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Unstable propagating reactions in sputter-deposited nanolaminates

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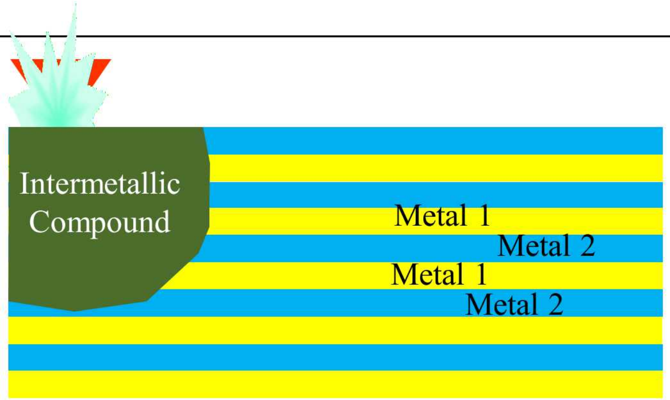
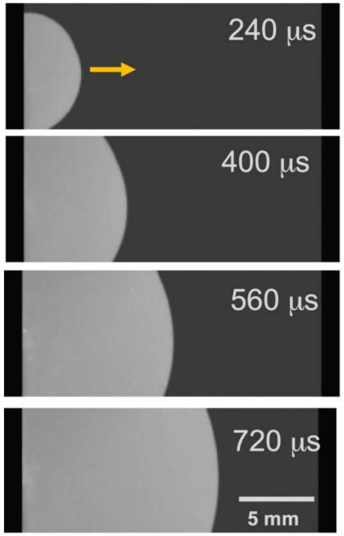
Many reactive multilayers undergo propagating reactions. Some are stable. Others are unstable.



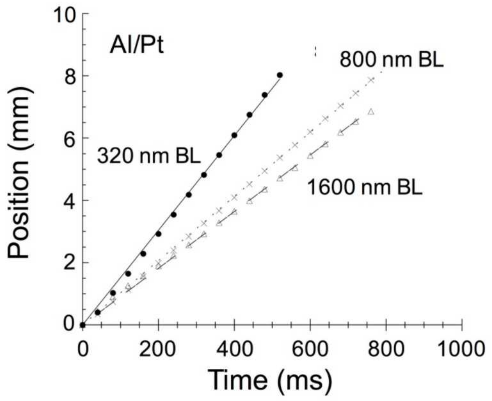
Example Systems:
Al + Pt -> AlPt + 100 kJ/mol.at.
Co + Al -> CoAl + 43 kJ/mol.at.

Stable propagating reactions:

- Smooth reaction front & uniform wave speed

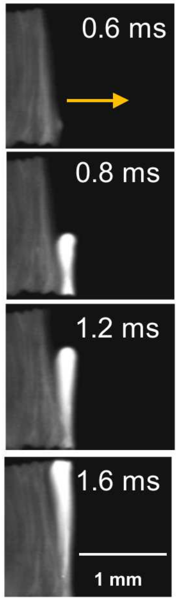


Videography



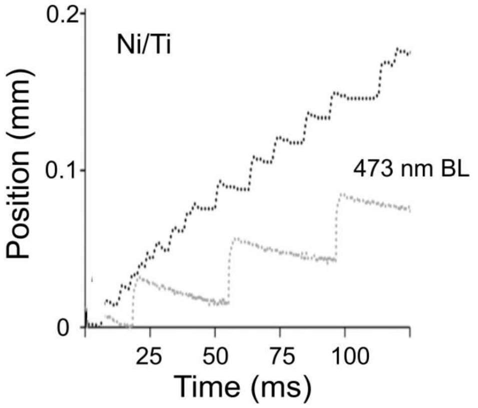
Unstable propagating reactions:

