design includes two reactants
- Single, out-of-plane periodicity for each multilayer (called bilayer thickness)
- Heats of formation, ΔH_o, for bimetals:
  Ti/2B : - 102 kJ/mol at.
  Al/Pt : - 100 kJ/mol at.
  Ni/Al : - 60 kJ/mol at.
  Co/Al : - 58 kJ/mol at.
- Review articles

1. Rogachev (Russ. Chem. Rev., 2008)
2. Weihs (in Metallic Films for Optical & Magnetic Applications, 2014)
3. Rossi (J. MEMS, 2007)
4. Adams (Thin Solid Films, 2015)



Al/Pt multilayer in Cross Section by TEM

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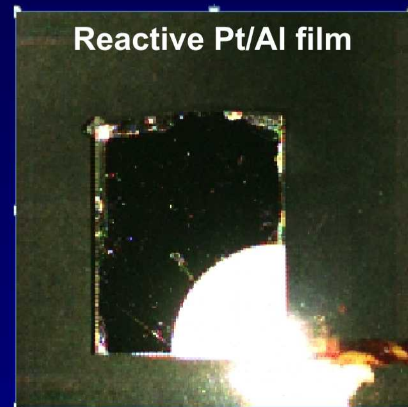

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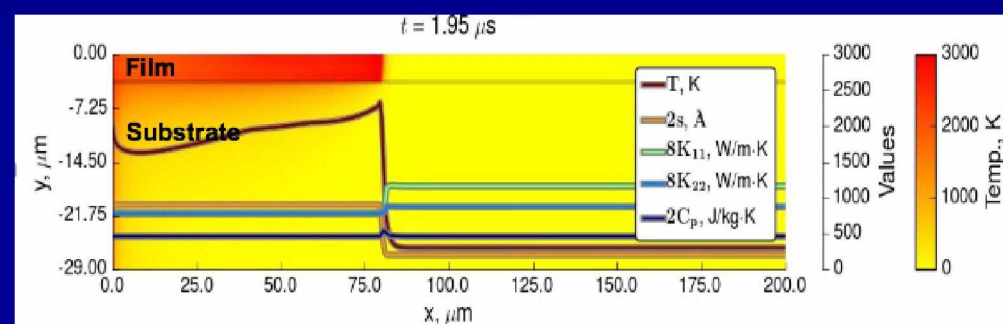
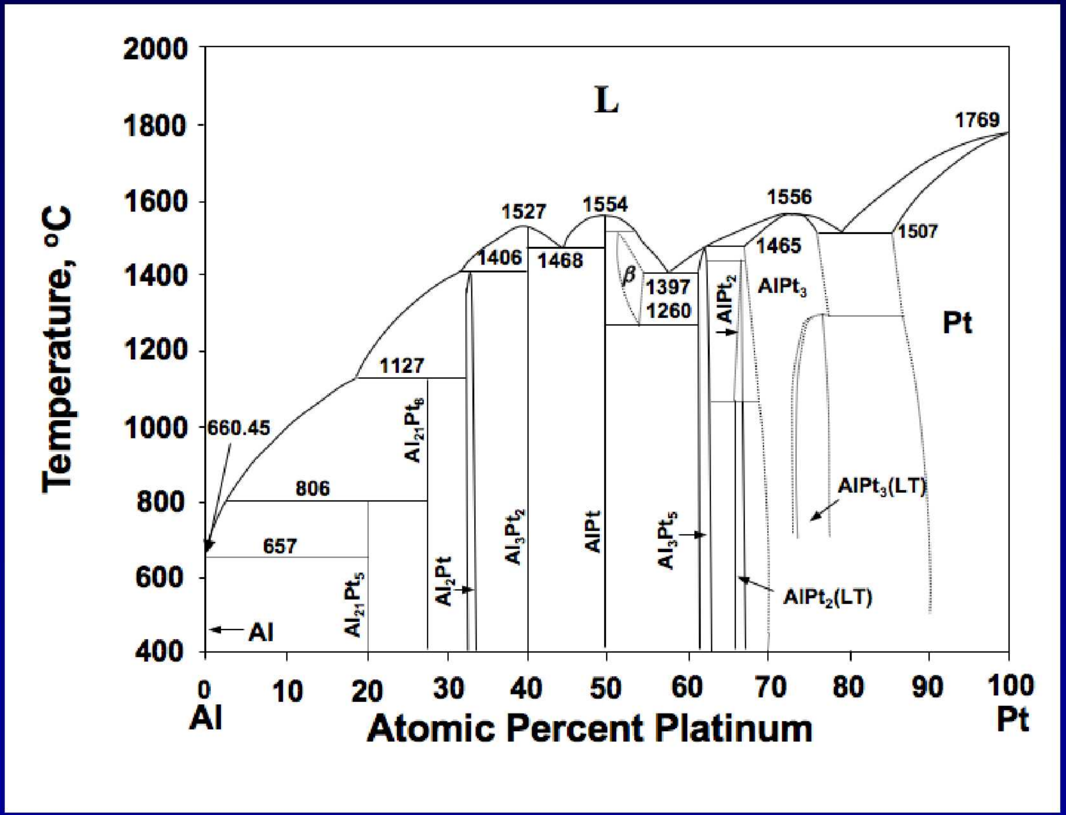


Finite element thermal model simulation of propagating reaction in Al/Pt film

Why Al/Pt?

- Known to have several exothermic stoichiometries.
- Eleven different thermodynamically stable phases.
- Previous demonstration of propagating reactions in equimolar Al/Pt.



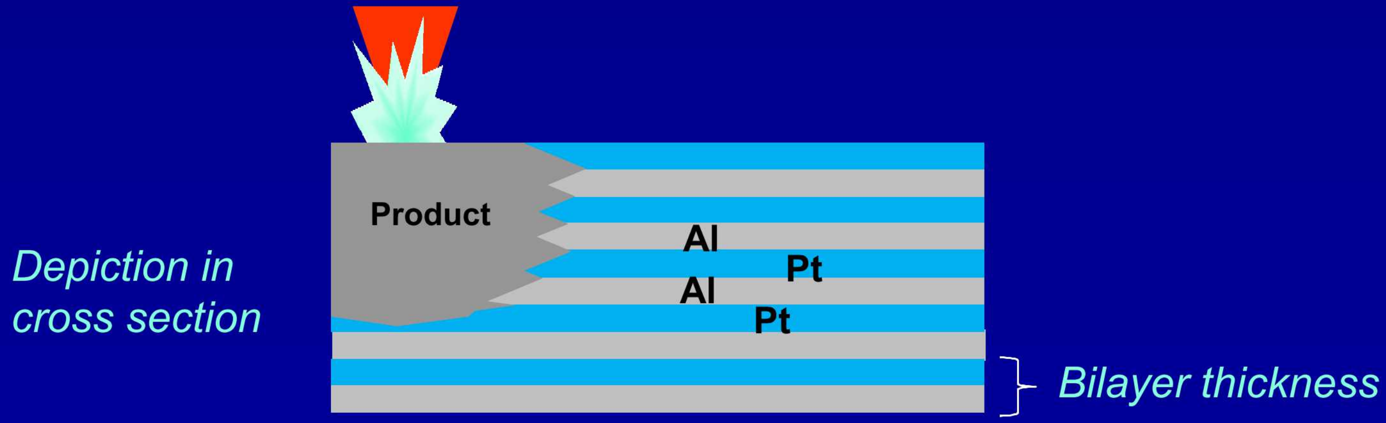
Phase Diagram redrawn from McAlister and Kahan, ASM 1986

