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Reaction instabilities in sputtered deposited nanolaminates and their effects on kinetics at the scale of reactant periodicity

Robert V. Reeves
Joseph R. Michael,
and David P. Adams

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Background and definitions

- "Gasless" Reactive Systems
  - Can produce novel materials
    - Combustion synthesis [a,b]
  - Reactants contained in initial mixture
  - Reactions progress without evolution of gases
  - High heat release
- High heat release and reaction persistence allows many uses:
  - Used for joining, brazing [Tim Weihs- JHU, Indium Corp.]

Reactants	-Q, [J/g]	T_{ad}, [K]
Co+Al	1280[c]	1911[c]
Ni+Al	1380[c]	1911[c]
Ti+2B	5520[c]	3498[c]
Ni+Ti	640[d]	1583[d]
$Fe+KClO_4$	920-1250 (84-88 wt% Fe)[e]	1570-1650[f]

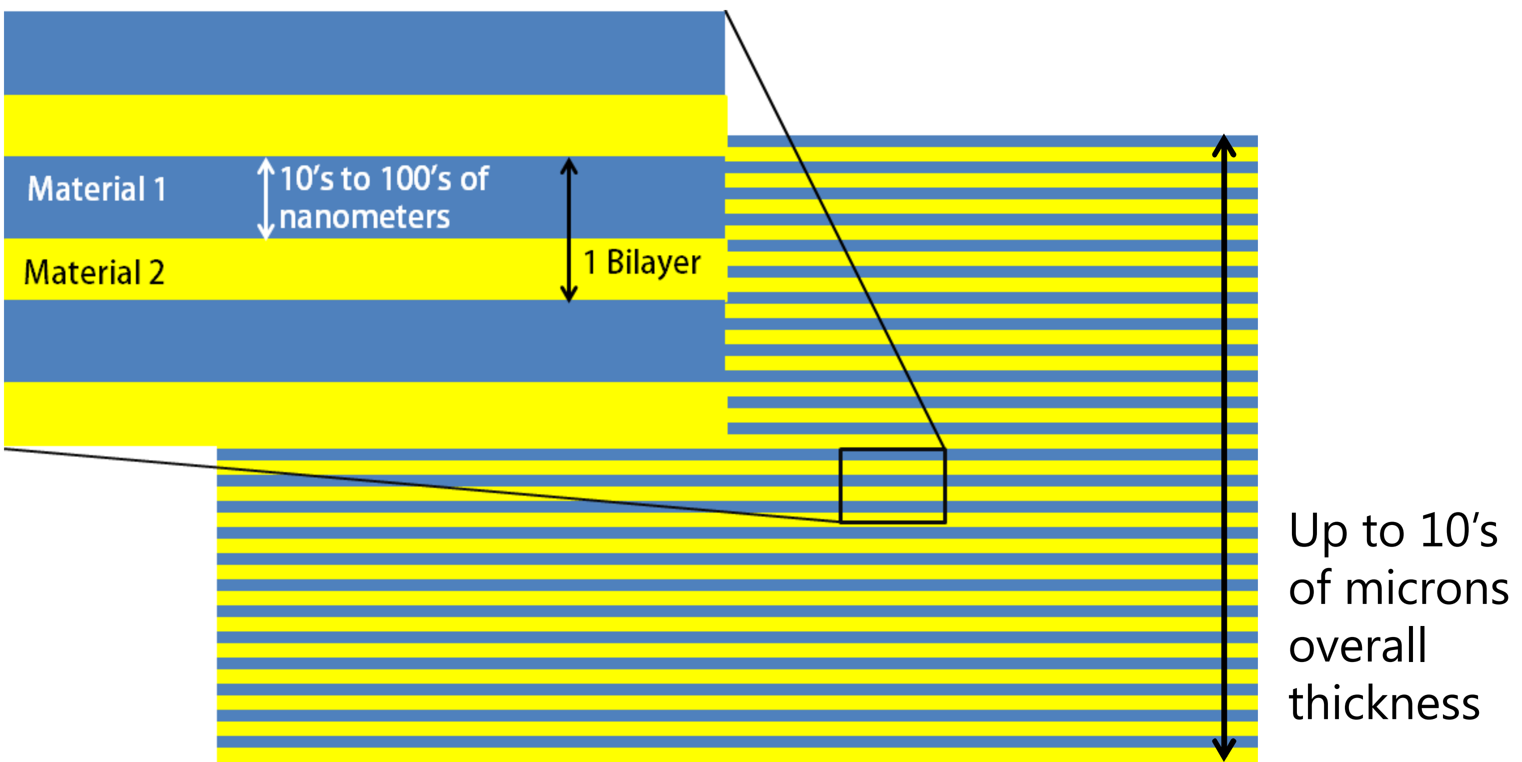
a. A.G. Merzhanov, Ceramics International **21**, 371 (1995)
b. Varma, A. S. Rogachev, A. Mukasyan, and S. Hwang, *Combustion Synthesis of Advanced Materials: Principles and Applications* (1998)
c. Fischer, S.H., Grubelich, M.C., SAND98-1176C
d. F.R. de Boer,,R. Boom, W.C.M.Mattens, A.R. Miedema, A.K.Niessen, *Cohesion in Metals Transition Metal Alloys*. 1989
e. Guidotti, R.A., SAND2001-2191
f. Calculated in CHEETAH 6.0 thermochemical program

Nanolaminates

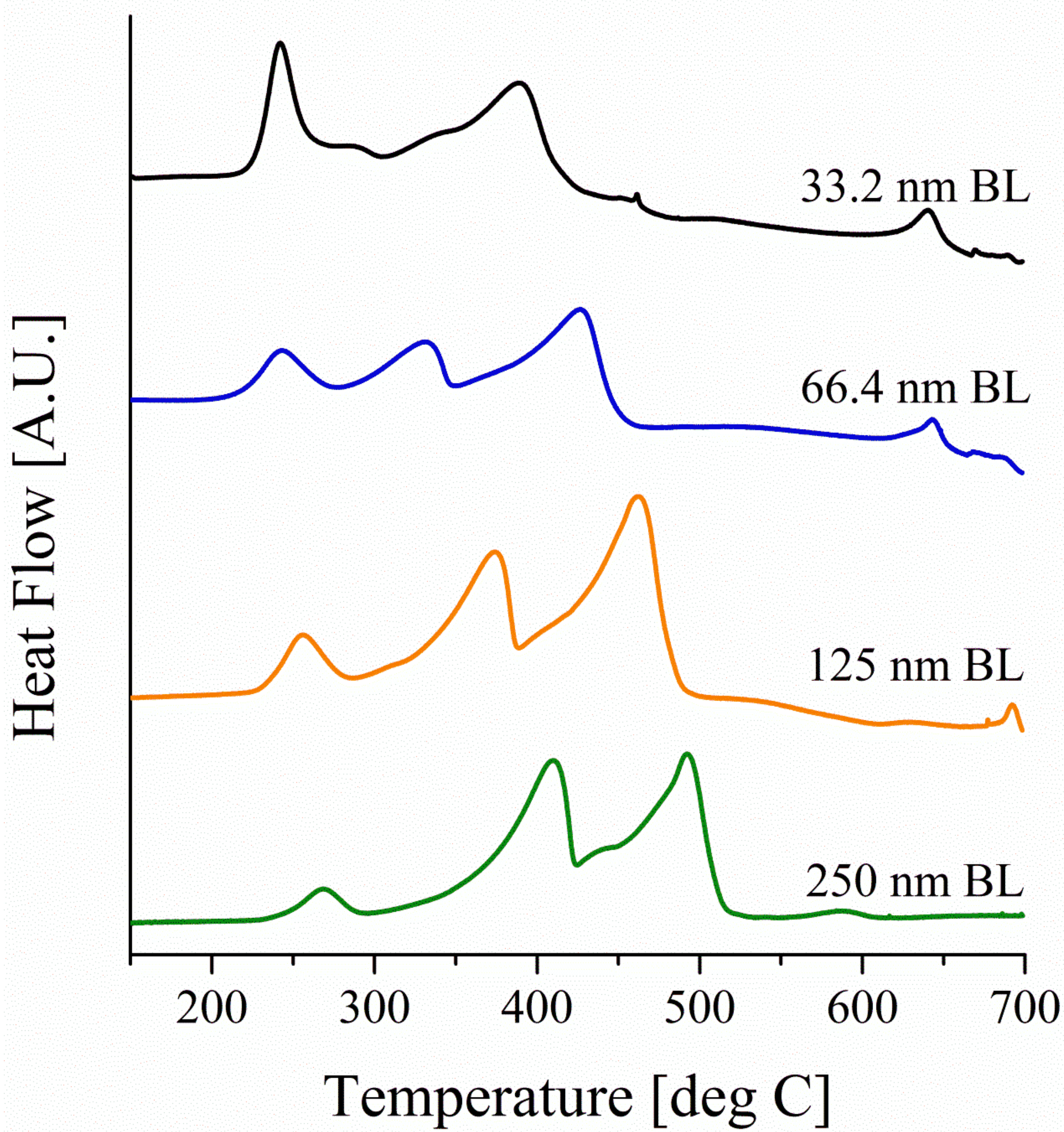
- $Co + Al \rightarrow CoAl; \Delta H_{exp} = -54 \frac{kJ}{mol_{atoms}}$

(de Boer, Boom, Mattens, Miedema, Niessen, *Cohesion in Metals*, 1988)

- Typical design of sputtered reactive foils
  - Used extensively by Weihs, Adams, Rogachev, others
  - Macroscale stacks of nanometric metal layers
  - Clean interfaces, high purity materials



DSC of Nanolaminates
Heat Release Characteristics (Co/Al)



- Reaction onset significantly below eutectic (659 ^{o}C)
- Solid state reactions dominate