- Nonuniform reaction front & varying wave speed



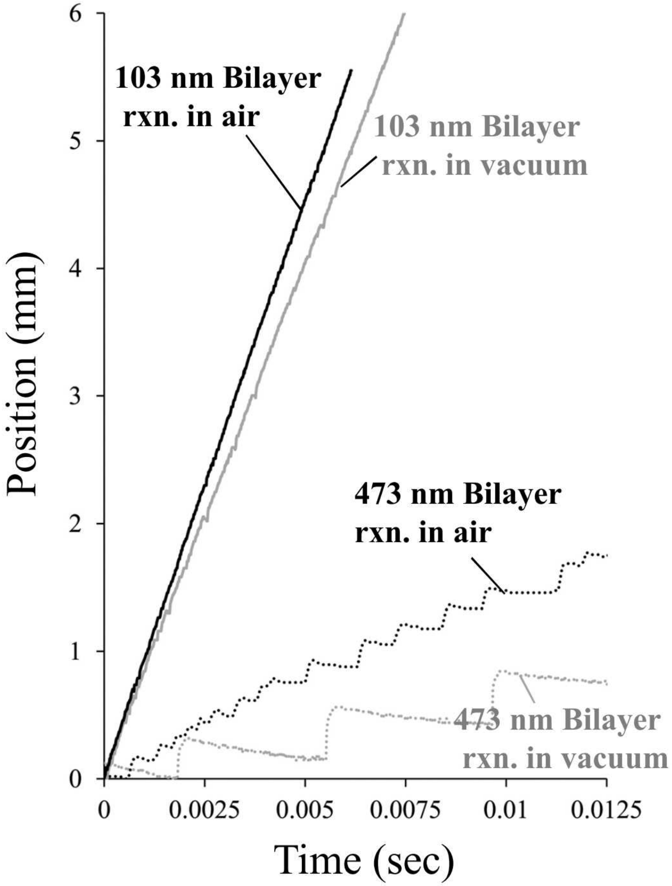
Videography

Each step = New spin band.

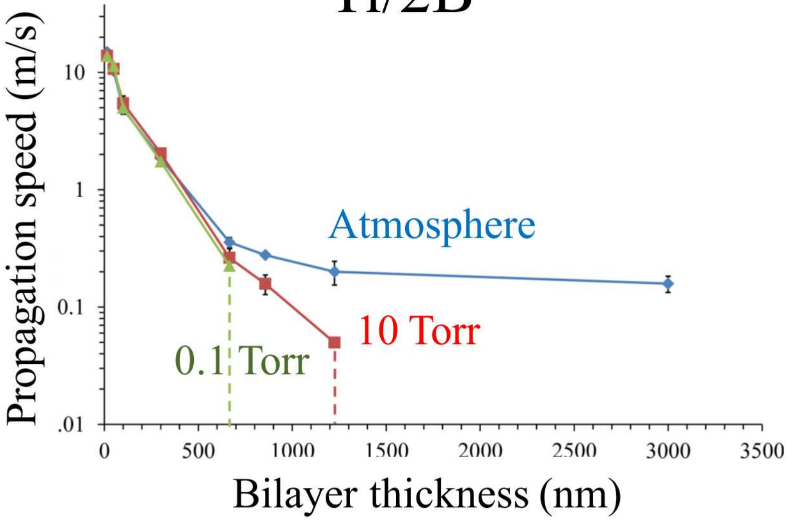


Propagating reactions are often affected by surrounding gaseous environment.

Ni/Ti



Ti/2B



Additional effects of gaseous environment:

- Increased average speed when reacted in air
  - increased spin band nucleation rate (Ni/Ti)
- Expanded range of reactive designs (Ni/Ti, Ti2B)

Question addressed in this study

Building on the idea that a minimum forward heat release rate is needed for a stable propagating reaction .....

Can certain intermetallic reactions be stabilized by prompt oxidation when tested in air?

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$Sc + Ag \longrightarrow ScAg$ (-0.32 kJ/g)