Goals and approach of current study

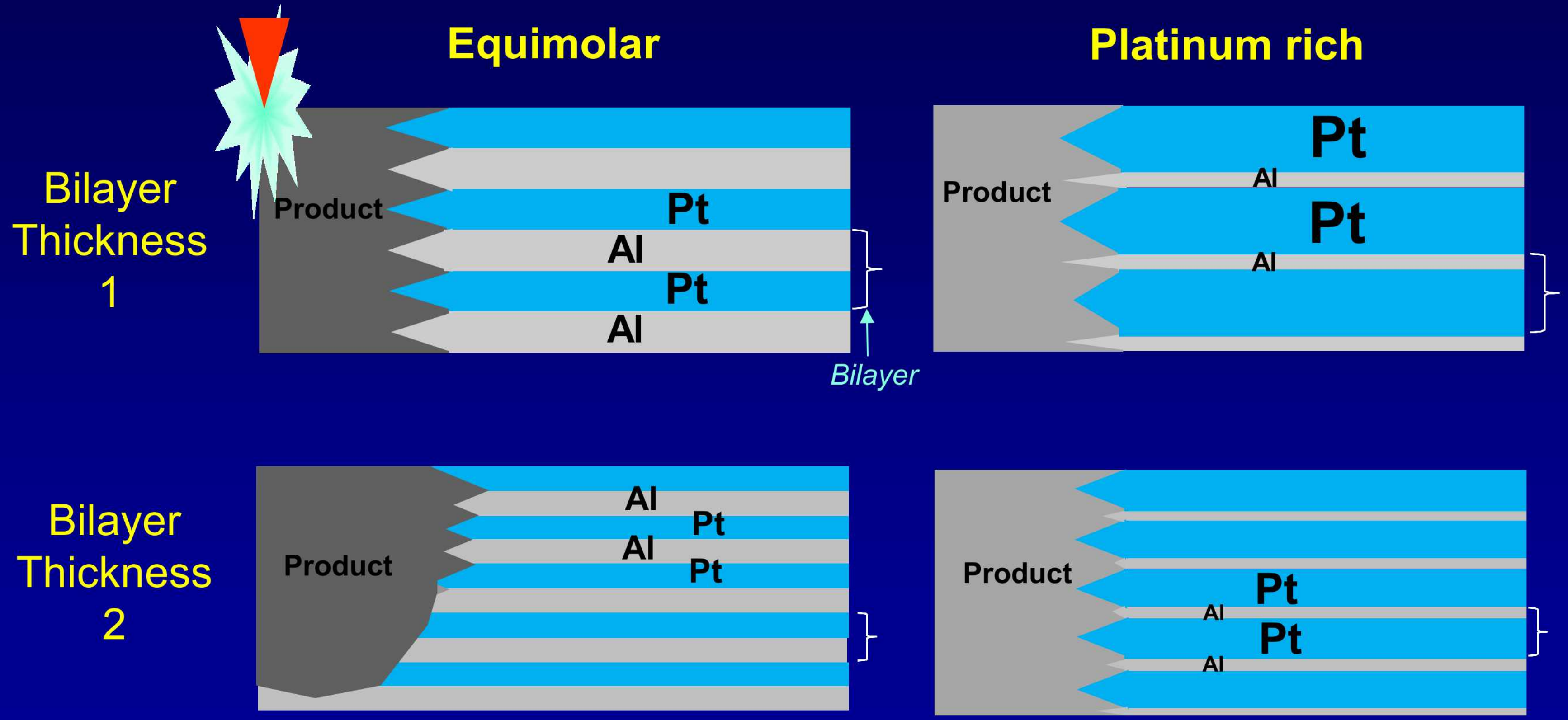
i) Determine the reactive range of Al-Pt multilayer stoichiometry which exhibit self-sustained, formation reactions when ignited at a point

ii) Investigate how ignition requirements vary with multilayer stoichiometry

iii) Explore how reaction wavefront speeds vary with multilayer stoichiometry.

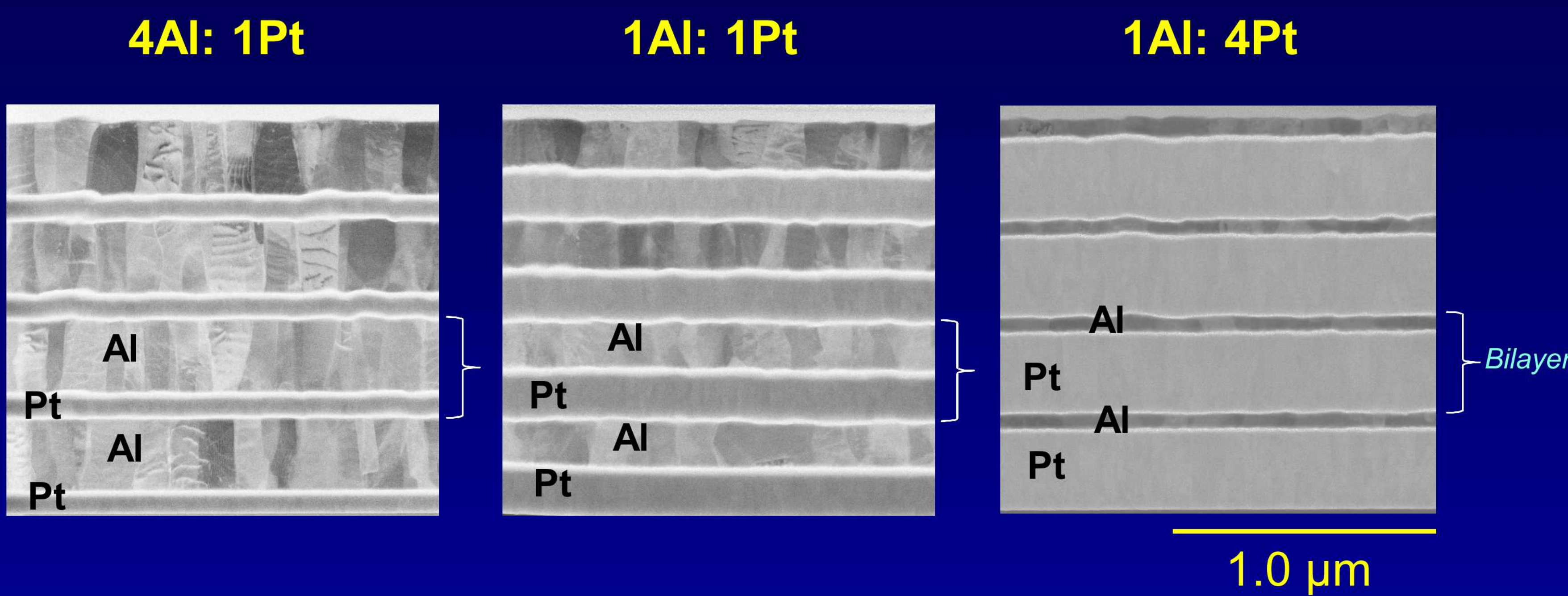


Multilayers have been made with different overall stoichiometry and periodicity



Stoichiometry varied from 9Al:1Pt to 1Al:9Pt.
Bilayer thickness varied from 10 nm to 1600 nm.
Total multilayer thickness fixed at 1.6 μm.

Example multilayers in SEM



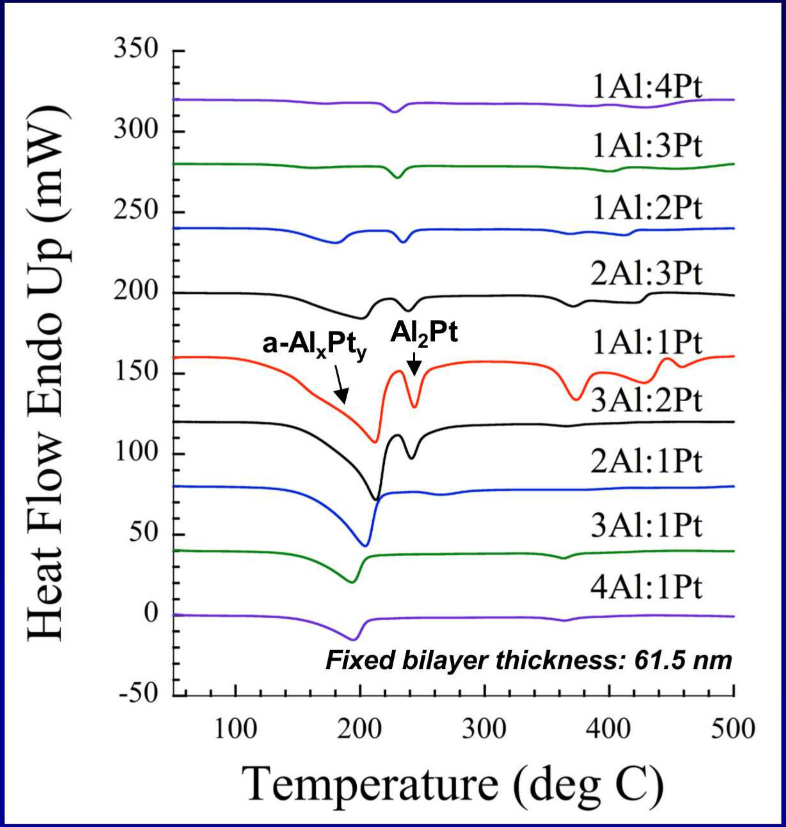
Each has a bilayer thickness of ~400 nm.

Differential Scanning Calorimetry is used to generate thermograms for Al/Pt.

- All Al_xPt_y stoichiometries studied here are characterized by exothermic rxns.

- First exotherms starts at ~100^{o}C.
  - Separate XRD confirms growth of amorphous interlayer (a-Al_xPt_y) is associated with first broad exotherm.