Experimental Material
Co/Al Nanolaminates

Foils with 33.2 nm BL and thinner have stable reaction fronts

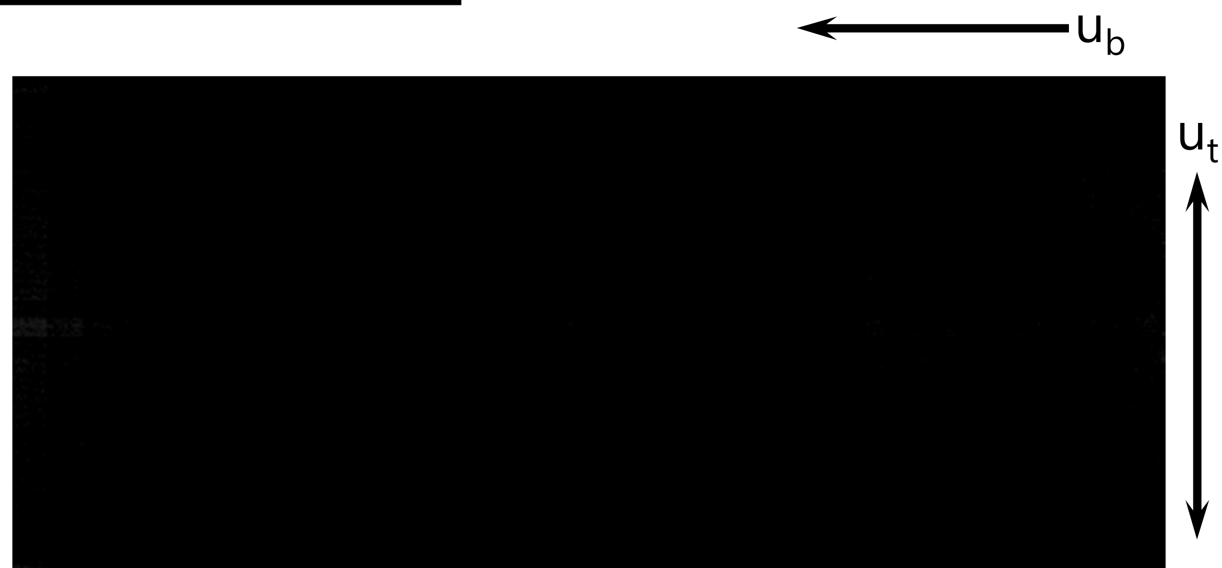
Total duration 3.125 ms

8.96mm window

Foils with 66.4 nm BL and thicker have unstable reaction fronts

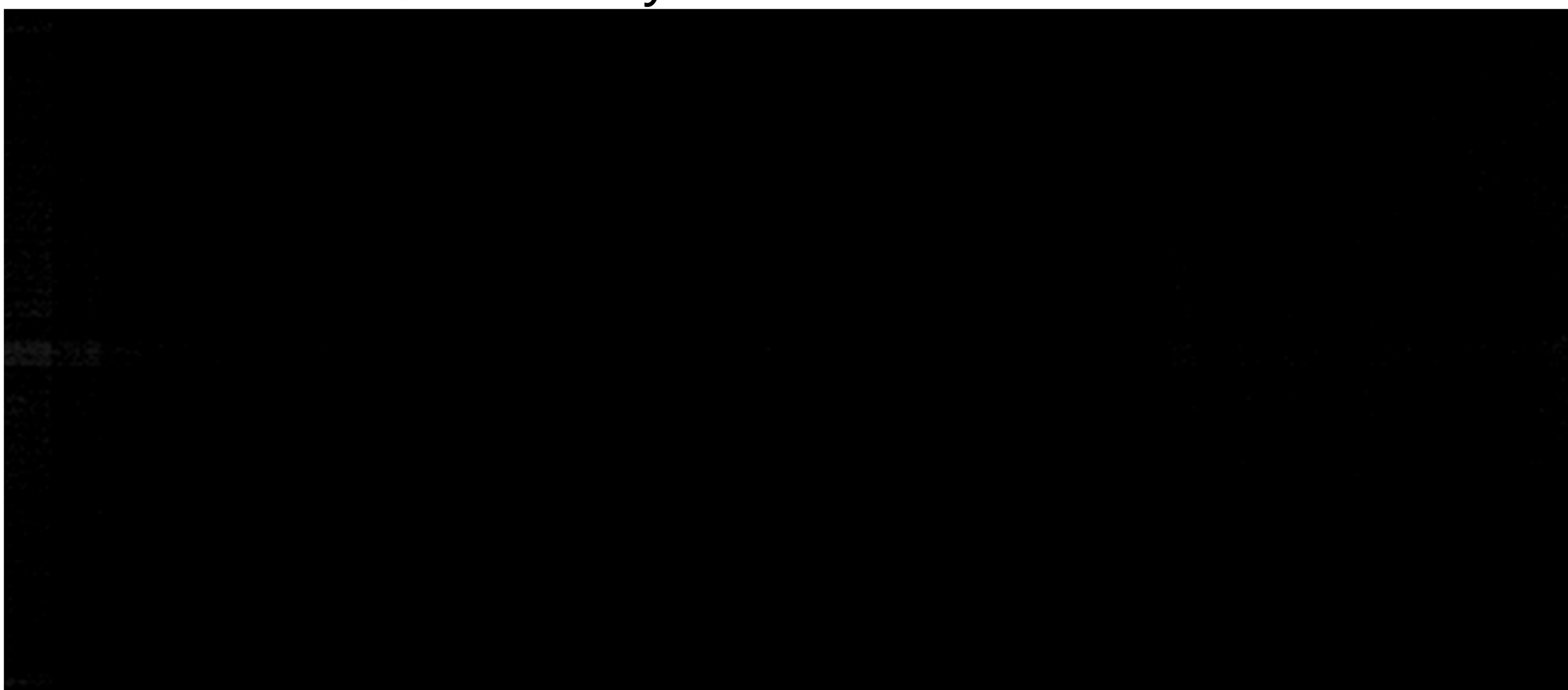
Total duration 11.7 ms

8.96 mm window

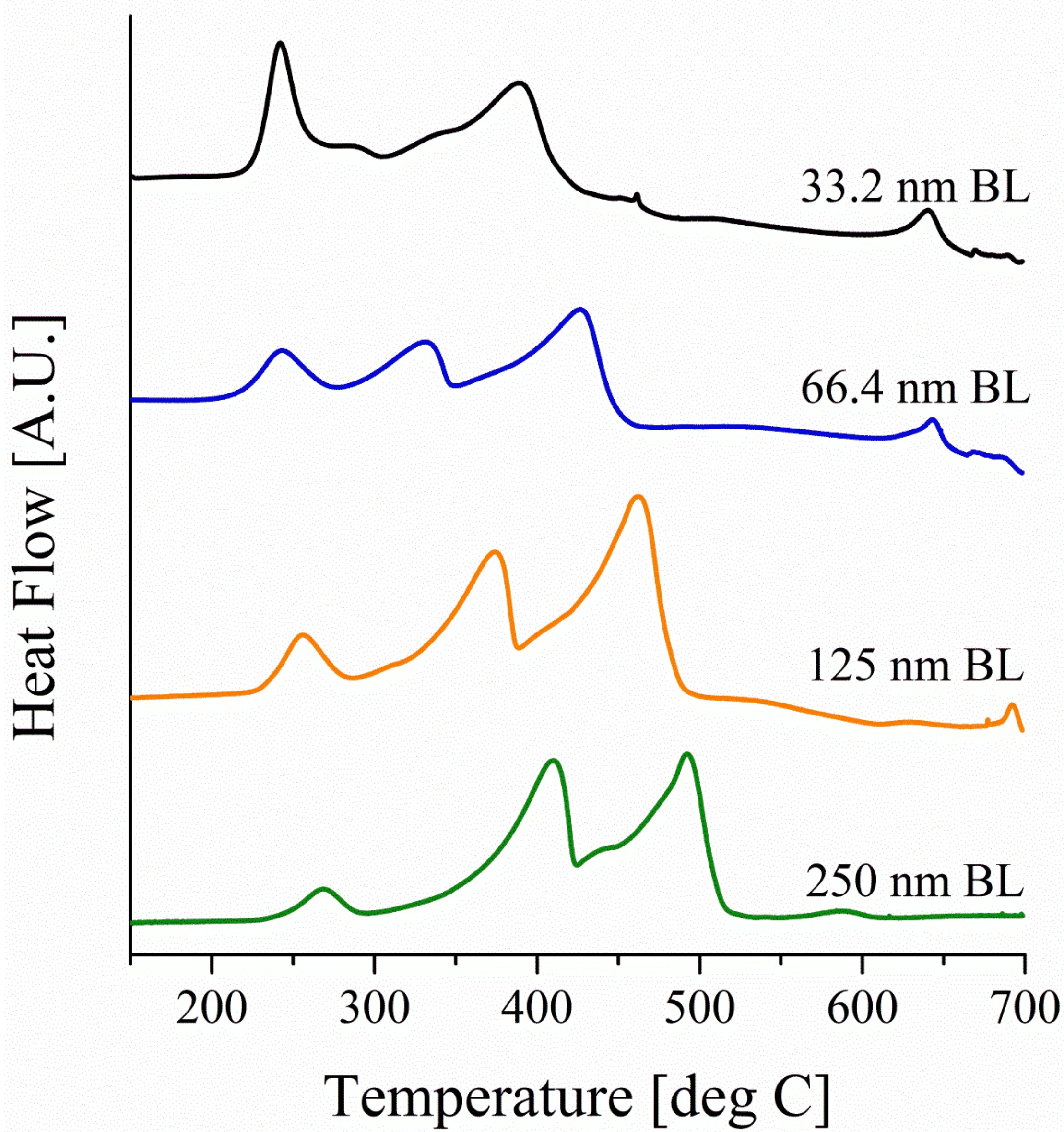


Experimental Motivation
Understanding and Controlling Stability

- Instabilities can be detrimental in typical application (joining)
- What are effects of initial temperature on reaction behavior?
- What does temp. dependent behavior inform us about local reaction kinetics/instability microstructure?



BL Dependent Behavior
Heat Release Characteristics

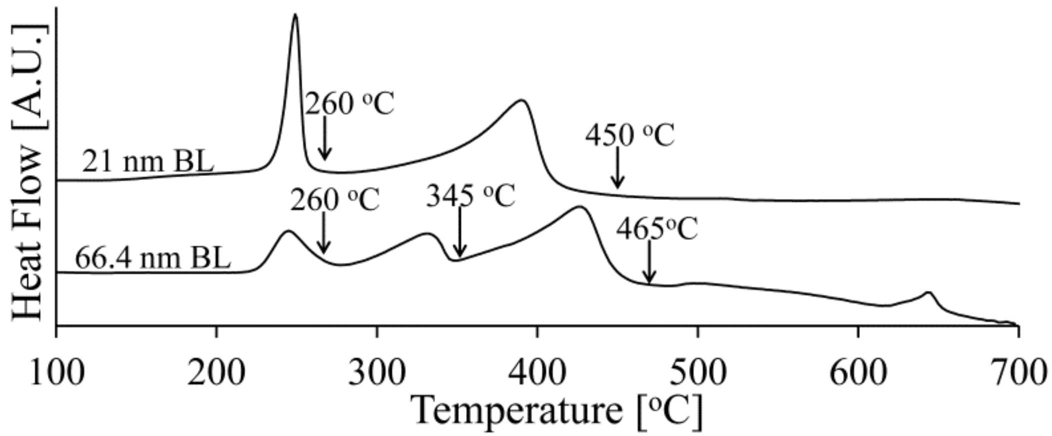


- Reaction progression changes with BL thickness during DSC heating
- Common to heterogeneous reactive materials
- Additional exotherm occurs in foils with BLs 50 nm and larger
- DSC heating not equivalent to self-propagating reaction

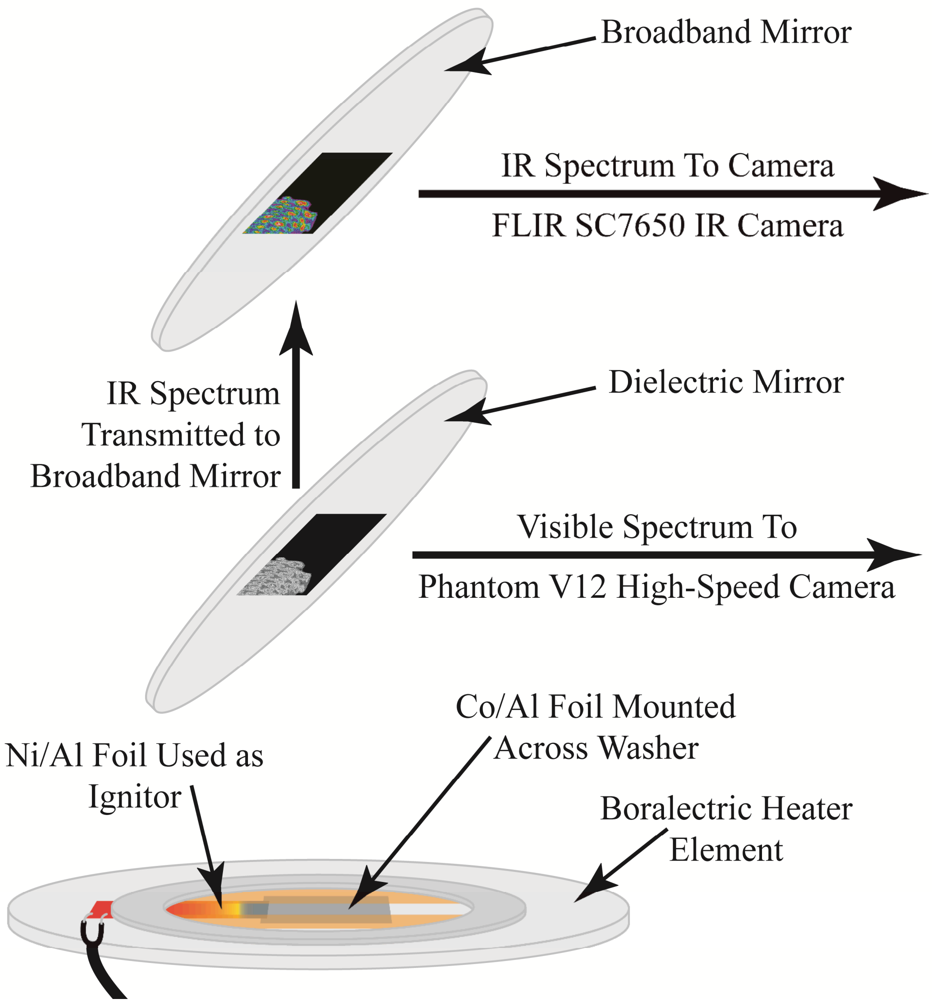
Quenched Samples – Phase ID

		Co	Al	Co_2Al_9	Co_4Al_{13}	Co_2Al_5	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

- Initial exotherm results in ~10 nm Co diffusion



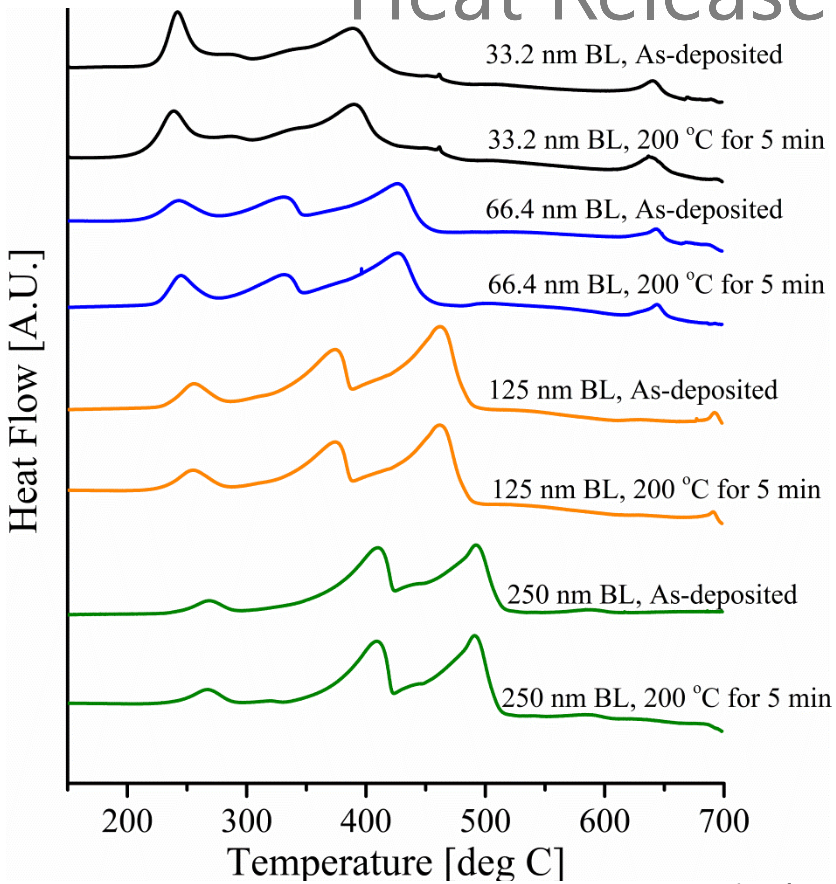
Propagating Reaction Test Setup
Simultaneous IR and Visible Light Imaging



- Heater element allows temperature control of foil
- Dielectric mirror separates emitted IR and visible spectra
- Gathered data gives temperature/spatial data wrt time

Effects of Preheating

Heat Release Characteristics

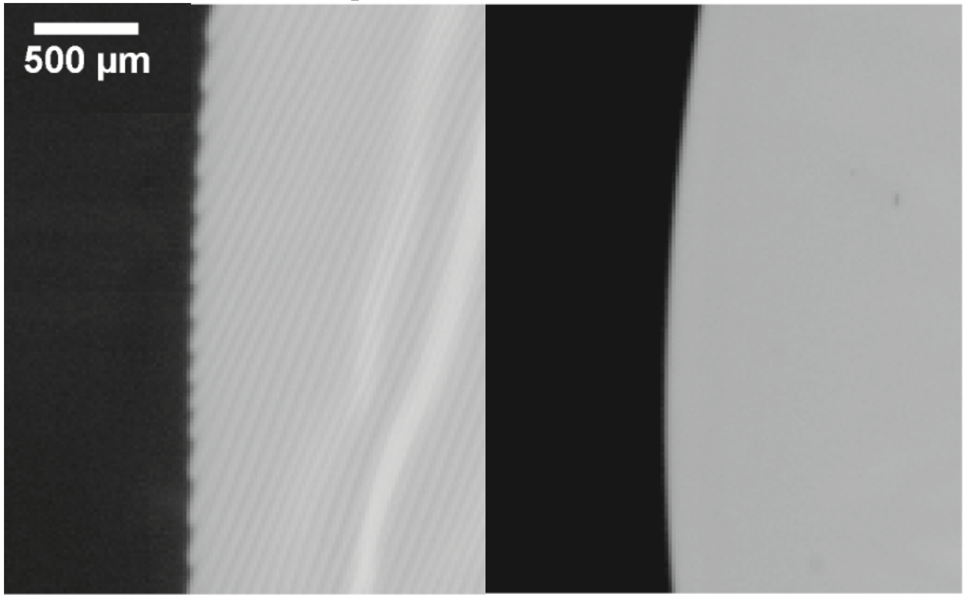


- Material held at 200 °C for 5 minutes
- Short times at elevated temperatures (below onset temp) have no effect on evolved heat
- E_a decreased for thick BLs
  - Possible grain coarsening

	As-Deposited Foils		After 5 min hold at 200 °C	
Bilayer Thickness	Total ΔH_f, [kJ/mol$_{atoms}$]	E_a,[kJ/mol$_{atoms}$]	Total ΔH_f, [kJ/mol$_{atoms}$]	E_a,[kJ/mol$_{atoms}$]
21 nm	-40.5 ± 1.0	27.5 ±0.1	-39.2 ± 0.9	28.9 ± 0.4
33.2 nm	-39.1 ± 1.5	28.2 ± 0.3	-44.6 ± 2.9	22.9 ± 5.3
66.4 nm	-45.7 ± 1.4	22.8 ± 5.2	-46.6 ± 1.6	27.9 ± 4.7
125 nm	-45.2 ± 1.9	30.8 ± 6.6	-45.7 ± 1.8	20.2 ± 7.1
250 nm	-46.2 ± 0.8	33.1 ± 6.5	-44.6 ± 1.8	14.2 ± 0.7

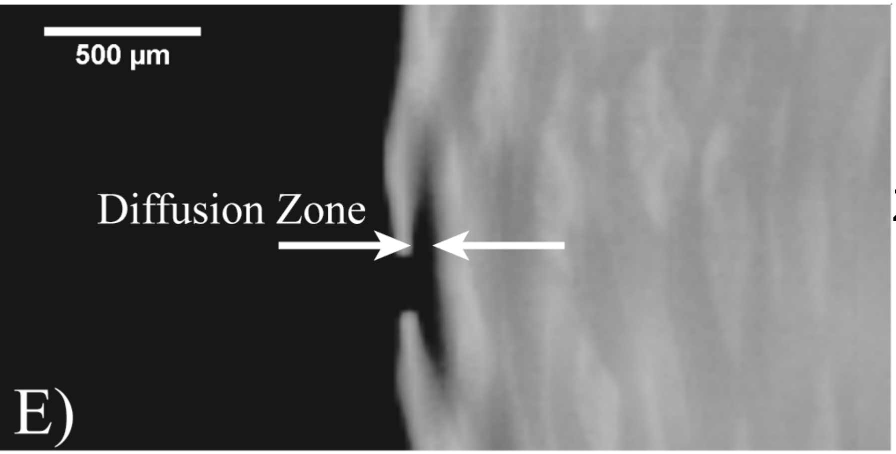
Stability is affected by BL thickness, initial Temperature