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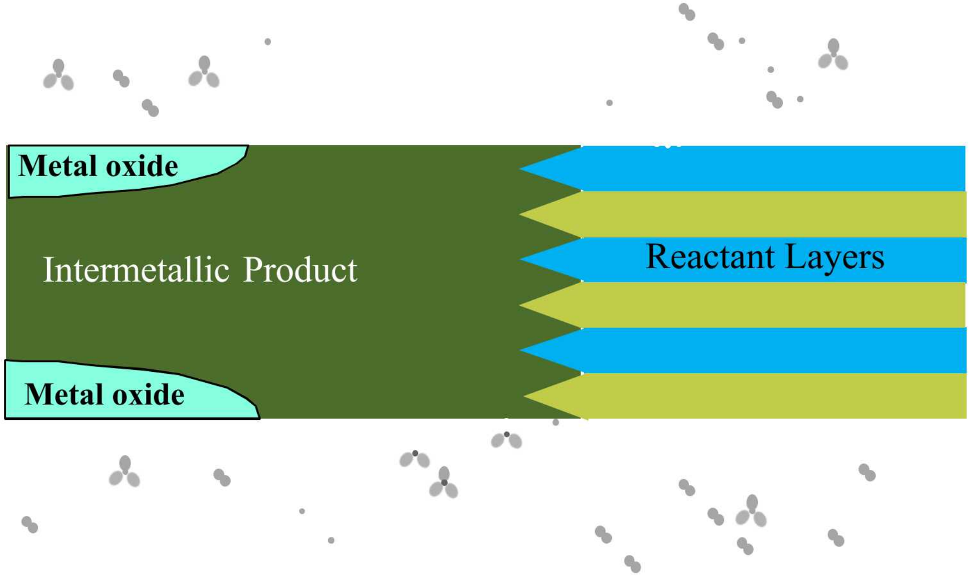
Subject of study: Sc/Ag

$$Sc + Ag \longrightarrow ScAg \ (-0.32 \text{ kJ/g})$$

$$4Sc + 3O_2 \longrightarrow Sc_2O_3 \ (-20.9 \text{ kJ/g})$$



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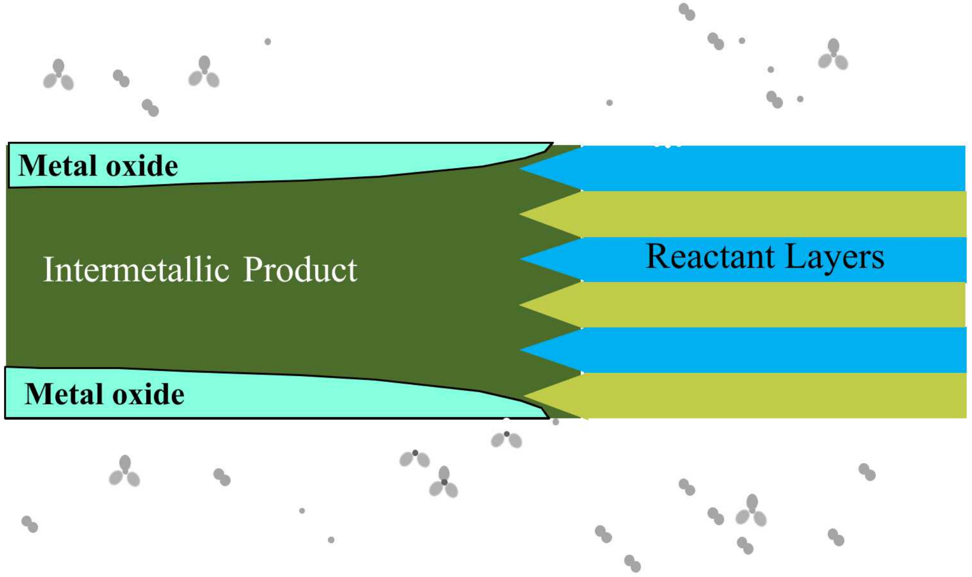
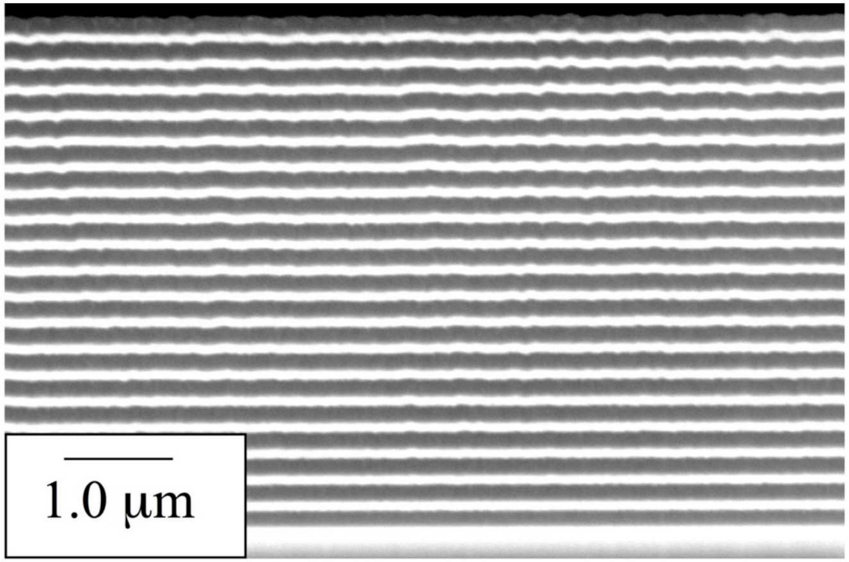