- Additional exotherms
  - associated with formation of different crystalline intermetallic phases (many cases starts with Al_2Pt)



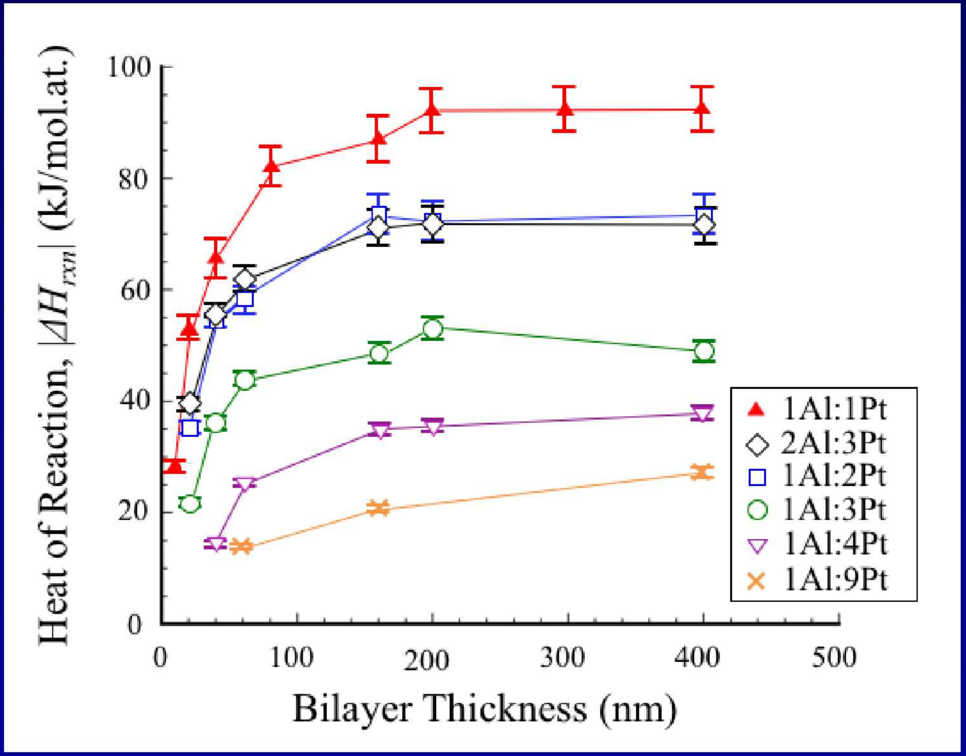
Heating rate: 40 degrees / minute
Gaseous environment: N_2
Perkin Elmer DSC system

Differential Scanning Calorimetry is used to measure heats of reaction for Al_xPt_y.

- All Al_xPt_y compositions studied here are characterized by exothermic reactions.

- Equiatomic AlPt exhibits largest $|\Delta H_o|$.

- Pt - rich multilayers have reduced stored chemical energy.



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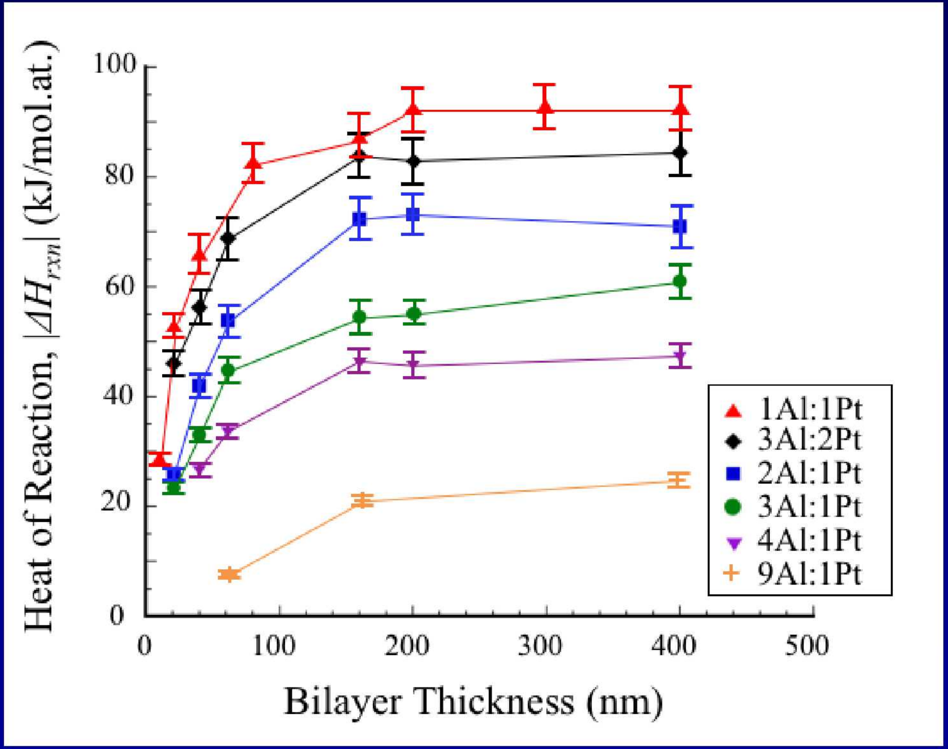
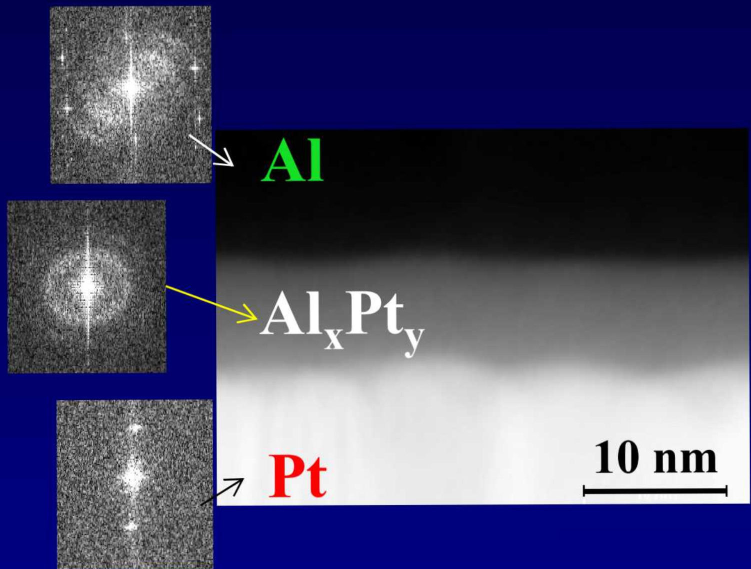
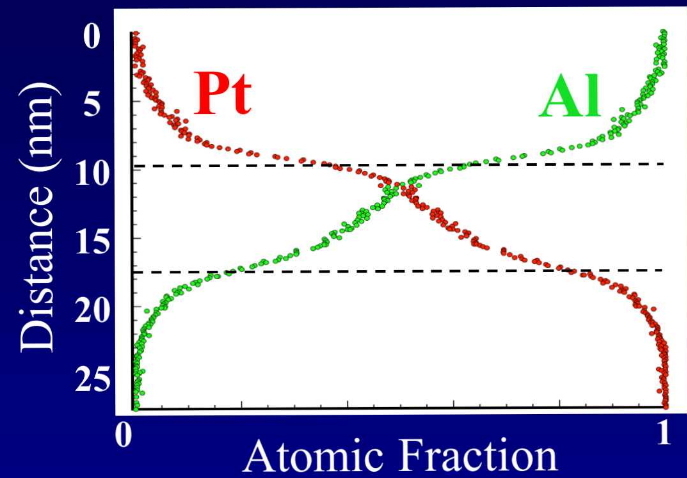
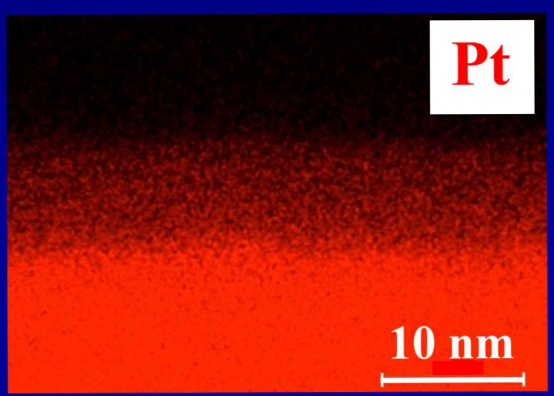
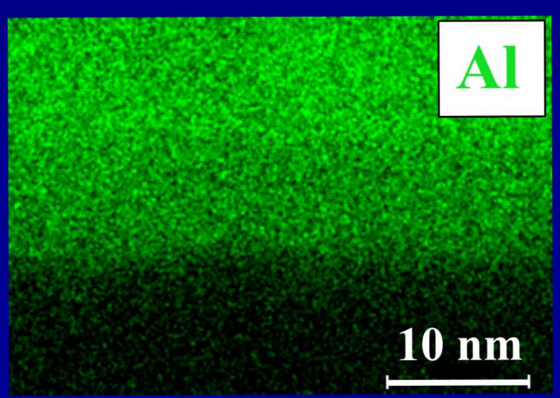