- 66.4, 75, 87.5 nm BLs transitioned to stability at elevated T_o



75 nm BL, T_o=25 °C

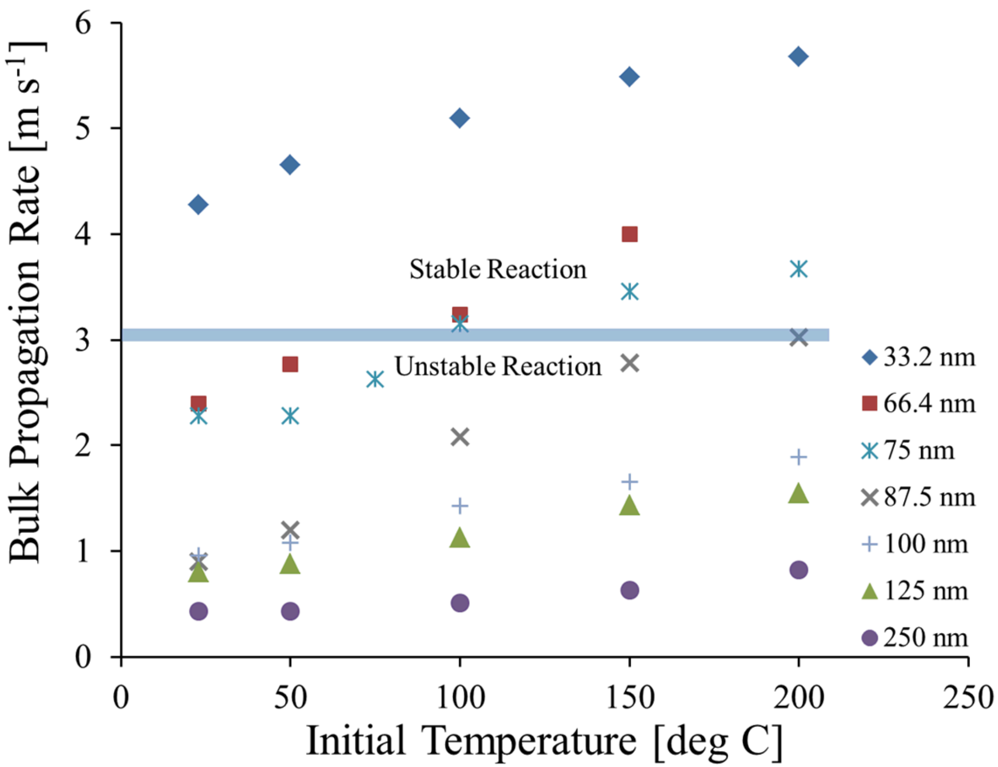
75 nm BL, T_o=150 °C



250 nm BL, T_o=25 °C

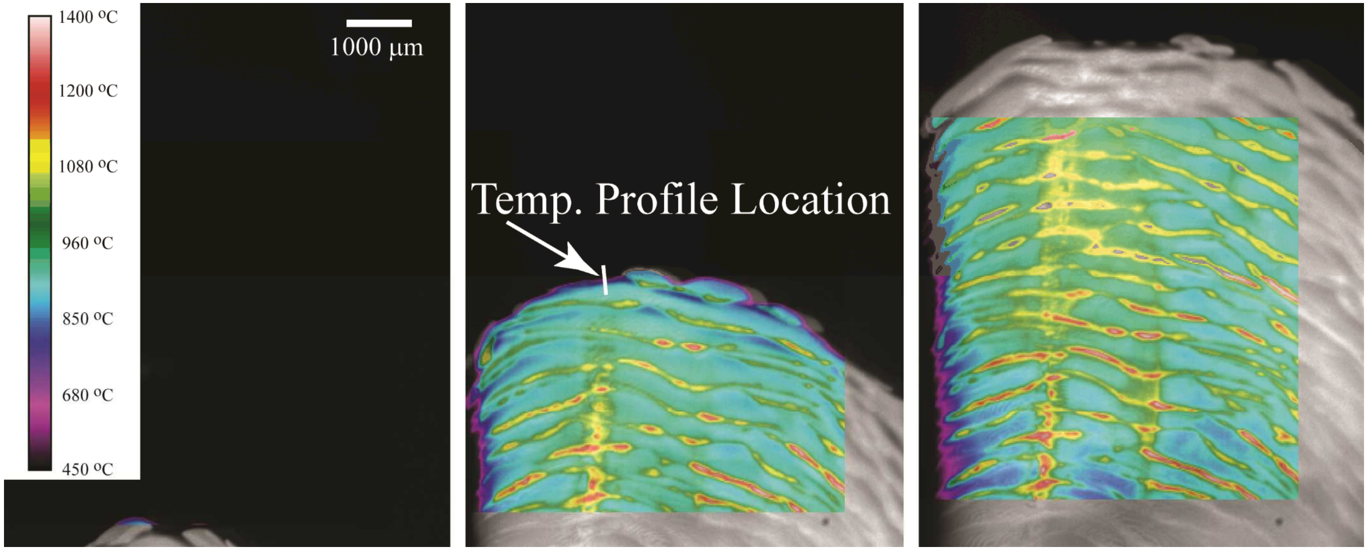
- Larger BLs unstable for all investigated T_o

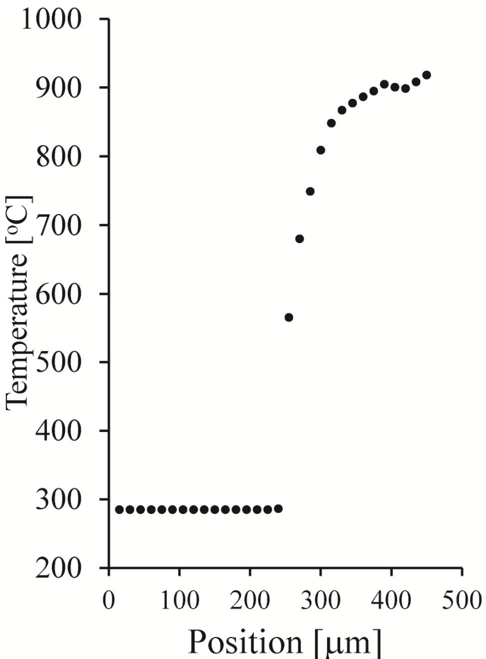
Macroscale Reaction Behavior
Temperature and BL Dependence



- Transition to stability takes place at $u_b \approx 3$ m/s for all BL designs
- Suggests a heat release rate for stability – system dependent, not BL dependent

Simultaneous IR/Visible Light Imaging





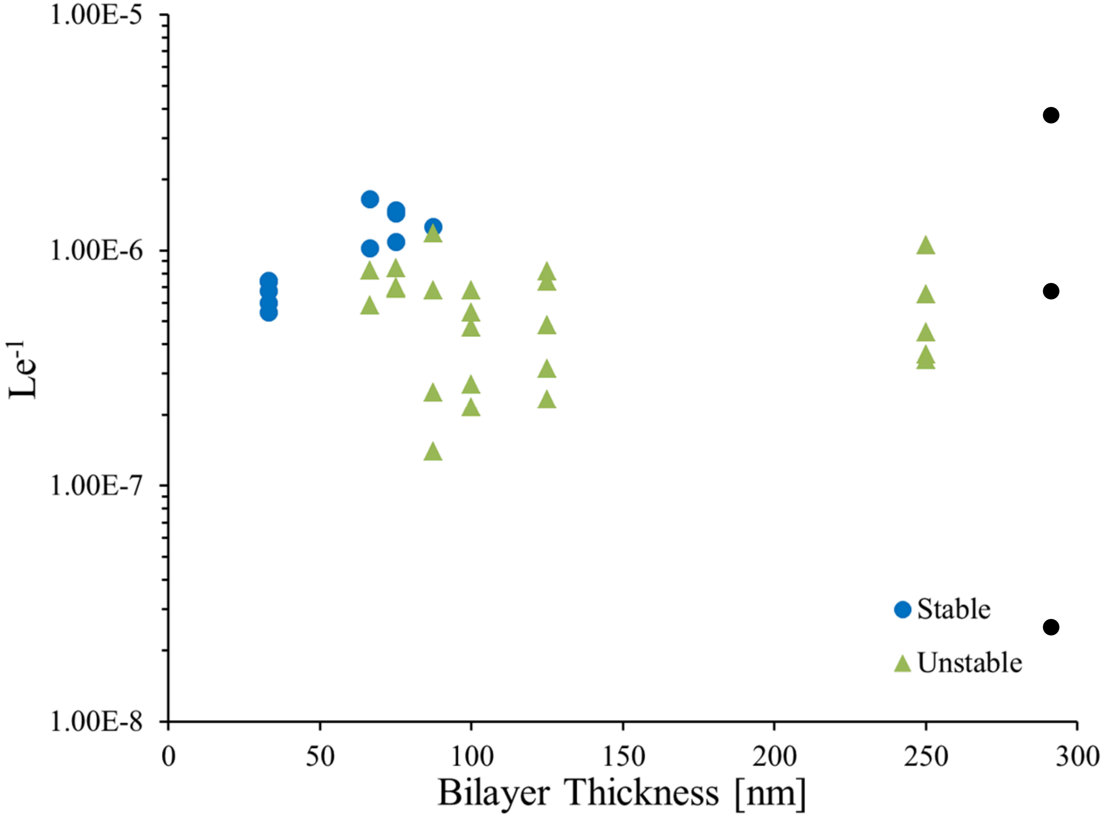
- Front can remain still for up to 1 ms
- Steep, unmoving temperature gradient at edge of transverse band
- Heat transfers from reacted material to unreacted material, but no significant self-heating occurs

Le^{-1} at Transition to Stability

- Using Armstrong's relationship,

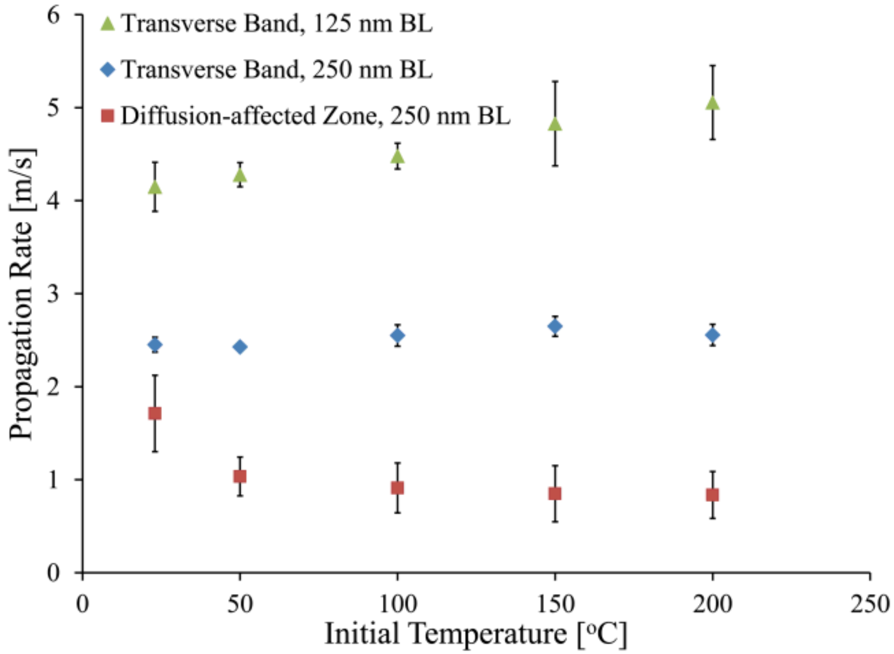
$$Le^{-1} = \frac{D}{\lambda} = \frac{u^2\delta^2 E_a (T_f - T_0)}{3\lambda^2 T_f{}^2 R} = \mathcal{A}\, exp\left(\frac{-E_a}{RT_f}\right)$$

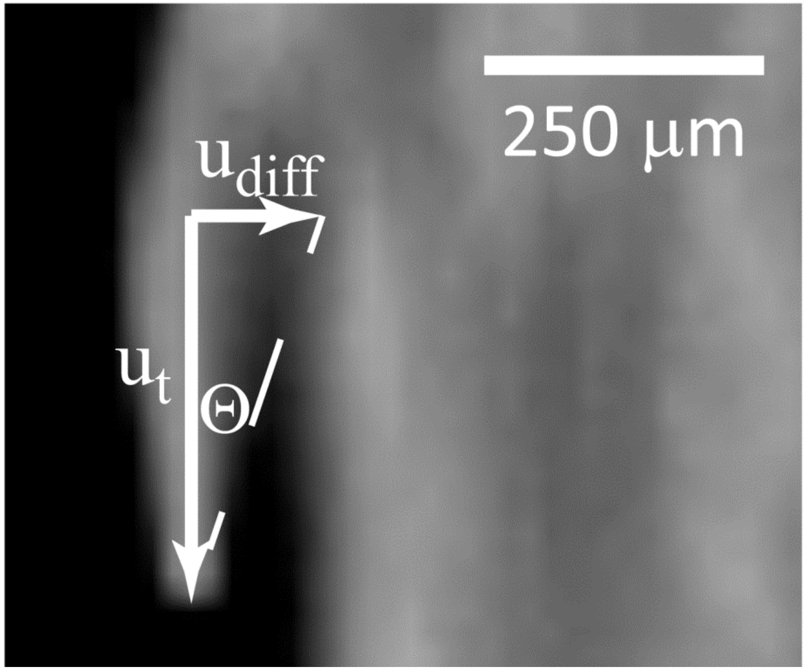
[R. Armstrong, Combust. Sci. Technol. **71,** 155 (1990)]



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

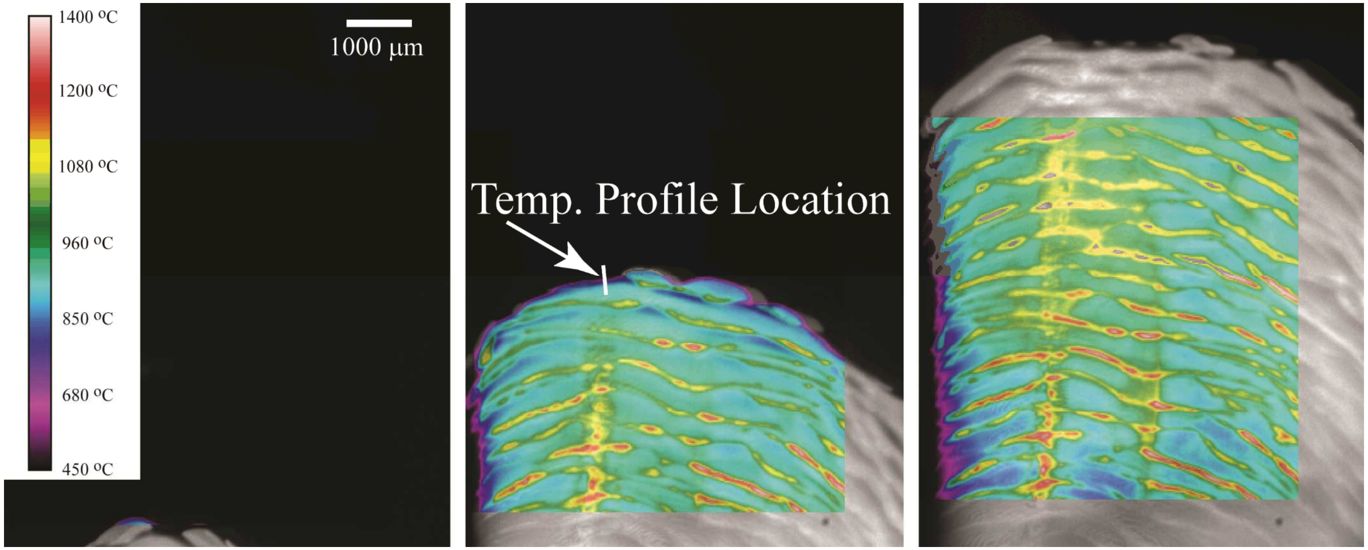
Propagation Rates Dependences on T_0

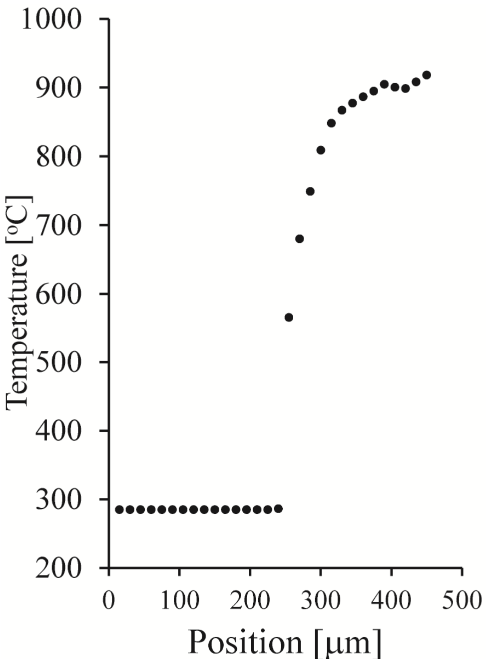




- U_t slightly increases with T_0 for 125 nm BL foils
- U_t has little dependence on T_o for 250 nm BL foils
- U_{diff} has a slight negative dependence on T_0 for 250 nm BL foils