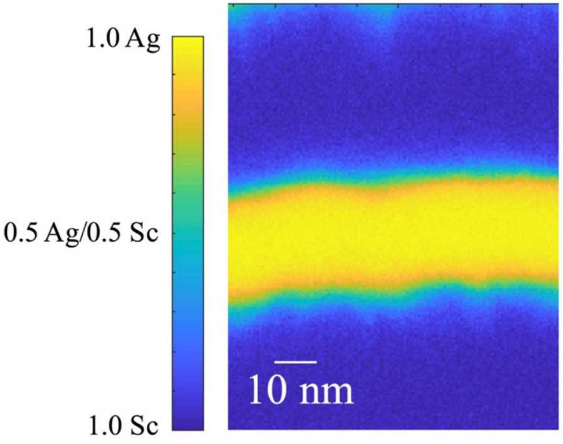
Layered structure and composition profiles are revealed by SEM and TEM/EDS.

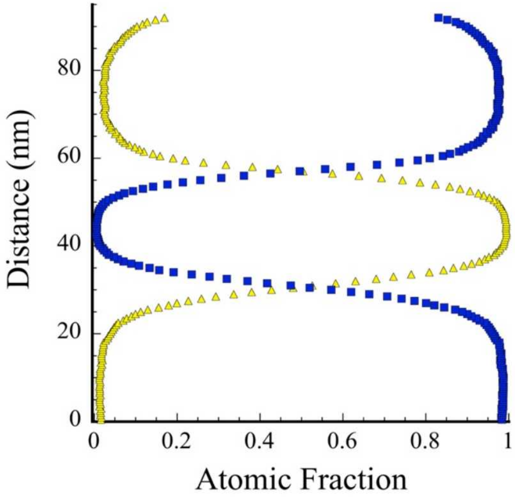
Secondary electron micrograph showing Sc/Ag multilayer in cross section

(constant $t_B = 250$ nm)



Compositional map TEM/EDS is obtained from sample with $t_B = 62.5$ nm





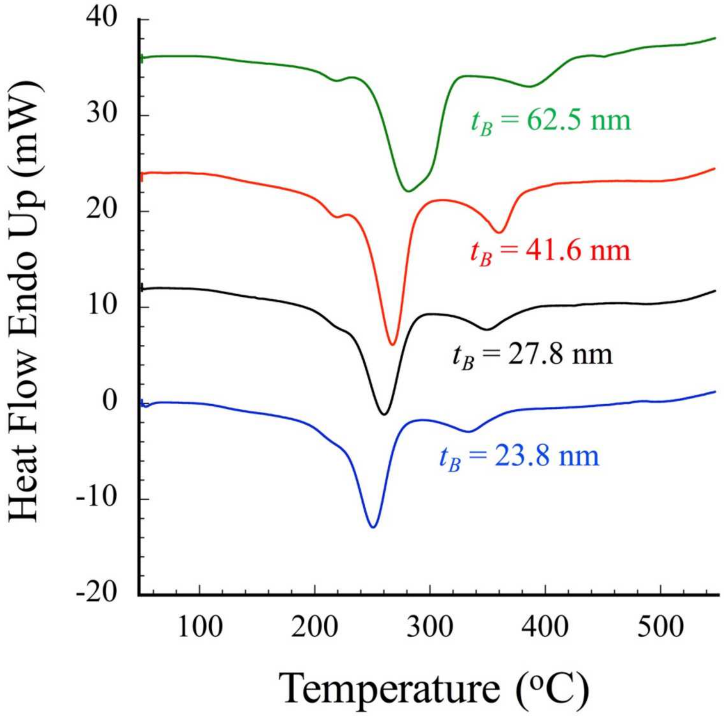
Premix thickness is ~ 8 nm when specifying boundaries at 15 and 85%