A close look at interfaces of a Al/Pt multilayer

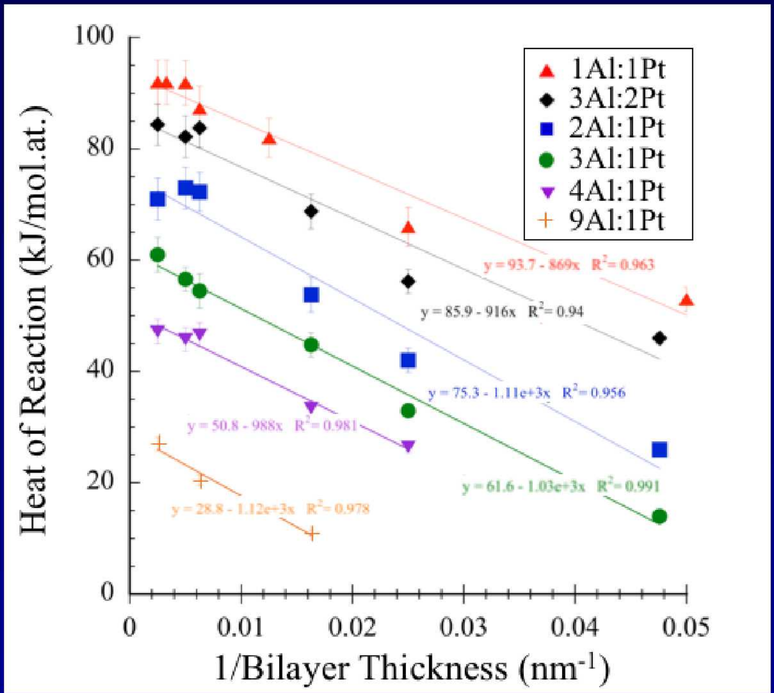


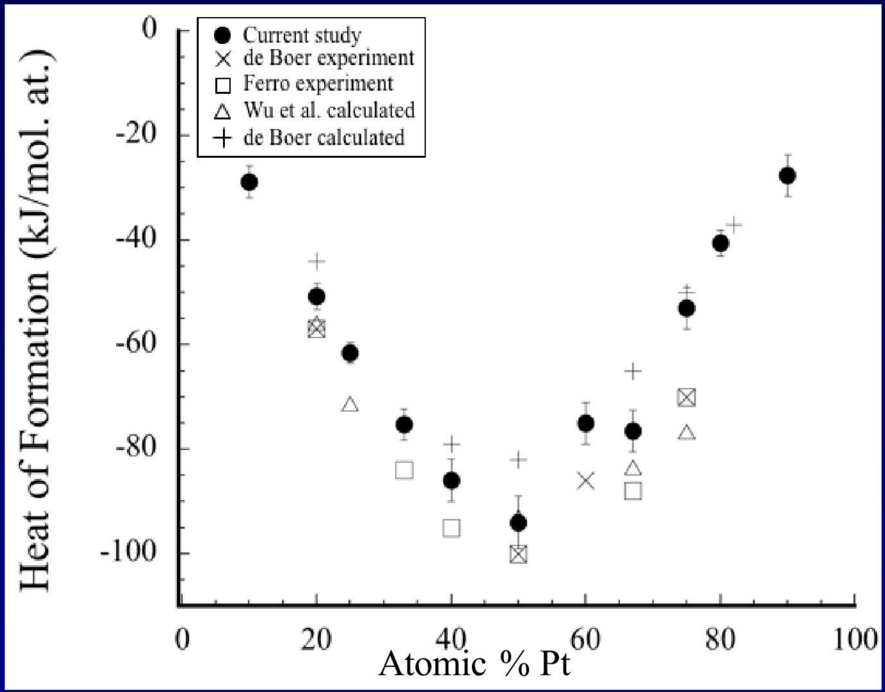






Heats of Formation Derived from measured Heats of Reaction





$$\Delta H_{rxn} = \Delta H_{Al_xPt_y} - \Delta H_{premix}\left[\frac{2\, w\, V_{Al_xPt_y}}{t_B\, V_{premix}}\right]$$