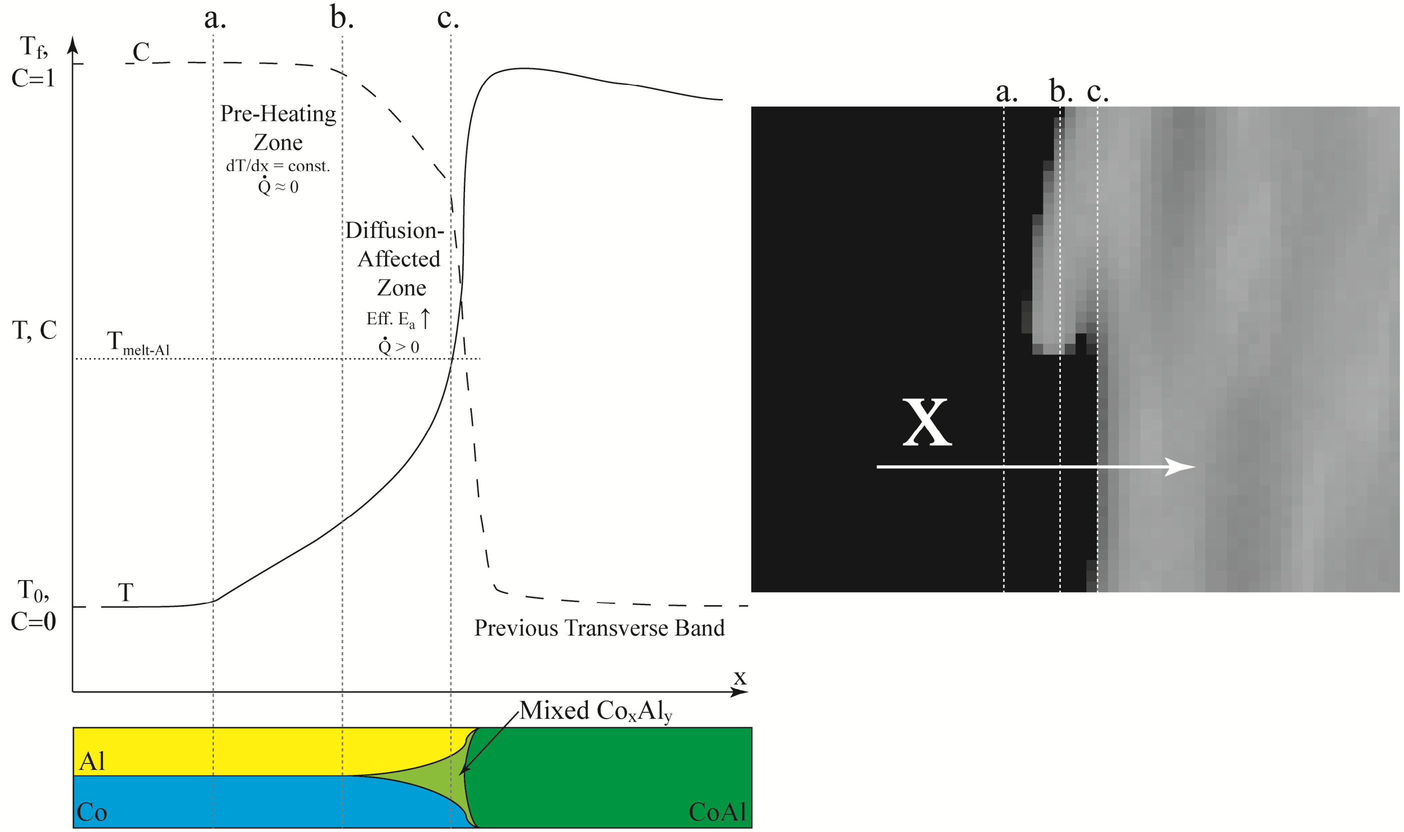
Simultaneous IR/Visible Light Imaging





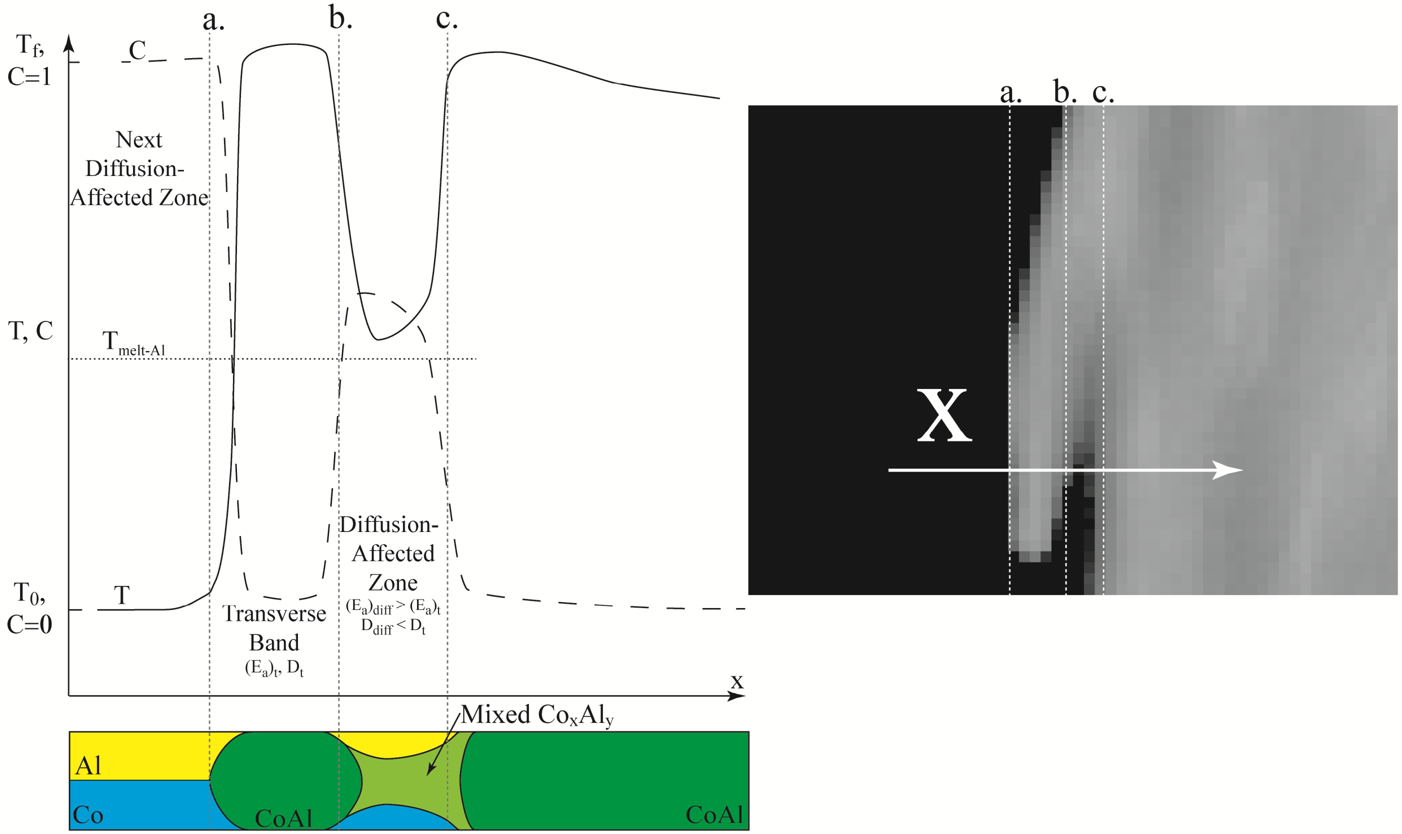
- Forward heat transfer w/o self-heating will be at conductive rates (<10[3])
- This might cause stationary reactions similar to initial DSC exotherm
- Solid state products could inhibit local reactions

Proposed Mechanism



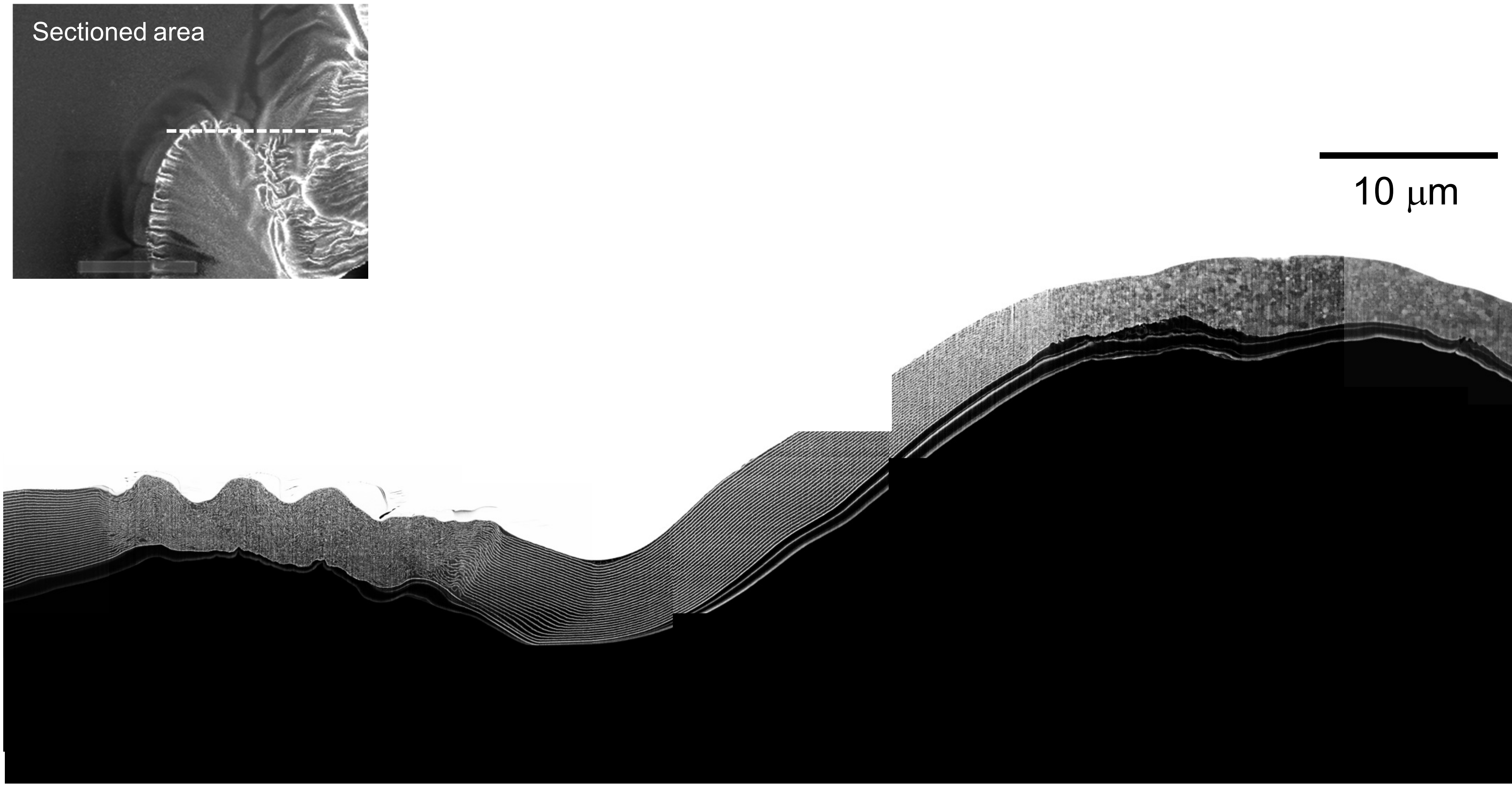
- At front edge of previous transverse band, heat is conducted into unreacted material
- Near transverse band, limited reaction occurs at Al/Co interface
- Farther ahead the local temperature rises, but remains below reaction onset threshold

Proposed Mechanism



- 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

Quenched samples that exhibit a 2-D instability show evidence for intermediate phases (Co_2Al_9).



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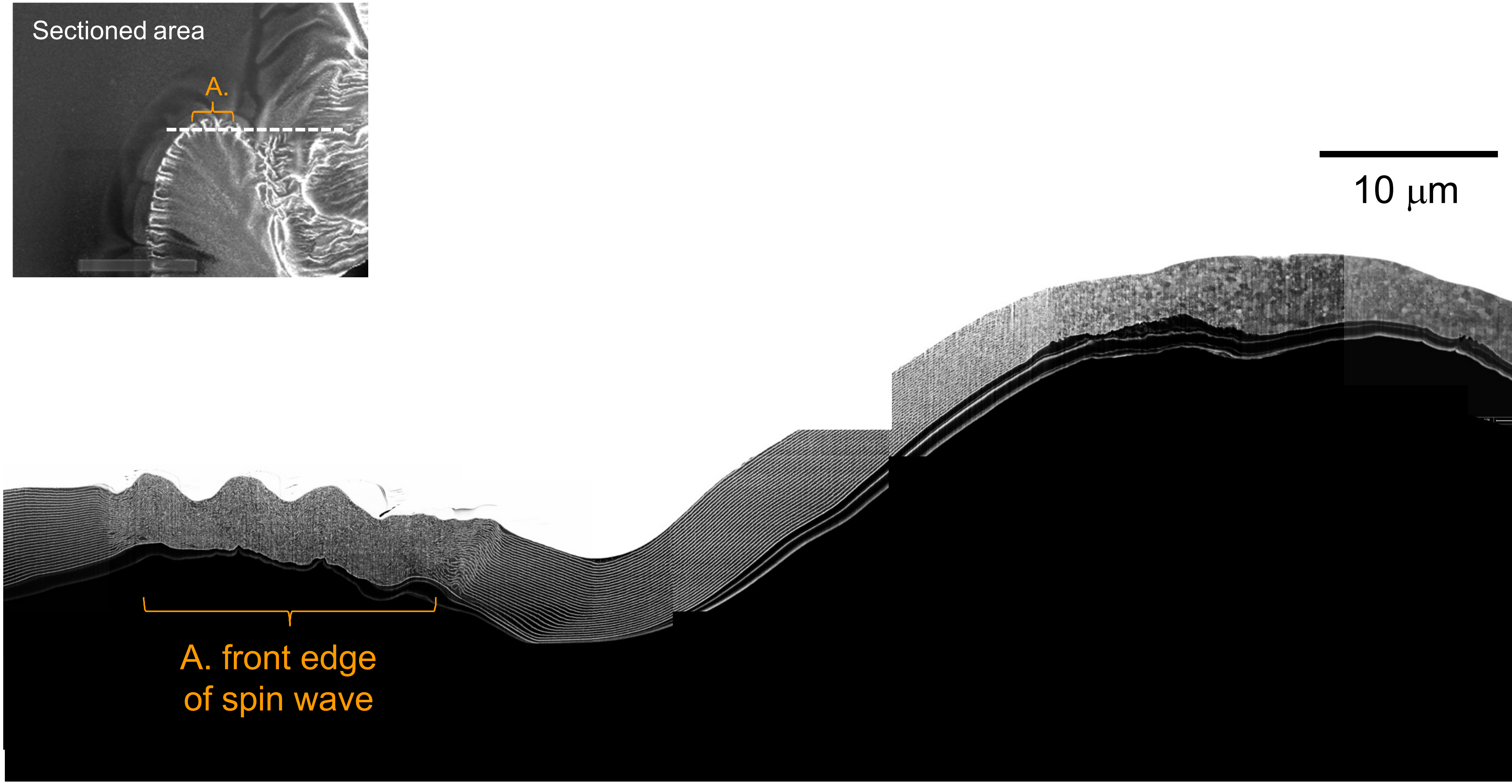