Differential Scanning Calorimetry (DSC) was used to obtain thermograms which ultimately were used to determine ΔH_{rxn}.

- All ScAg multilayers were characterized by multiple exotherms.

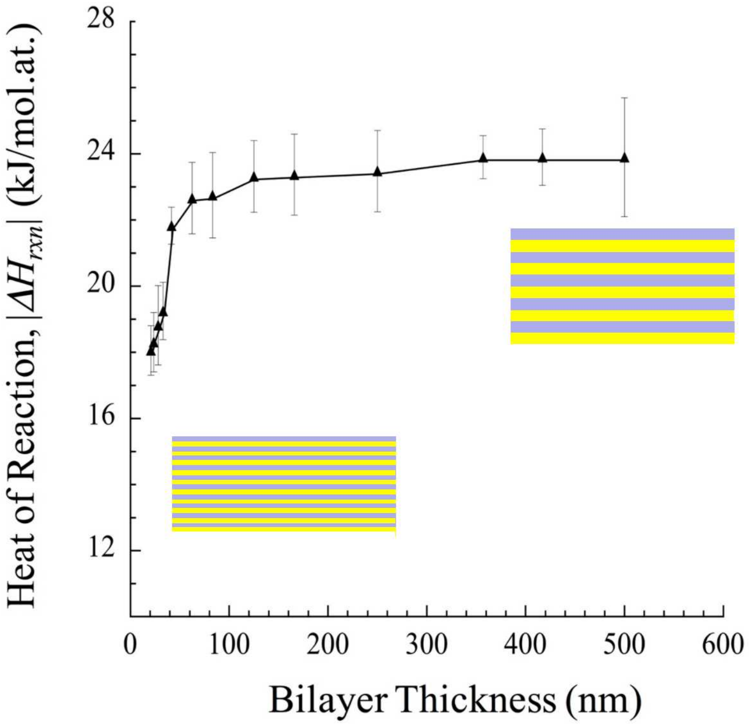
- First exotherms starts at ~200°C.
  - Separate XRD confirms growth of amorphous interlayer initially

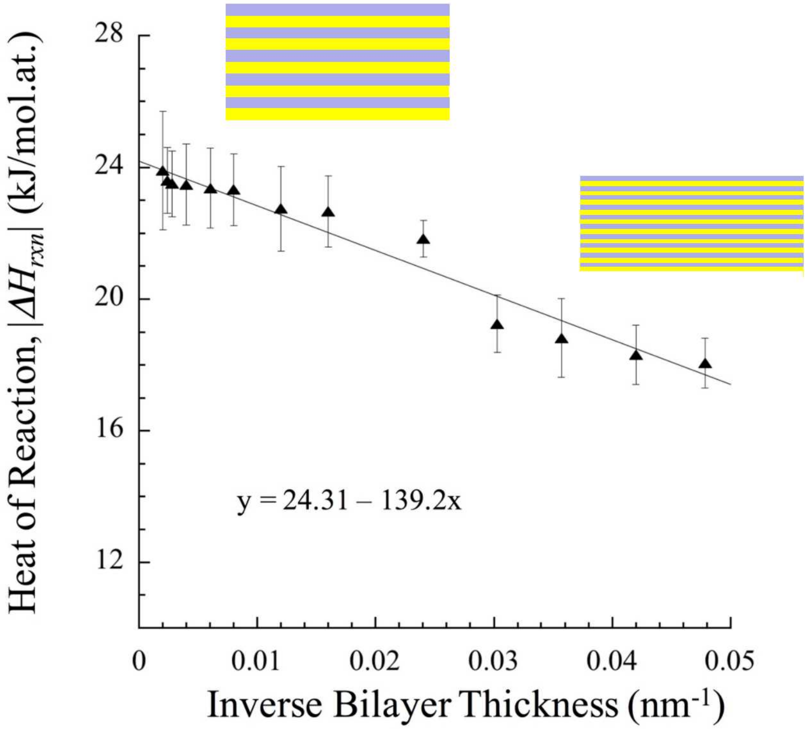
- Additional exotherms
  - Formation of Ag_2Sc then ScAg



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

Heats of formation are determined from measured heats of reaction.