Measured Heat of Reaction

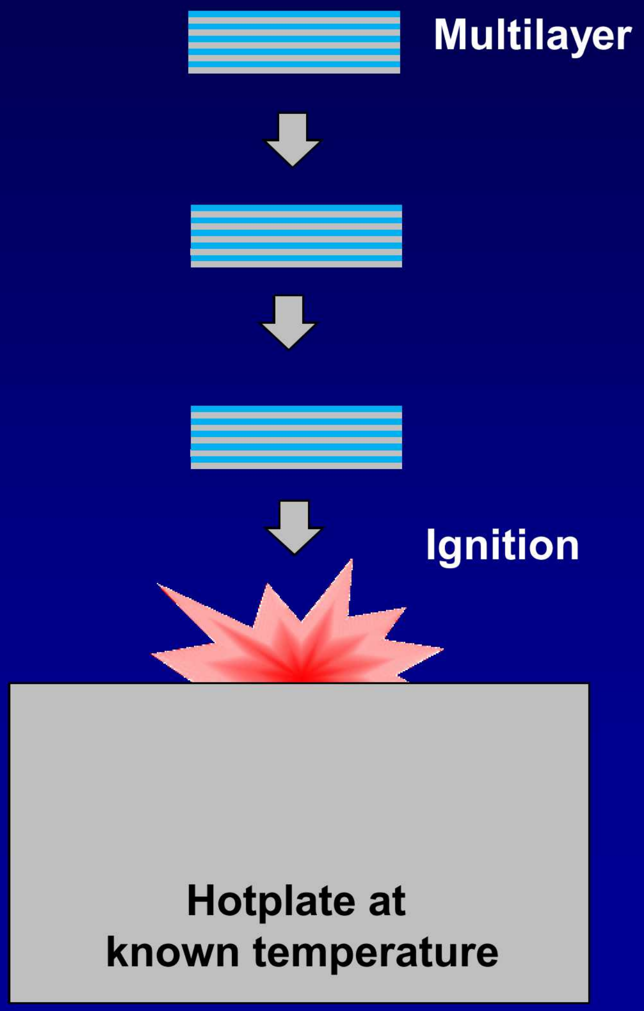
Heat of Formation

Energy lost via premixing

w = premix thickness
t_B = bilayer thickness
V = molar atomic volume

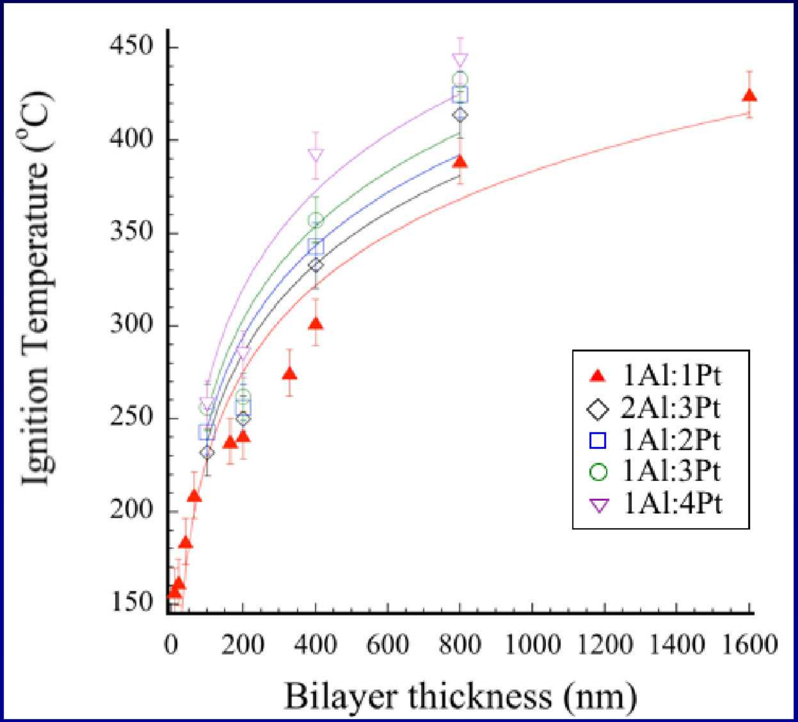
Thermal Ignition Experiments

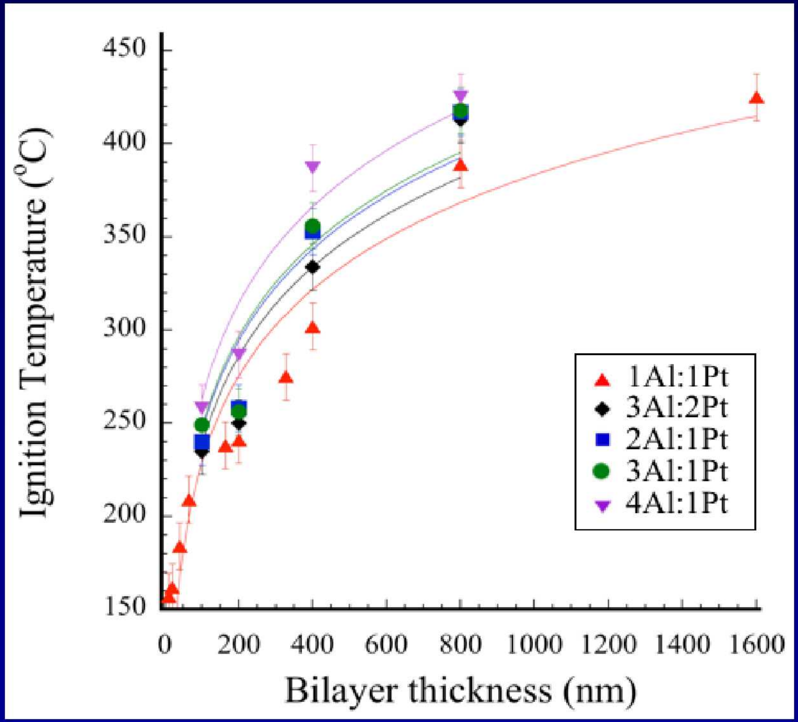
- Equilibrate hotplate at known temperature (in air)
- 1 mm^2 sample is tossed onto hotplate to contact on planar face
- Observed during contact to view one of two behaviors:
  - Ignition (evidenced by bright flash and burst into microscopic debris.
  - No ignition (subtle changes in shape, slight discoloration due to oxidation)



References for method: Fritz et al., 2013 J. Appl. Phys.

Ignition Temperatures vary with Bilayer Thickness and Stoichiometry



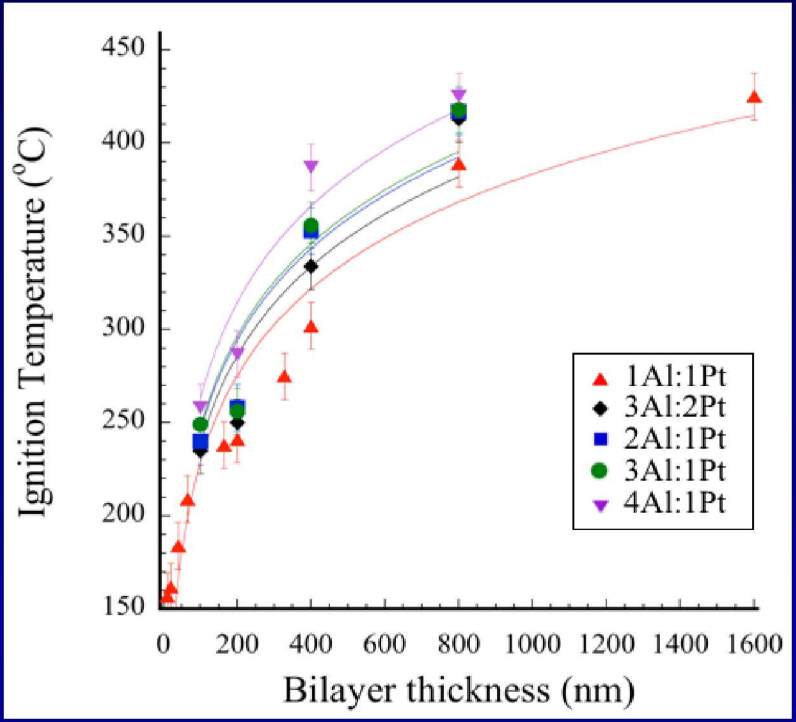


- Ignition temperature increases with bilayer thickness for each molar ratio.
- Equimolar multilayers exhibit lowest ignition temperatures.

Trends of Ignition Temperature (T_{ig}) vs. Bilayer Thickness are Consistent with Predicted Dependencies from Fritz et al.

Analytical expression for T_{ig}, from Fritz et al., 2013 J. Appl. Phys.

$$T_{ig} = \frac{E_a / R}{\ln\left[\left[\frac{2\, t\, \Delta H_{rxn}\, D_o\, R_T}{t_B\, w}\right]\frac{f}{n(1-n)}\right]}$$



w = premix thickness
t_B = bilayer thickness
ΔH_{rxn} = heat of reaction
R_T = thermal resistivity
t = thickness of multilayer
E_a = activation energy for mixing reactants
N = molar fraction

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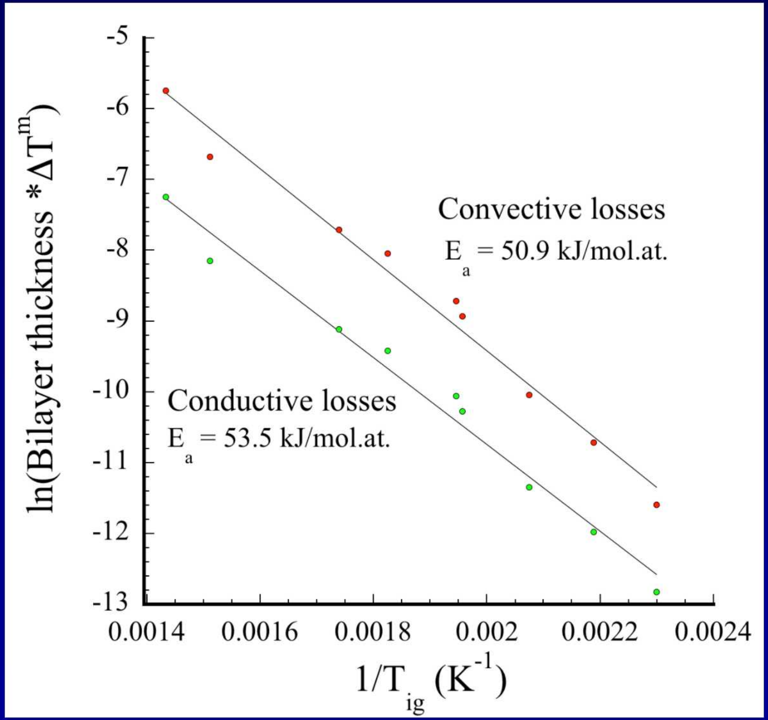


Activation energies derived from this analytical approach should be associated with the solid state diffusion of reactants.

High Speed Videography of Propagating Wave

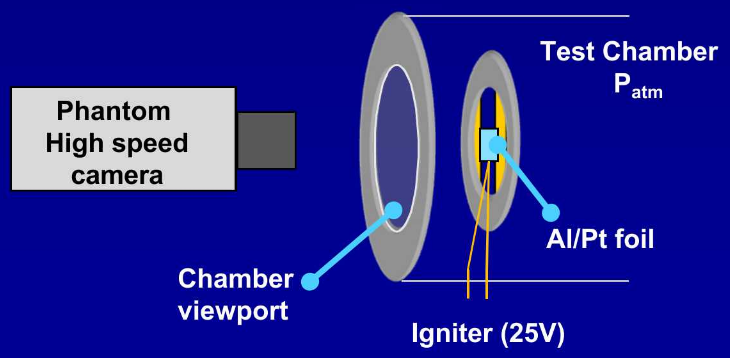
Tested as freestanding foils

Point ignition in air

No preheat above room temperature

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

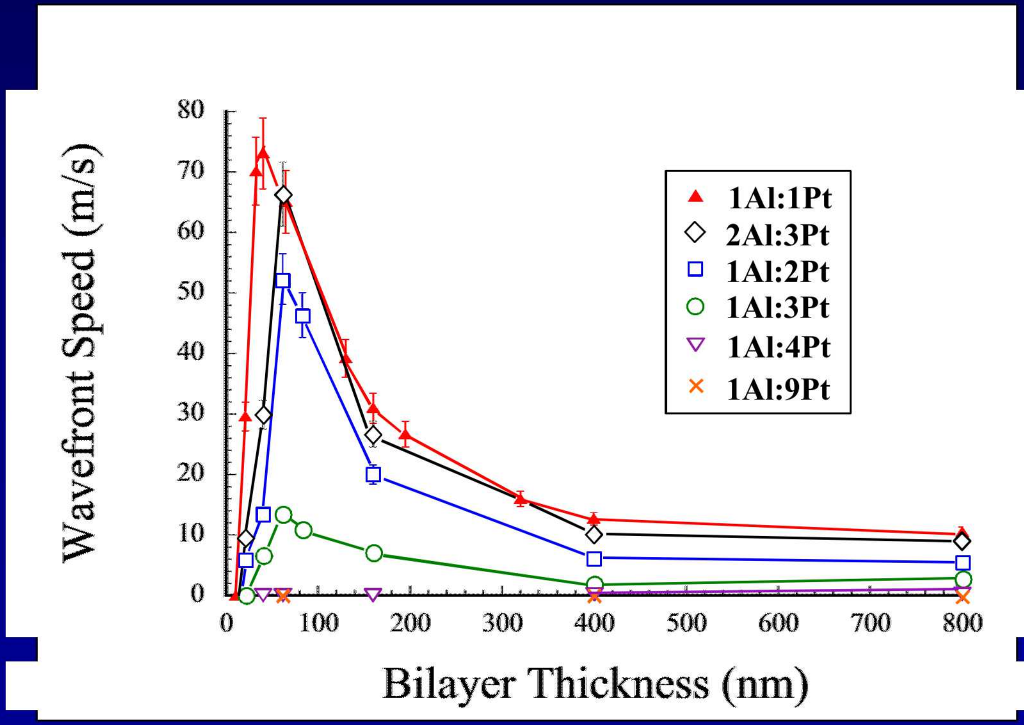
Position is plotted versus time to determine speed