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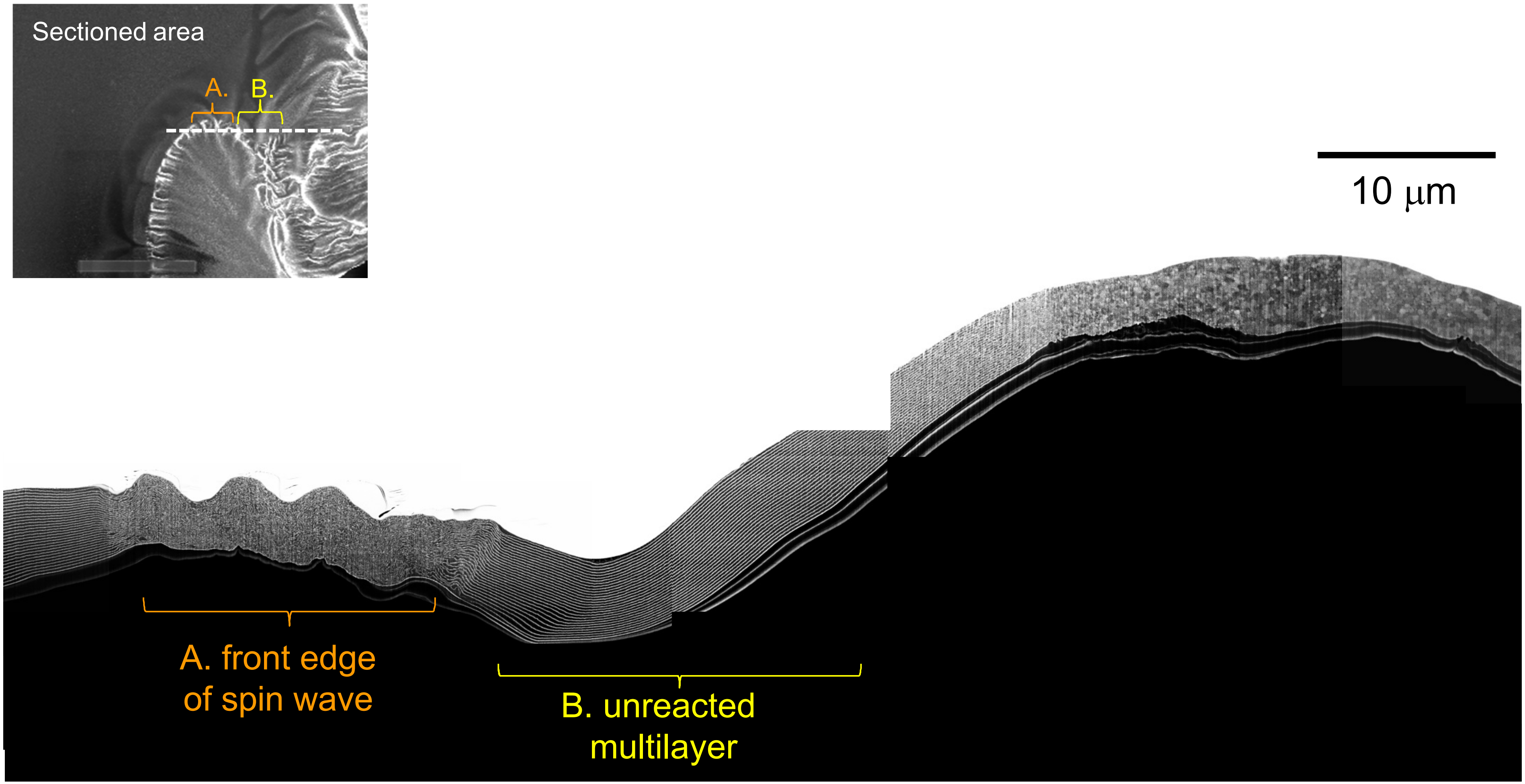

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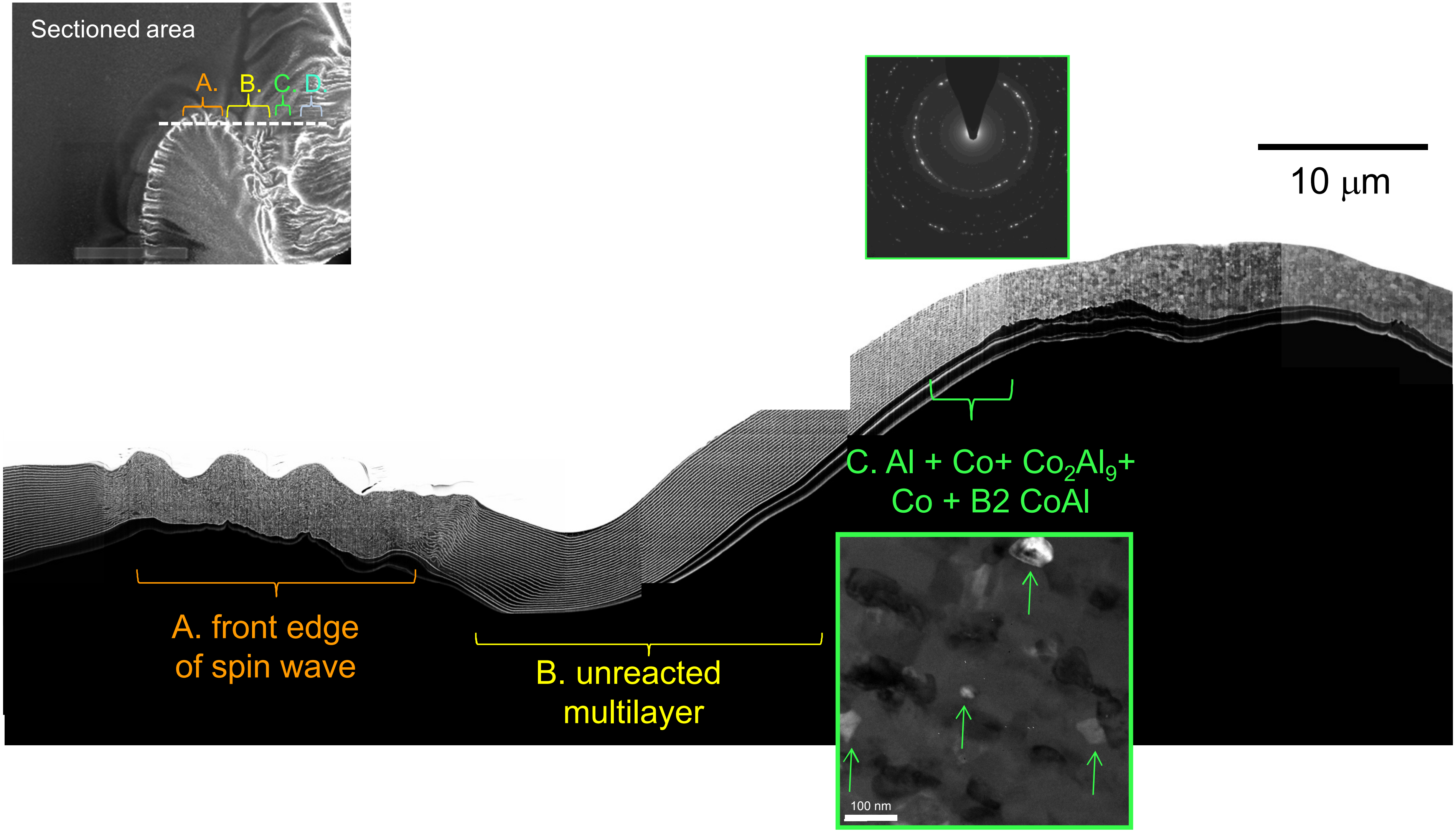

Dark field TEM of Co_2Al_9

uses (111) reflection
corresponds to d = 3.8 Å

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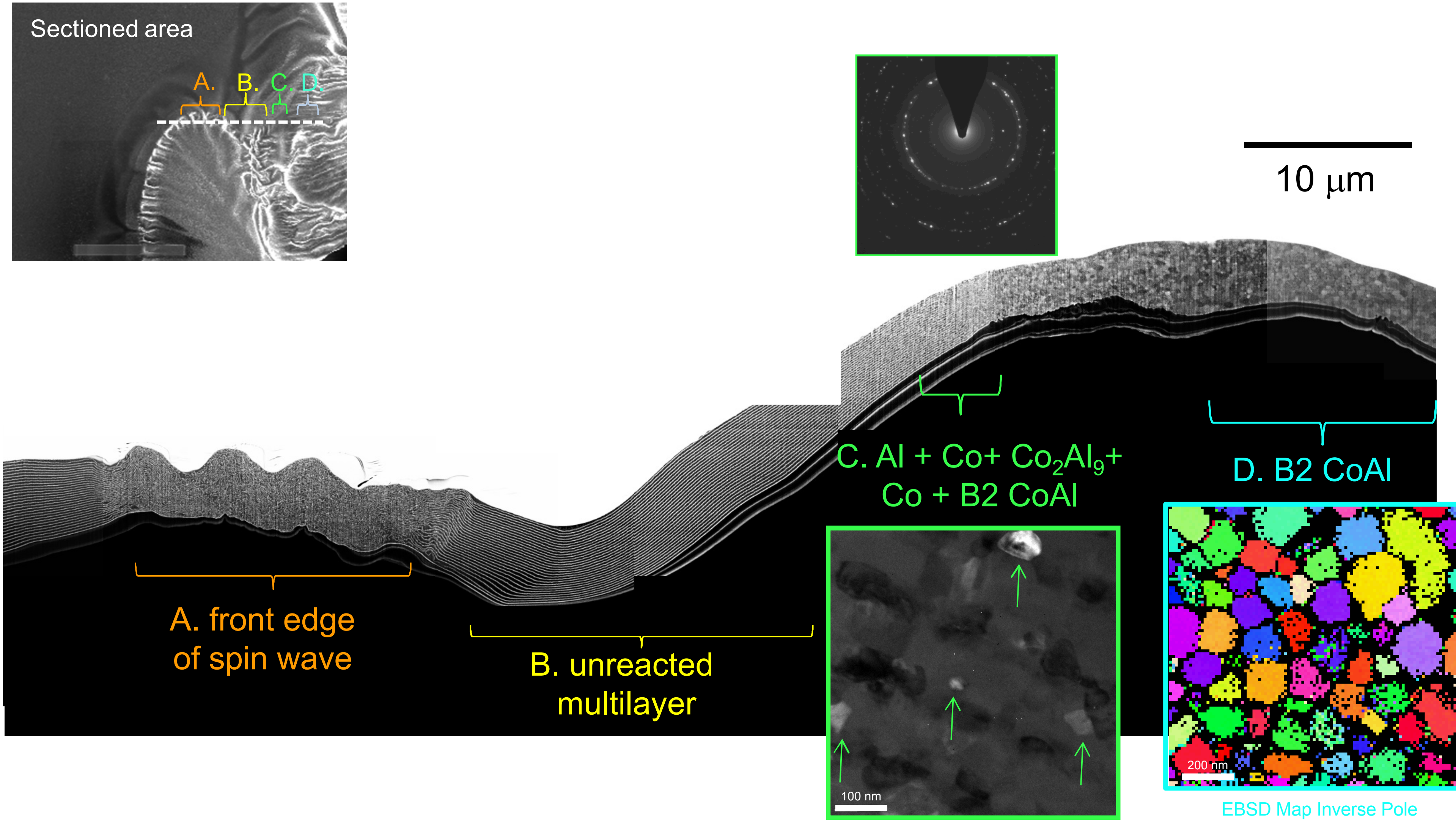


Dark field TEM of Co_2Al_9
uses (111) reflection
corresponds to d = 3.8 Å

EBSD Map Inverse Pole Figure x from B2 CoAl reflection

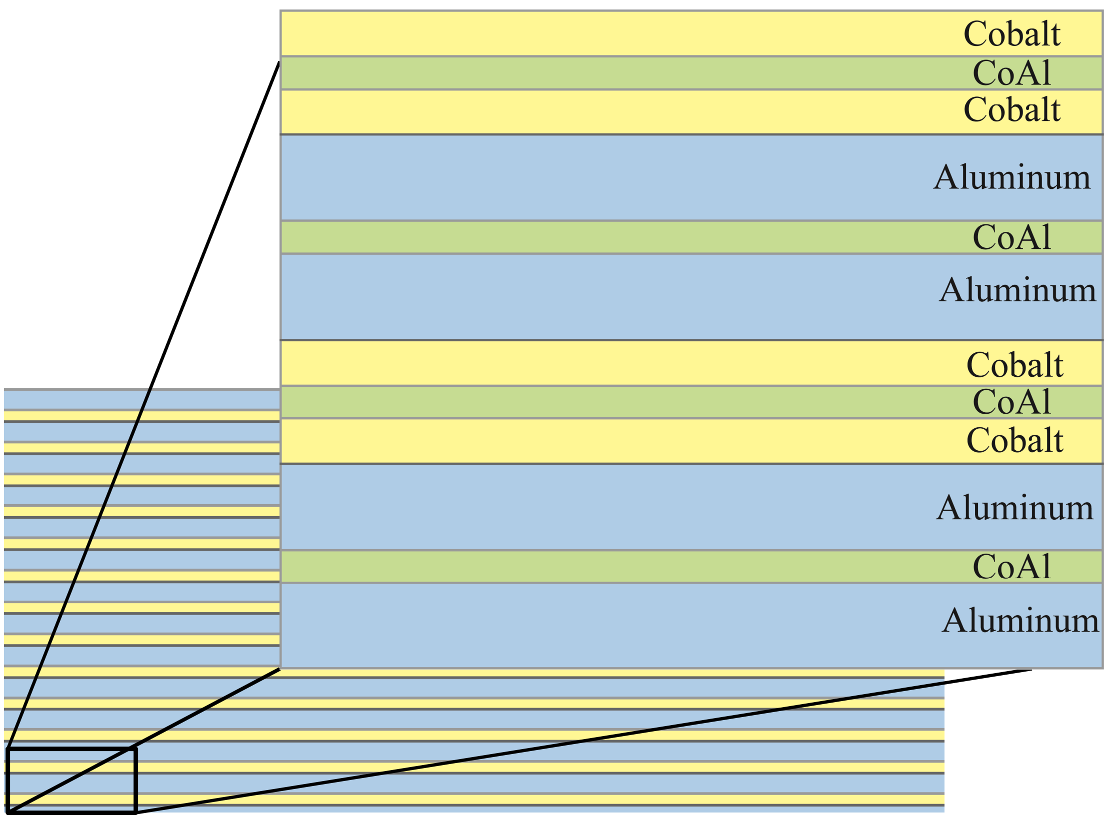
Multilayer Design

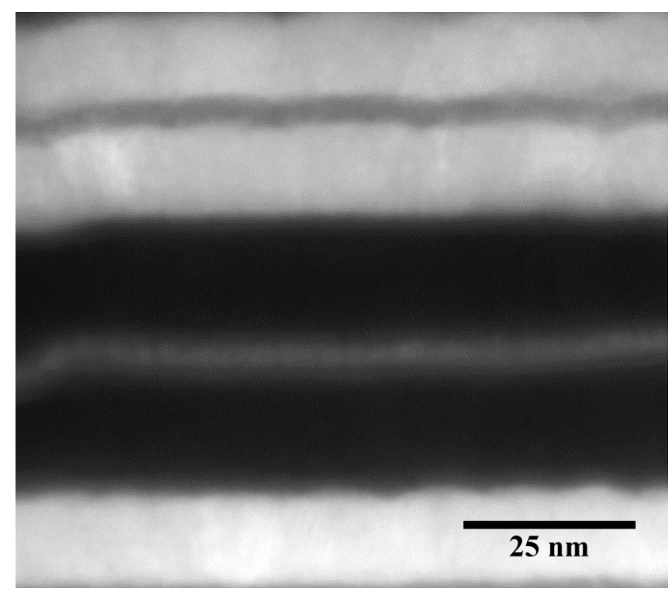
Dilution Designs to vary β

- Design for variation of β
  - Layers of CoAl product are deposited *within* each reactant layer
  - Reactive interfaces and diffusion distances are unchanged from the baseline multilayer design
  - Total volumetric dilution from 0% to 30%

- $\beta = \frac{E_a}{R{T_{ad}}^2}(T_{ad} - T_0)$

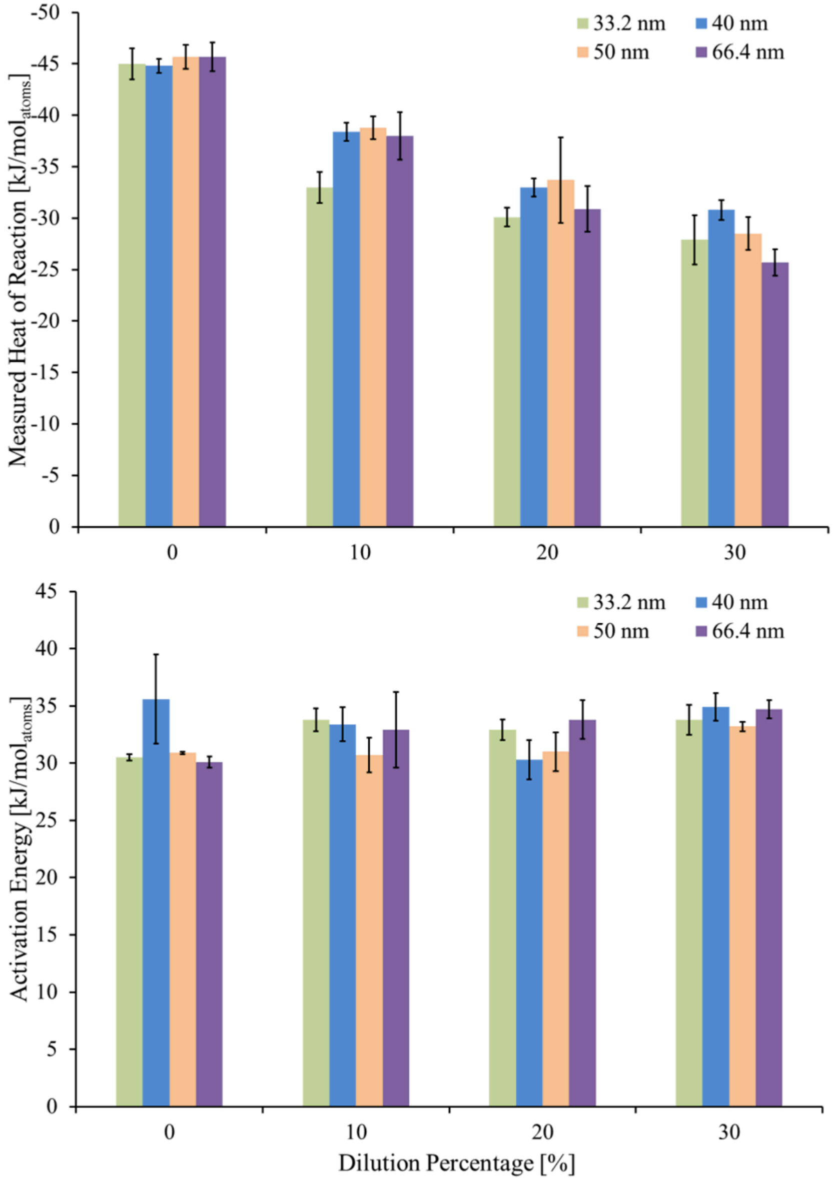
  so increasing CoAl dilution decreases T_{ad}, increasing *b*