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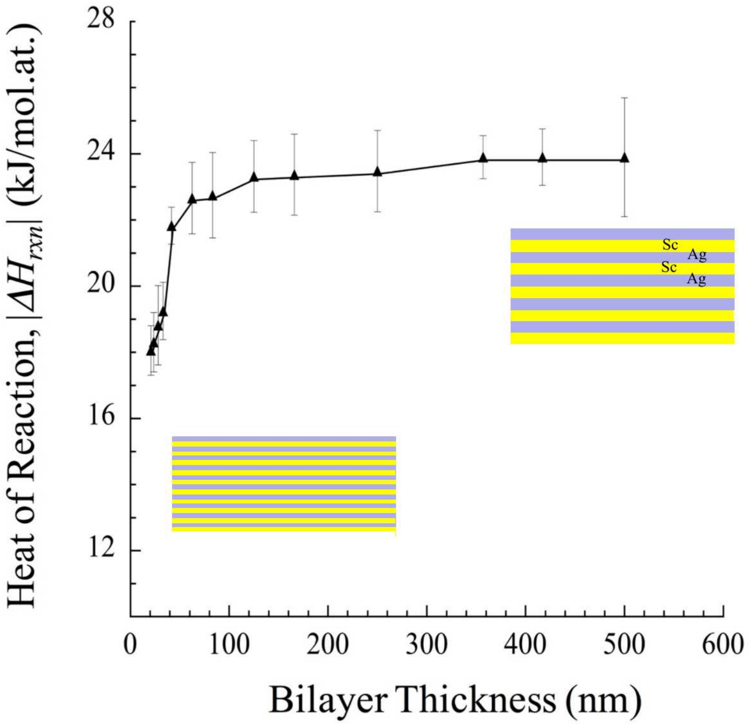
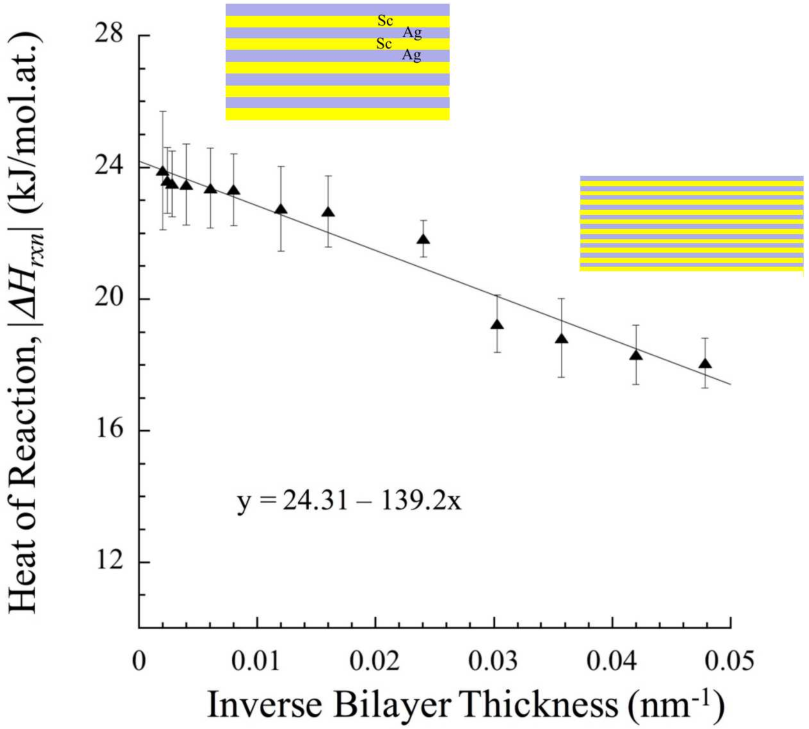
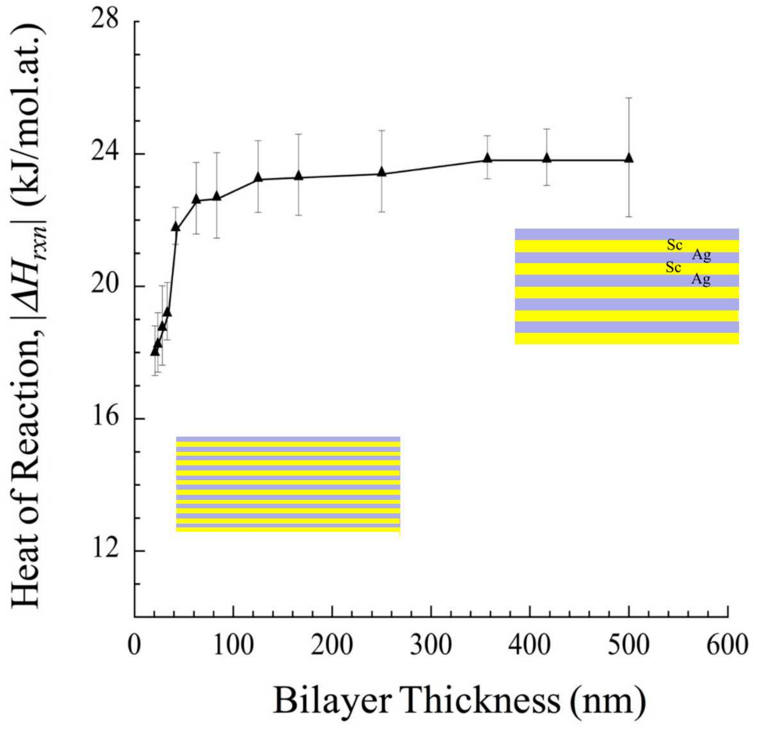