Equiatomic Al/Pt, bilayer thickness: 50 nm

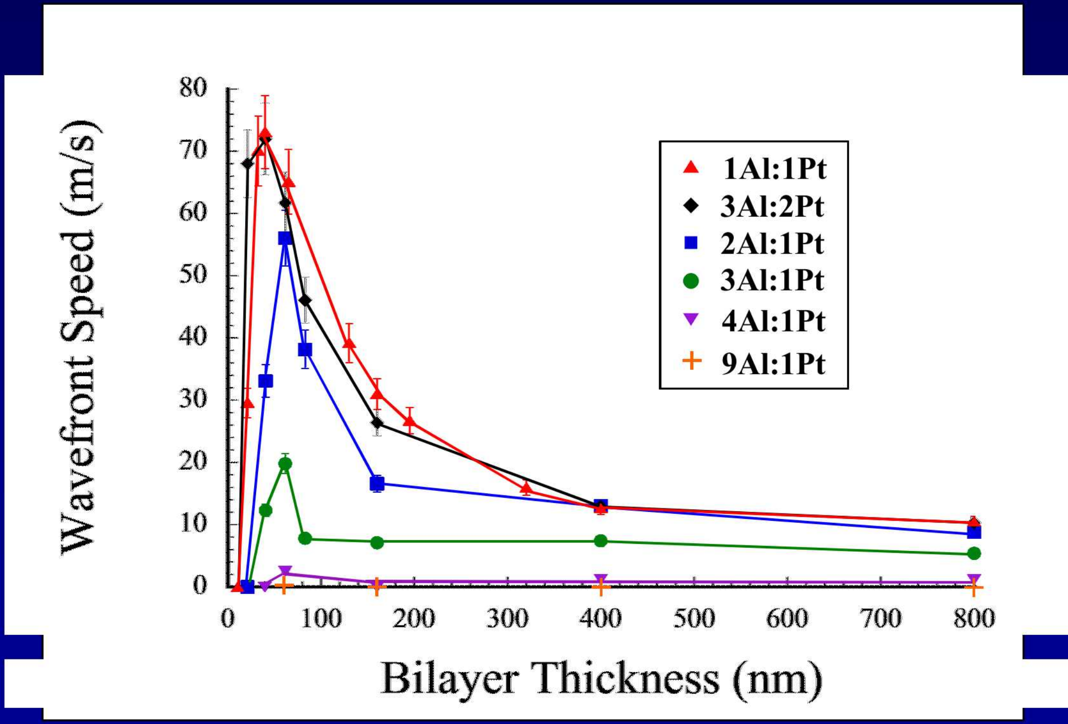
Multilayers having Pt - rich compositions exhibit self–propagating reactions.

- Equiatomic AlPt exhibits largest reaction rate.
- Pt-rich multilayers exhibit decreased propagation speeds as %Pt is increased.
- Traditional bilayer thickness dependence is observed for several compositions.



Multilayers having Al - rich compositions exhibit self–propagating reactions.

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



Summary

- Sputter-deposition provides the necessary control of stoichiometry, purity and dimension for detailed studies of structure-composition-property relationships.

- The range of reactive stoichiometry for Al/Pt multilayers is large: spans at least 20 to 80 at.% Pt.
  - Attributed to a substantial heat of formation across molar range.

- Equimolar Al/Pt multilayers exhibit the lowest ignition temperatures
  - Attributed to largest heat of reaction.

- Equimolar Al/Pt multilayers exhibit the most rapid propagating reactions
  - Attributed to largest heat of reaction and adiabatic temperatures.

- Ignition and self-propagating reaction rates vary with bilayer thickness.

EXTRA SLIDES

Analytical models predict how propagation speed is affected by various multilayer properties.

From Armstrong and Koszykowski assuming no premixing

$$v_{flame}^2 = \frac{3A \exp(-E/RT_{max})\, RT_{max}^2 \;\lambda^2}{\delta'^2 E(T_{max} - T_o)}$$

A = Arrhenius prefactor
R = gas constant
λ = average thermal diffusivity
δ' = ¼ of bilayer thickness

E = activation energy for mass diffusion
T_{max} = maximum temperature during steady propagation
T_0 = ambient temperature

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From Armstrong and Koszykowski assuming no premixing

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T_{max} varies with composition

A = Arrhenius prefactor
R = gas constant
λ = average thermal diffusivity
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$$v_{flame}^2 = \frac{3A \exp(-E/RT_{max})\, RT_{max}^2 \;\; \lambda^2}{\delta'^2\, E(T_{max} - T_o)}$$

From Mann, Weihs et al. (1997)
Accounted for premix, and assumed intermixed region is fully reacted final phase

$$v_{flame}^2 = \left(\sum_{n=odd} \frac{k_n}{\alpha_n^3} \right) \frac{A \exp(-E/RT_{max})\, RT_{max}^2 \;\; \delta' \lambda^2}{E(T_a - T_o)}$$

A = Arrhenius prefactor
R = gas constant
λ = average thermal diffusivity
δ' = ¼ of bilayer thickness
k_n = Fourier coefficients

E = activation energy for mass diffusion
T_{max} = maximum temperature during steady propagation
T_0 = ambient temperature
T_a = adiabatic temperature
α_n = Fourier eigenvalues

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

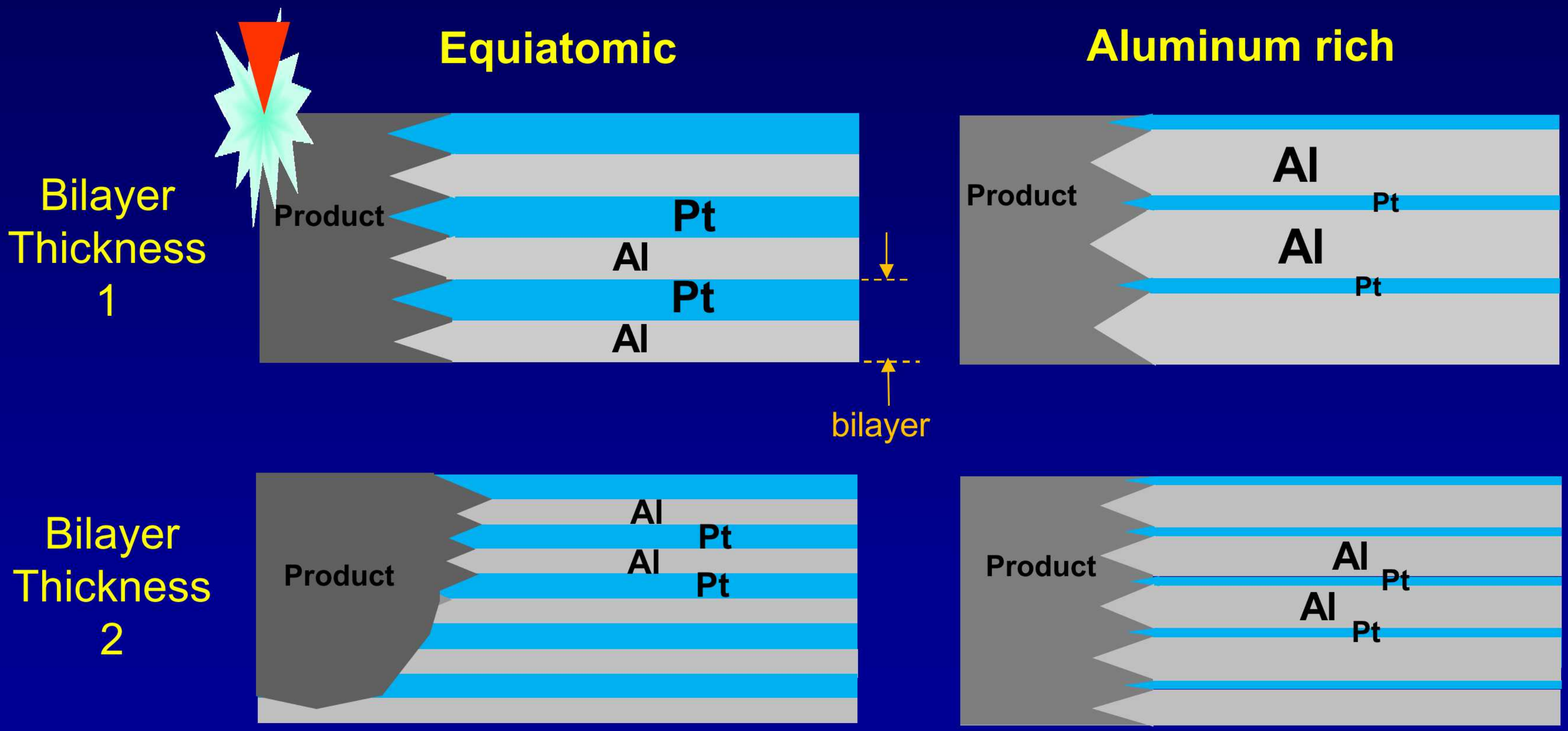
<u>Multiple deposition systems</u>
10^{-9} - 10^{-8} Torr base pressure
Ar sputter gas
In-situ quartz crystal monitors