Calorimetry

Determination of ΔH and apparent E_a



- Heat release directly measured from DSC
- Apparent E_a determined by Kissinger method

Le^{-1} at Transition to Stability

- Using Armstrong's relationship,

$$Le^{-1} = \frac{D}{\lambda} = \frac{u^2 \delta^2 E_a (T_f - T_0)}{3\lambda^2 {T_f}^2 R} = \mathcal{A}\, exp\left(\frac{-E_a}{RT_f}\right)$$

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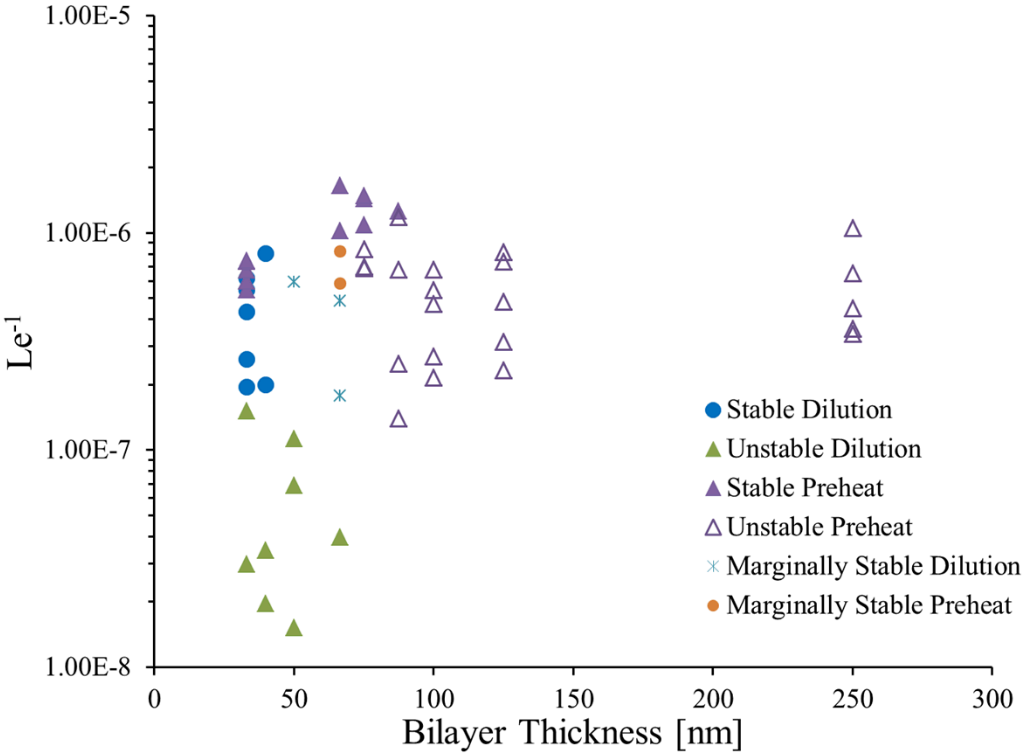
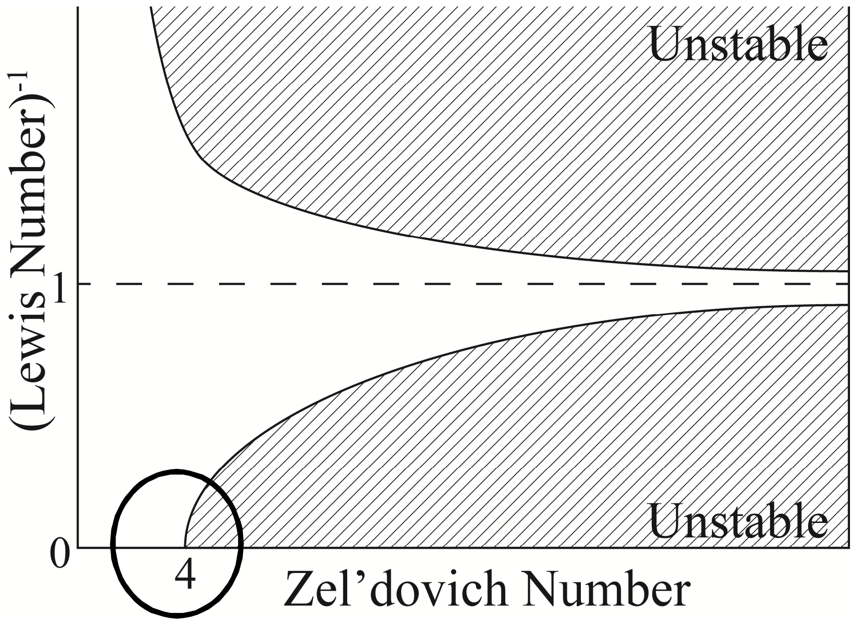


- Thinner BLs exhibit stable front at lower *Le^{-1}*
- Assuming constant λ, thicker BLs require higher mass diffusivity (reaction rates) for stability
- Fits with idea of critical heat transfer rate

Reaction Wave Stability



- Above chart from Aldushin and Kasparyan [1,2], discussed by Merzhanov and Rumanov[3]

- Lewis Number, $\frac{\alpha}{D} = \frac{\kappa}{D\rho c}$
  - Compares Mass Diffusion and Thermal Diffusion rates
  - Typical $L_e \approx \frac{10^{-1}}{10^{-3}\ to\ 10^{-7}}$ for gasless systems
- Zel'dovich Number,

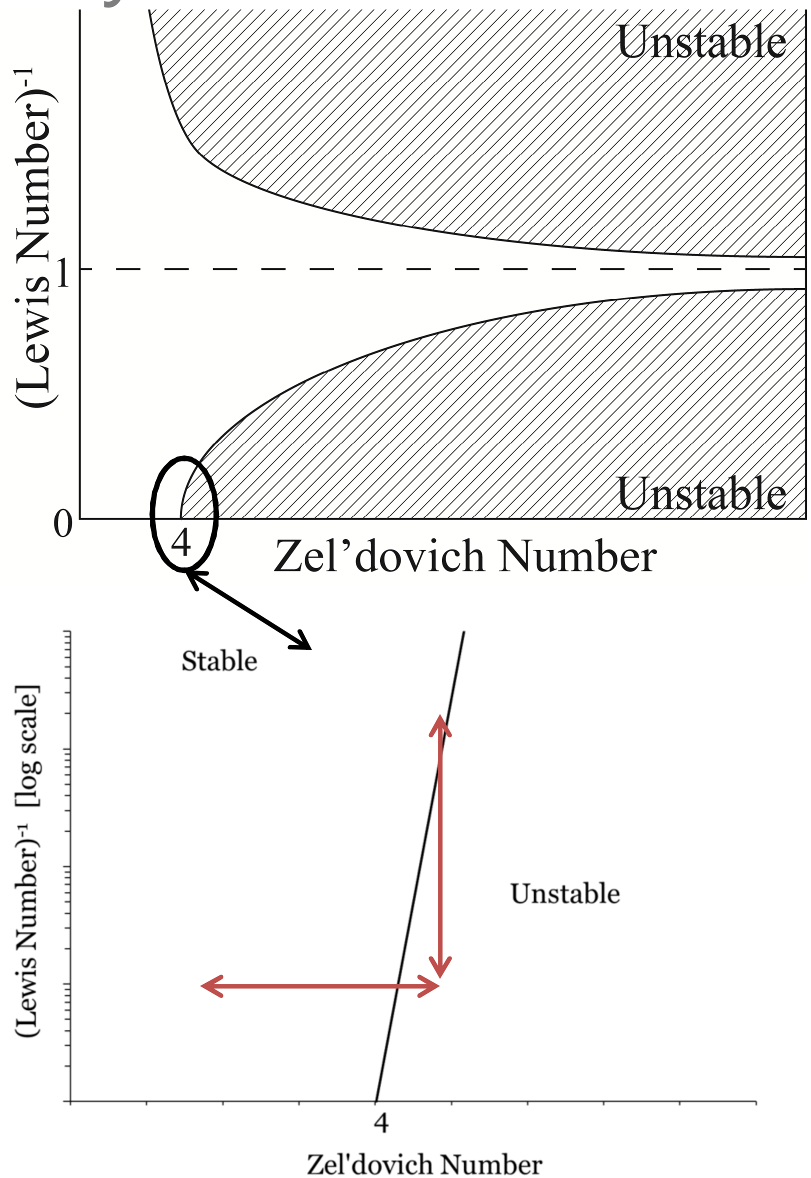
$$\beta = \frac{E_a}{R{T_{ad}}^2}(T_{ad} - T_0)$$

  - Compares temperature dependence of reaction to adiabatic flame temp.

[1] *Sov. Phys. Dokl*, **24**, 29, 1979
[2] *Akad. Nauk SSSR*, **247**, 1112, 1979)
[3] *Reviews of Modern Physics*, **71**, 4, 1999

Experimental Plan

Vary *Le* and *b* to determine stability boundary

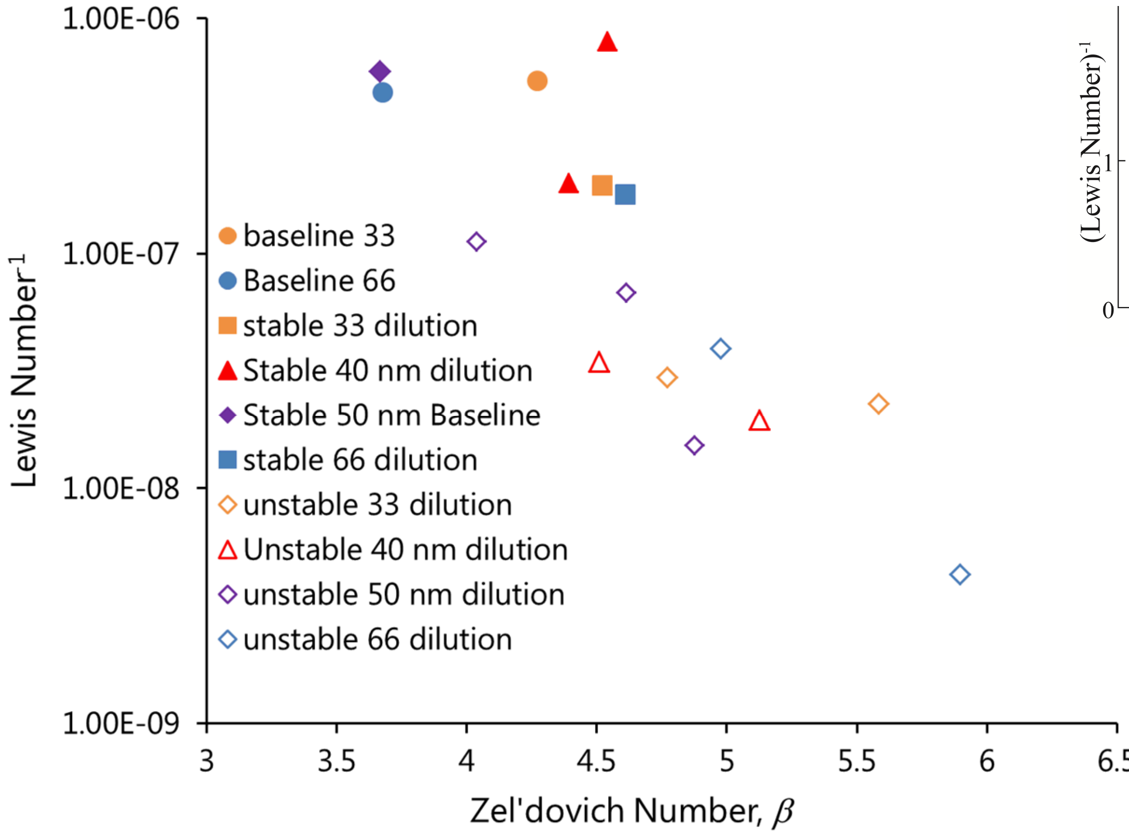


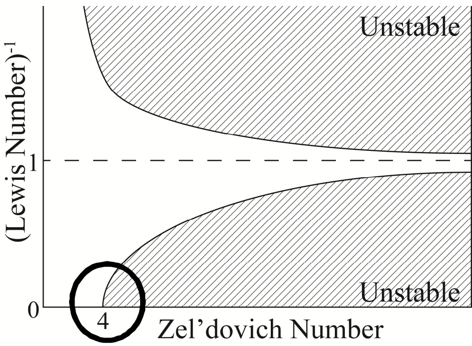
- Lewis Number
  - $Le^{-1} = \frac{D}{\lambda} = \frac{u^2 \delta^2 E_a (T_f - T_0)}{3\lambda^2 {T_f}^2 R} = \frac{u^2 \delta^2 \beta}{3\lambda^2}$

- Zel'dovich Number, $\beta = \frac{E_a}{R{T_f}^2}\left(T_f - T_0\right)$
  - Reduce adiabatic flame temperature through dilution

Stability Criteria

Experimental vs. Analytical

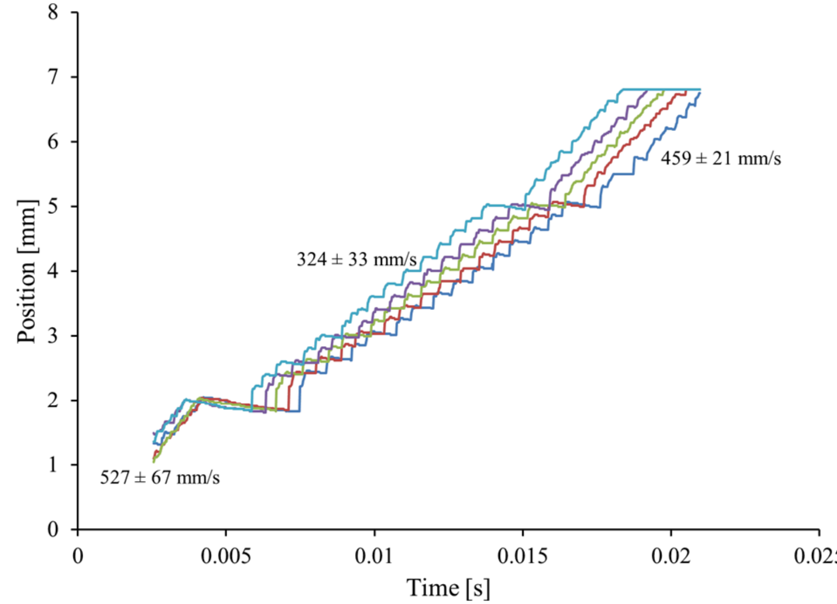


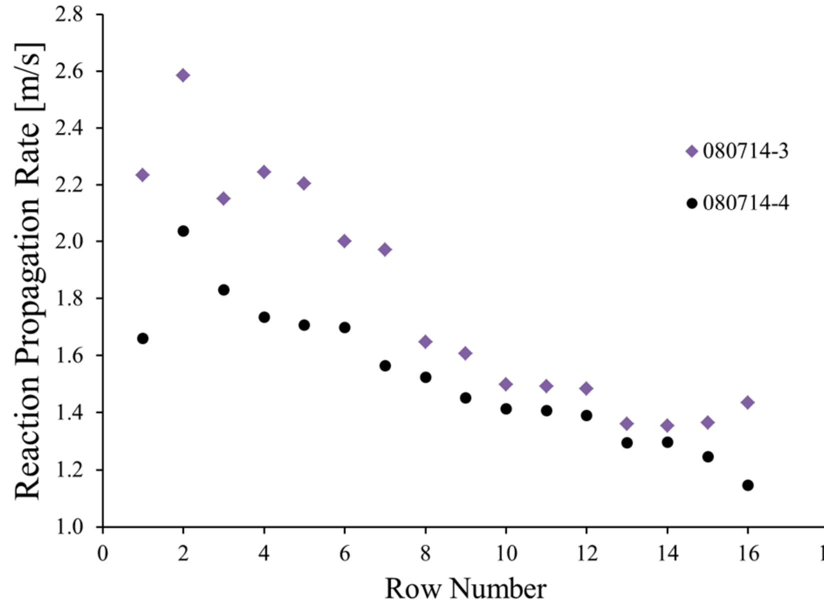


- Plotting on Le^{-1}-β axes, get approximate regions of stability
- Stability boundary similar between BL designs