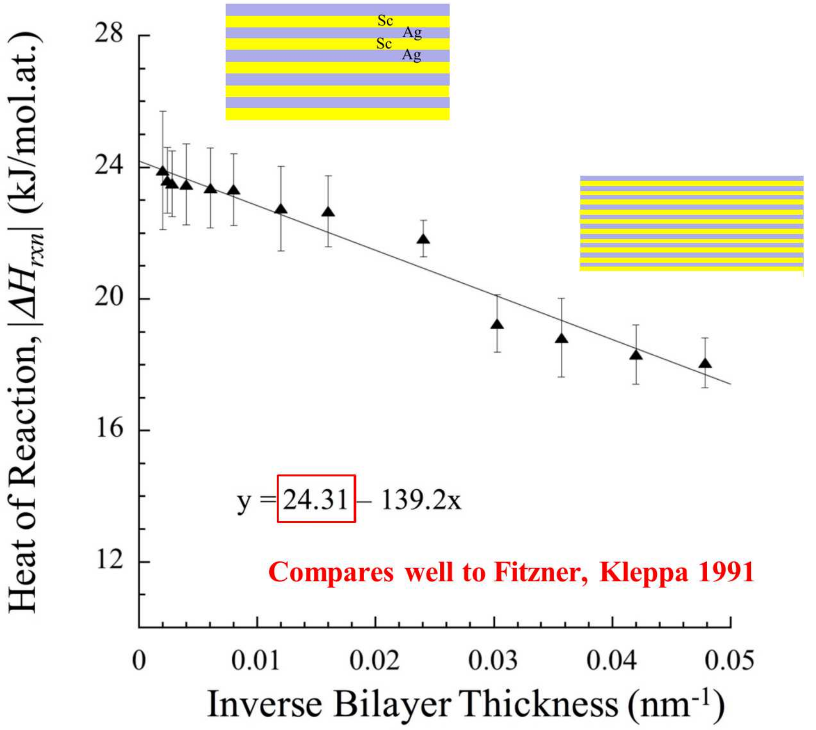


$$\underset{\substack{\uparrow\\ \textbf{Measured}\\ \textbf{Heat of}\\ \textbf{Reaction}}}{\Delta H_{rxn}} = \underset{\substack{\uparrow\\ \textbf{Heat of}\\ \textbf{Formation}}}{\Delta H_{ScAg}} - \underbrace{\Delta H_{premix}\left[\frac{2\,w\,V_{ScAg}}{t_B\;V_{premix}}\right]}_{\substack{\uparrow\\ \textbf{Amount lost via}\\ \textbf{premixing}}}$$

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

Heats of formation are determined from measured heats of reaction.