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

<u>Other:</u>
Adjust film thicknesses to
compensate for densities

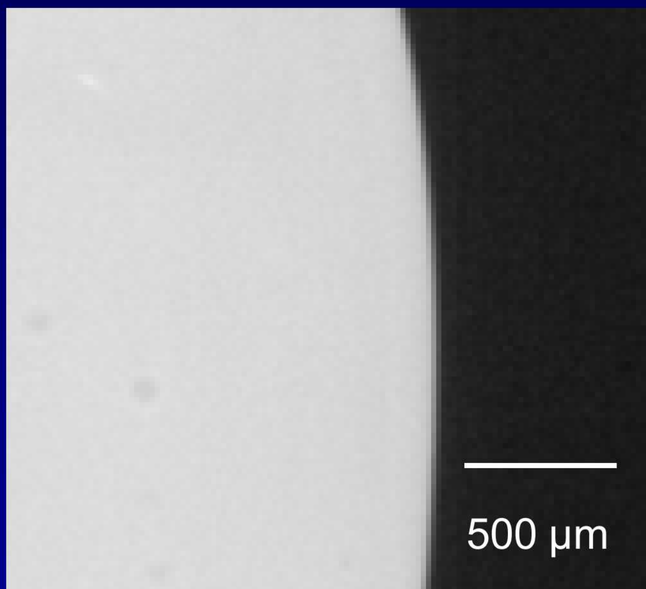
Generally, multilayer is peeled off to ‘create’ a foil for testing.

Design of multilayer design that vary net composition and bilayer thickness.

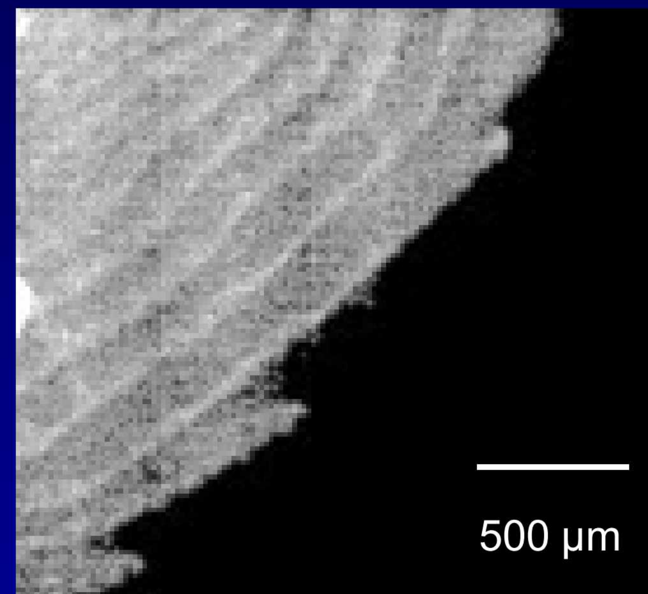


We account for Al and Pt densities in design.

Most multilayers undergo stable propagation. A few designs near the limits of stoichiometry exhibit instabilities.



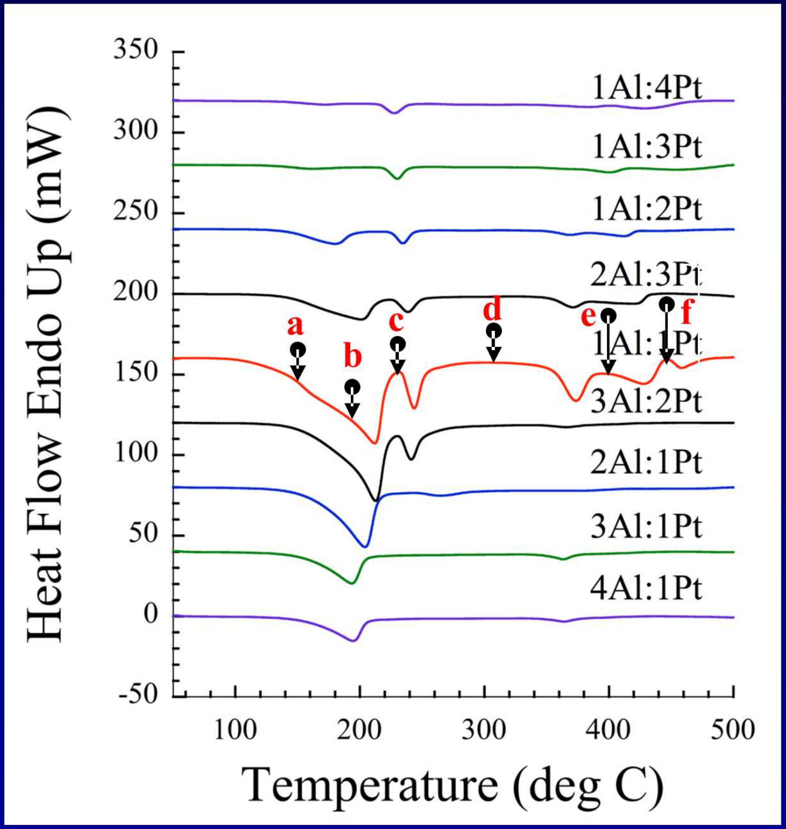
All other compositions,
designs (i.e., bilayer thicknesses)