Instability/Structural Anomaly Interaction

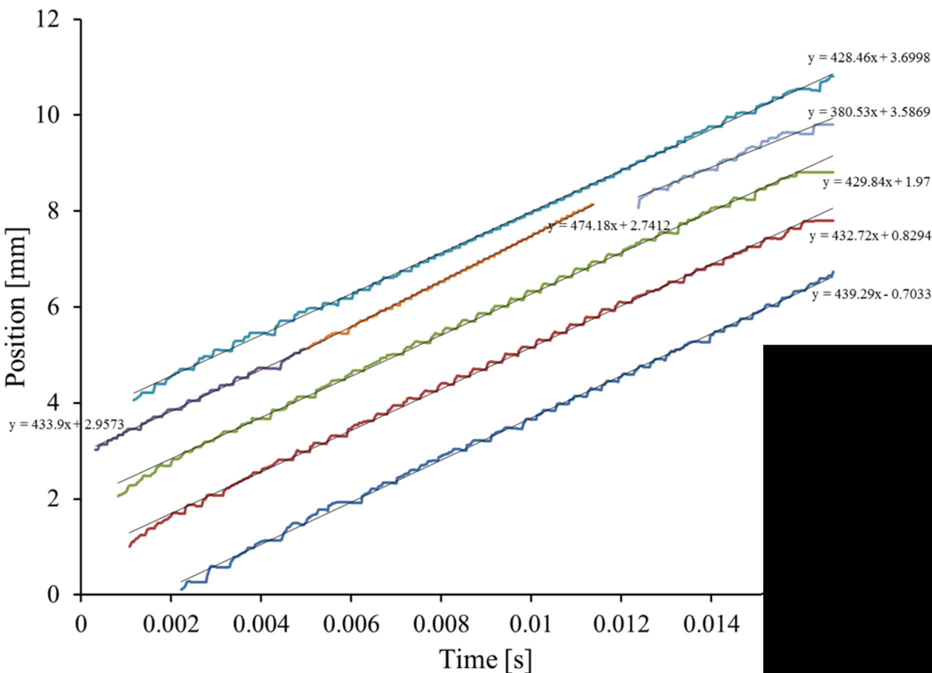
Arrays of Holes Slow Transit





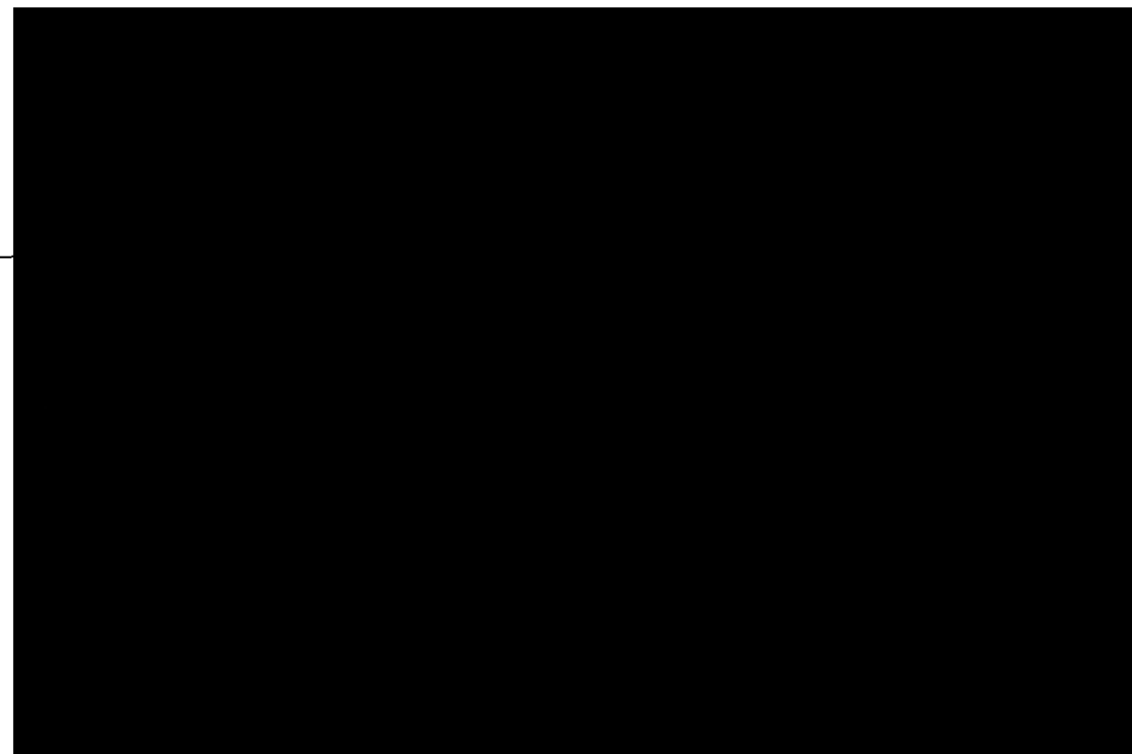
Holes affect heat flow, inducing transverse bands at length scale of spacing. Bulk propagation rate slows in porous region.

Instability/Structure Interaction



Slotted holes provide little impediment to heat flow.

Propagation is either unimpeded or accelerated



Conclusions

- Experiments show some BL designs can switch stability behavior by affecting the heat transfer conditions
- All transitions to stability occur at a common bulk propagation rate
- Disparate reaction kinetics likely occurring in diffusion-affected zones and transverse bands
- Quench experiments result in microstructures reflecting proposed mechanism

Acknowledgements

- Eric Jones
  - Thin film growth
- Cathy Sobczak
  - Thin film growth
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  - SEM images and montage
- Lisa Lowery
  - Many, many FIB sections

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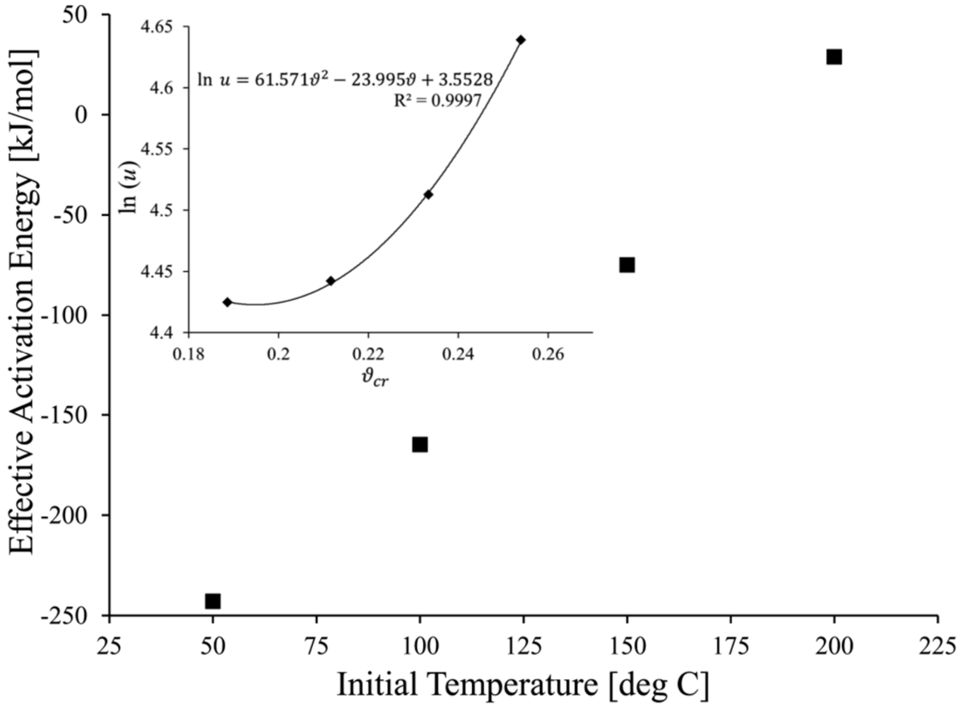
- Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

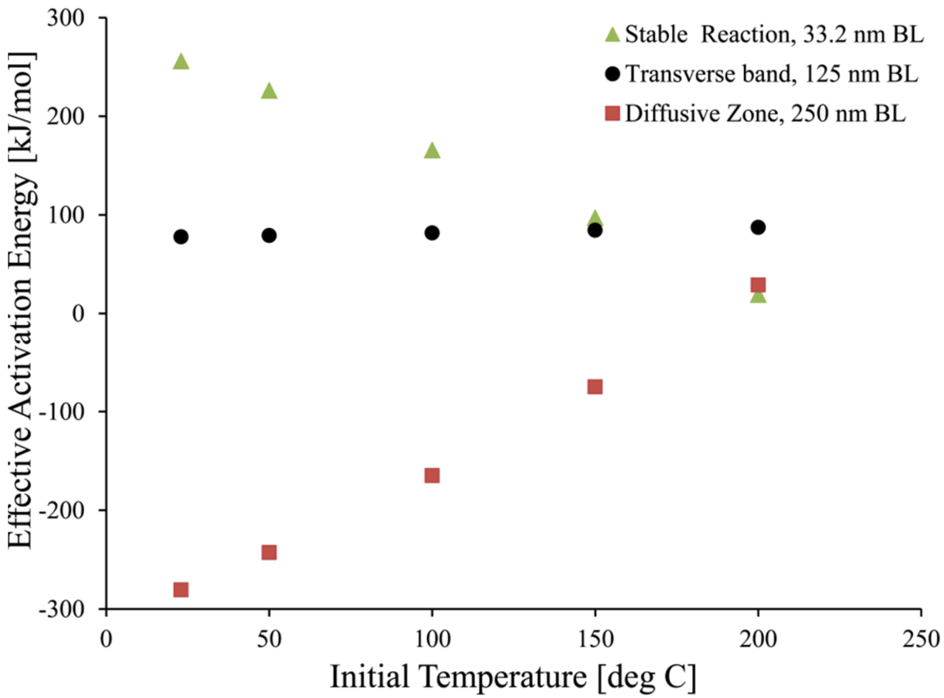
Additional slides

Conclusions

- Experiments show some BL designs can switch from unstable to stable reaction fronts by increasing T_0
- All foils transitioned to stability at a common bulk propagation rate
- Calculations show greater diffusion rates required for stability in thicker BL foils
- Dark regions between transverse band ("diffusion-affected zones") exhibit high-E_a behavior
  - Conduction heats material causing limited reaction
  - Product layer forms at interface, inhibiting reaction
- Disparate reaction kinetics likely occurring in diffusion-affected zones and transverse bands

Local Variation in Effective Activation Energy



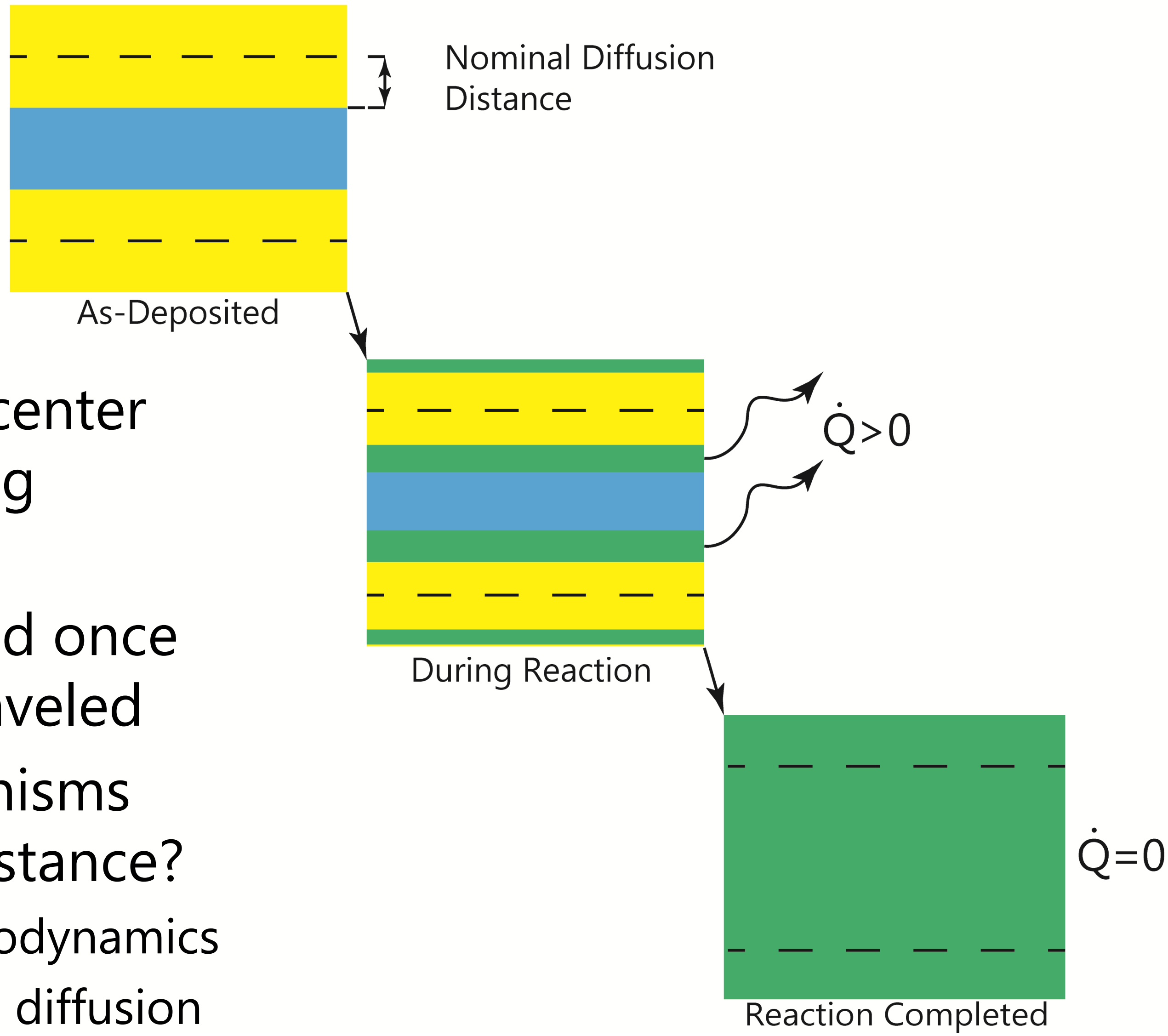


- E_a decreases with T_0 for stable bulk reaction
  - Increased local kinetics
- E_a is unaffected by T_0 for transverse reaction bands
  - Region is dominated by heat transfer
- E_a increases with T_0 for reactions in the diffusion-affected zones
  - Higher initial temp possibly producing more robust product films

Conclusions

- Can grow thin films that can well isolate effects of diffusion and mass dilution
- Variation in *Le* and *b* can introduce reaction instabilities, as predicted by theory
- Induced instabilities in Co/Al laminates limited to 2-D spinning instability
- Similar but not identical stability limits between BL designs
- Need dimensionally dependent heat release and mass transfer terms in the basic transport equations for analytical criteria and predictive models

Nanolaminates
Typical Reaction Progression

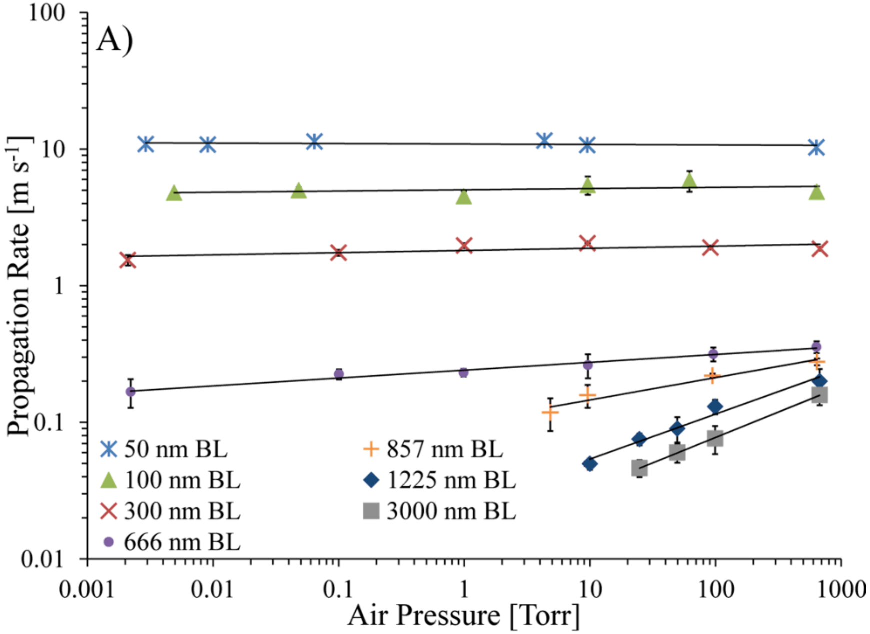


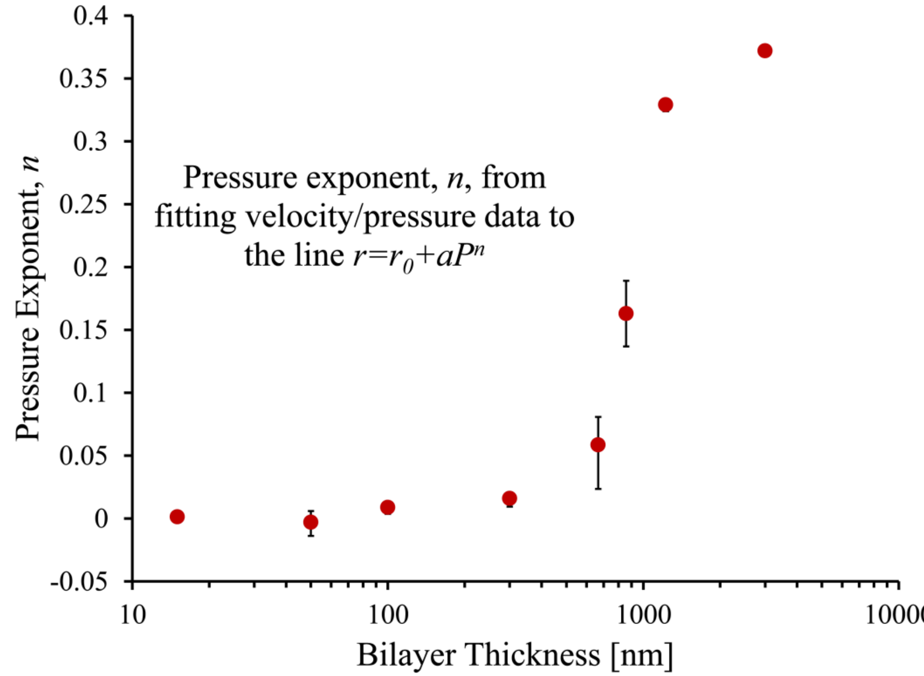
- Atoms diffuse to center line of neighboring reactant layer
- Final phase formed once this distance is traveled
- Can other mechanisms affect diffusion distance?
  - Dissipative thermodynamics
  - High temperature diffusion

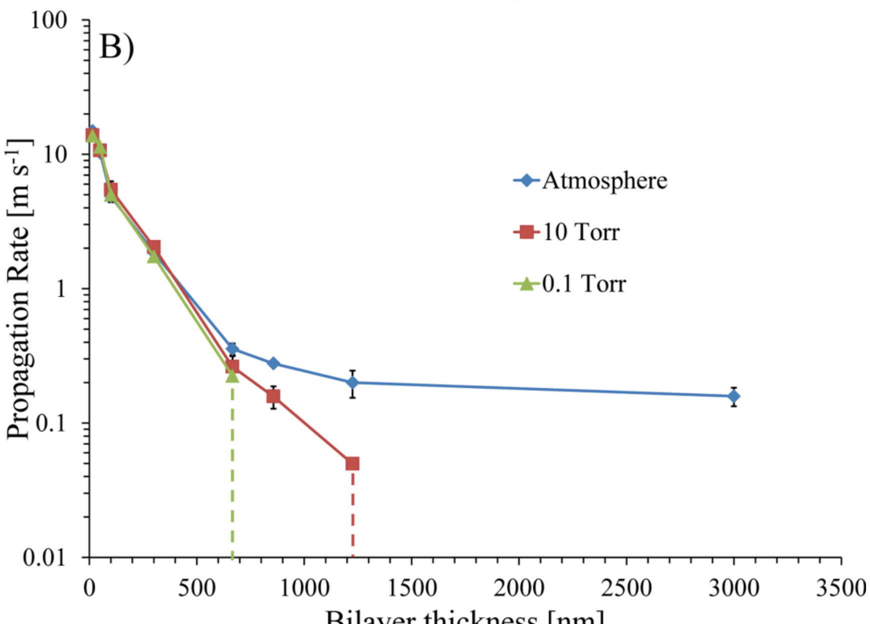
Reaction Initiation

- Despite all positive attributes, thermally ignited materials can suffer from instabilities
  - Reaction behavior dependent on forward heat transfer
- Mechanical loading can input energy faster than thermal diffusivity

Pressure dependence by bilayer







- Thick bilayers: strong pressure dependence
- Thin bilayers: little pressure dependence
- Transitional BL thickness lies between 667 and 857 nm
- Atmosphere extends range of BL thicknesses that propagate

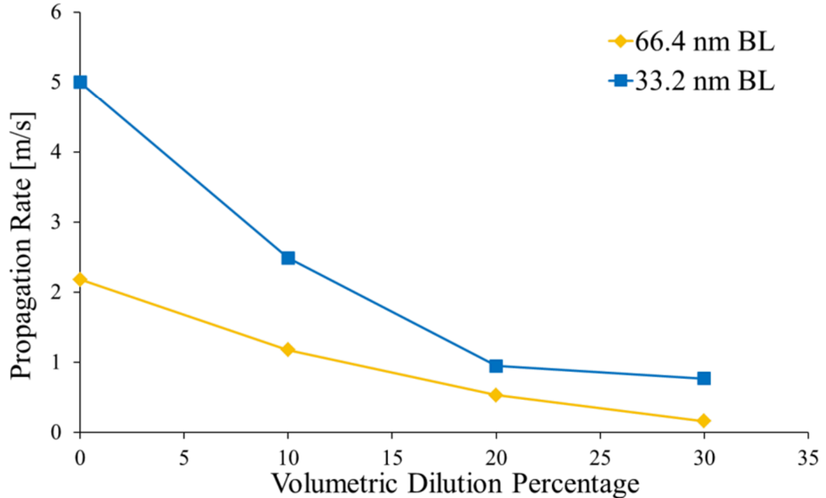
Propagation Rates

Co/Al Nanolaminates
33.2 nm BL Th.
Diluted with CoAl Alloy
Volumetric Percent CoAl Noted
Air Pressure = 10.0 mTorr

1 s Real Time = 1 ms Reaction Time

Co/Al Nanolaminates
66.4 nm BL Th.
Diluted with CoAl Alloy
Volumetric Percent CoAl Noted
Air Pressure = 10.0 mTorr

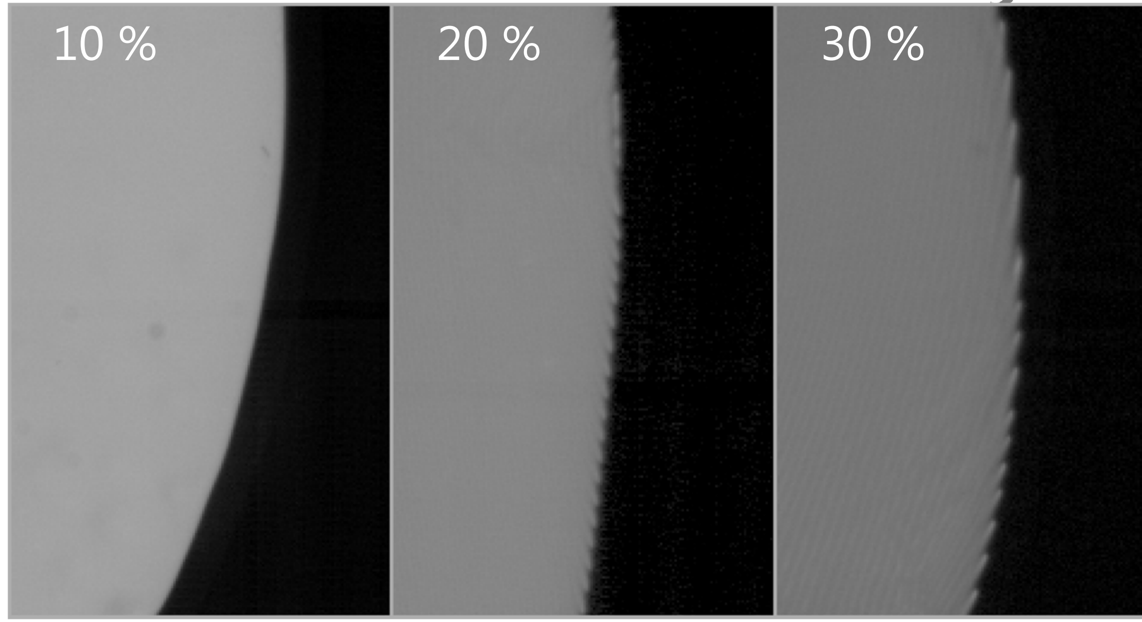
1 s Real Time = 1 ms Reaction Time

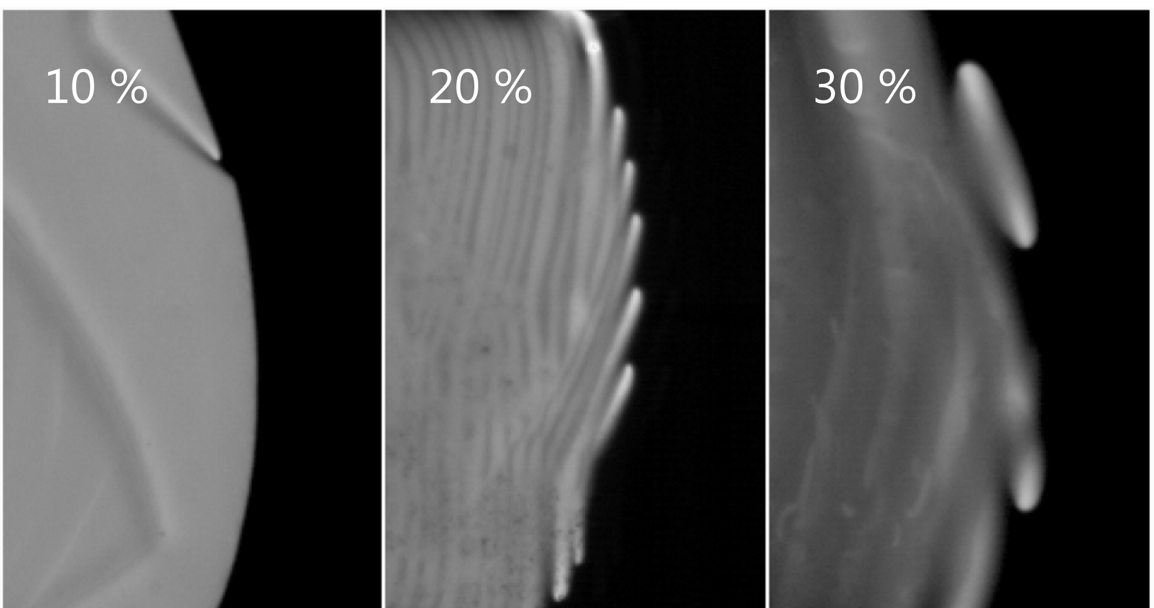


Dilution– Reaction Front Stability

33.2 nm BL

10% Dilution –
Stable front, u = 2.49 m/s
20% Dilution –
Spin instability appears, u = 0.95 m/s
30% Dilution –
Spin instability is more apparent, u = 0.77 m/s





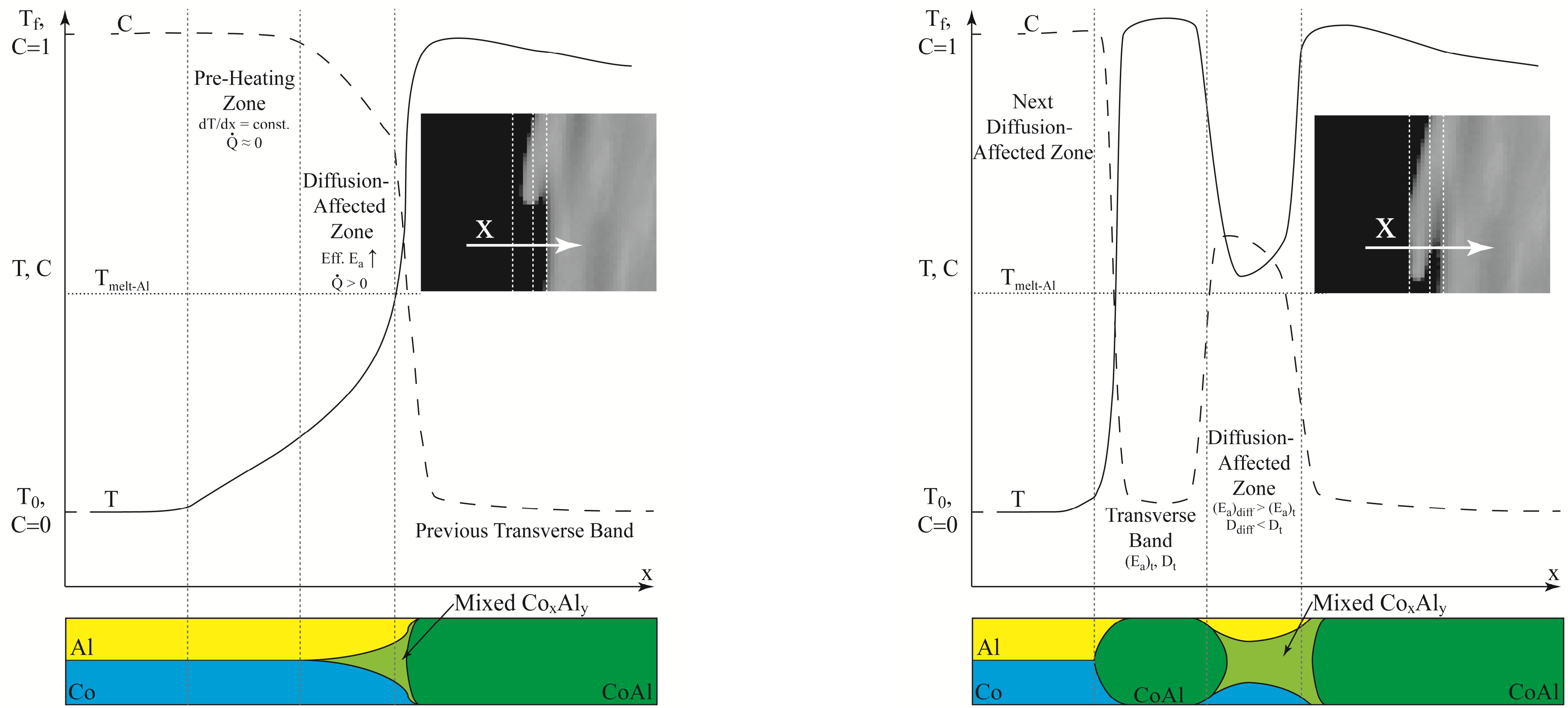
66.4 nm BL

10% Dilution –
Spin instability appears, u = 1.18 m/s

20% Dilution –
Spin instability appears, u = 0.53 m/s

30% Dilution –
Spin instability becomes very large and irregular, u = 0.16 m/s

Proposed Mechanism



- 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