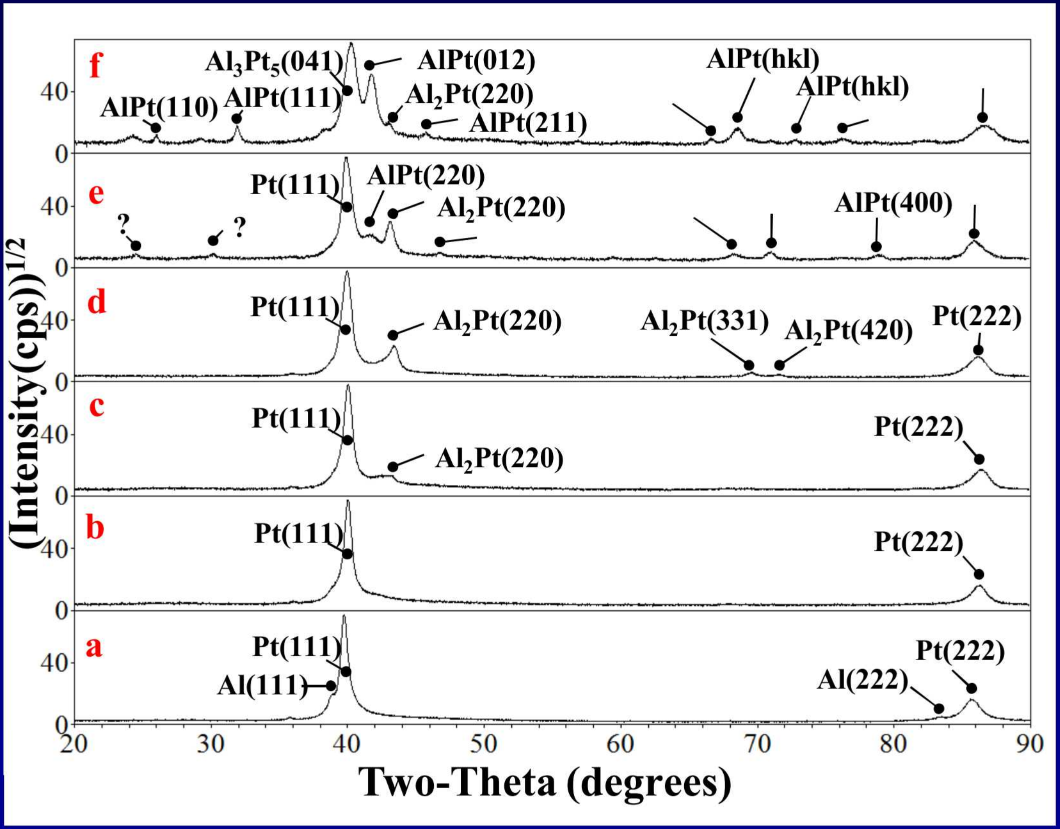


1 Al: 4 Pt
Bilayer thickness = 800 nm

Rogachev predicts unstable modes near concentration limts

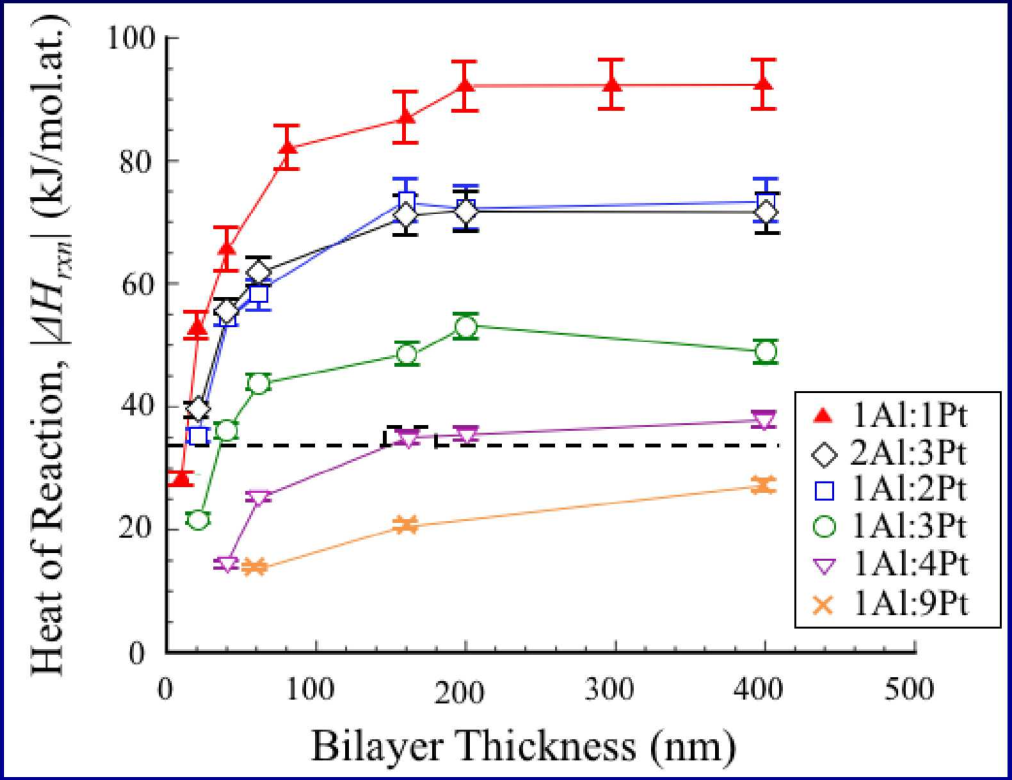
XRD reveals phase evolution associated with exotherms in DSC.





Exothermic release greater for mixing (associated with growing amorphous phase)

Differential Scanning Calorimetry is used to measure heats of reaction for Al_xPt_y.



Symbols above dashed line indicate reactivity (i.e., ignition, propagating reaction).

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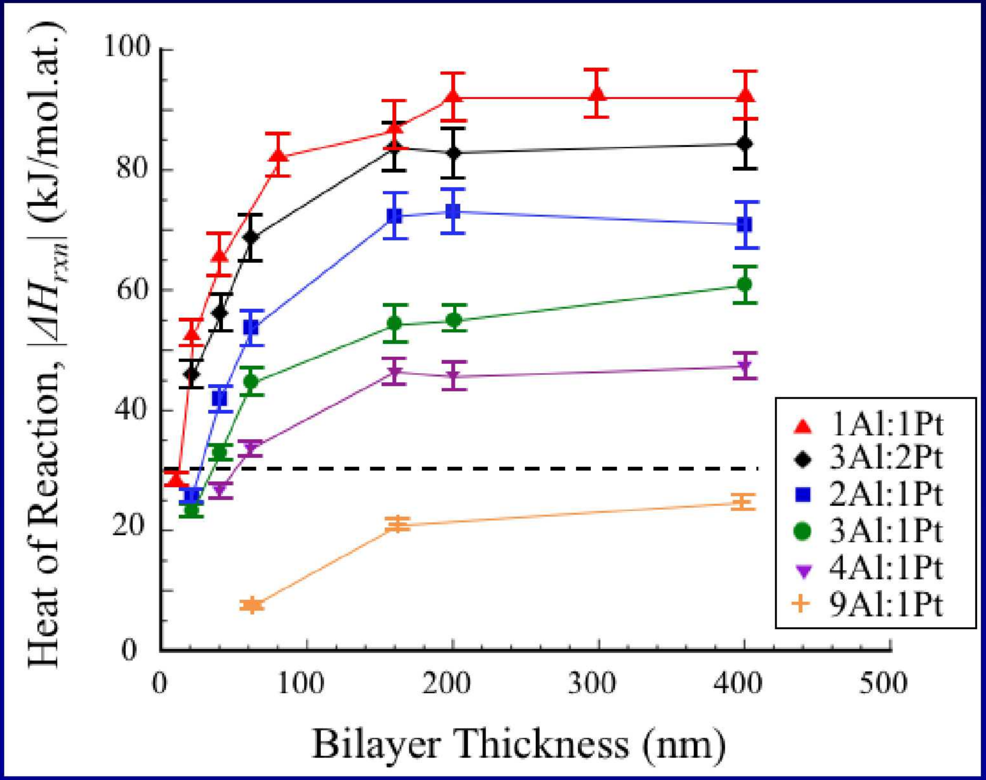

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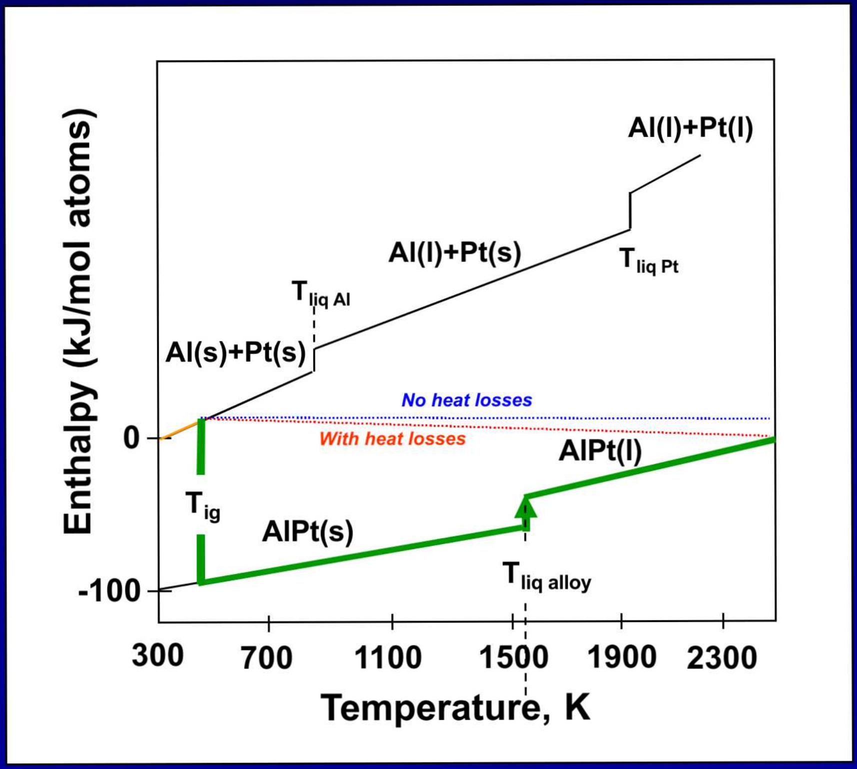
We turn to measurements of stored chemical energy for explaining trends in flame speed with bilayer thickness and composition.

Two anticipated examples shown.

Equiatomic



Non-equiatomic