Compares well to Fitzner, Kleppa 1991

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

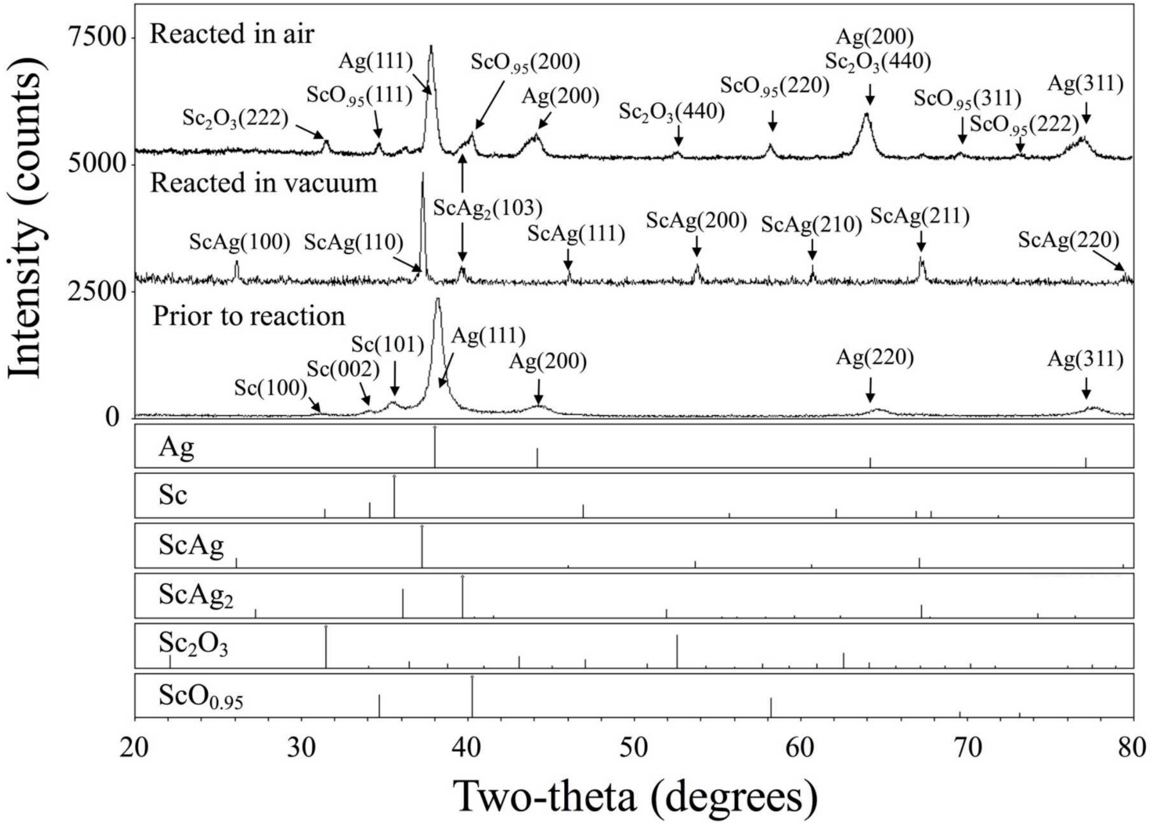
Measured Heat of Reaction

Heat of Formation

Amount lost via premixing

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

X-ray diffraction shows evidence of substantial oxidation of Sc/Ag when reacted in air.



Example has bilayer = 41.7 nm

A question remained: would oxidation occur promptly in a manner that influences wave stability in this system?

High speed videography of propagating waves is used to evaluate front morphology and speed.

Tested as freestanding foils

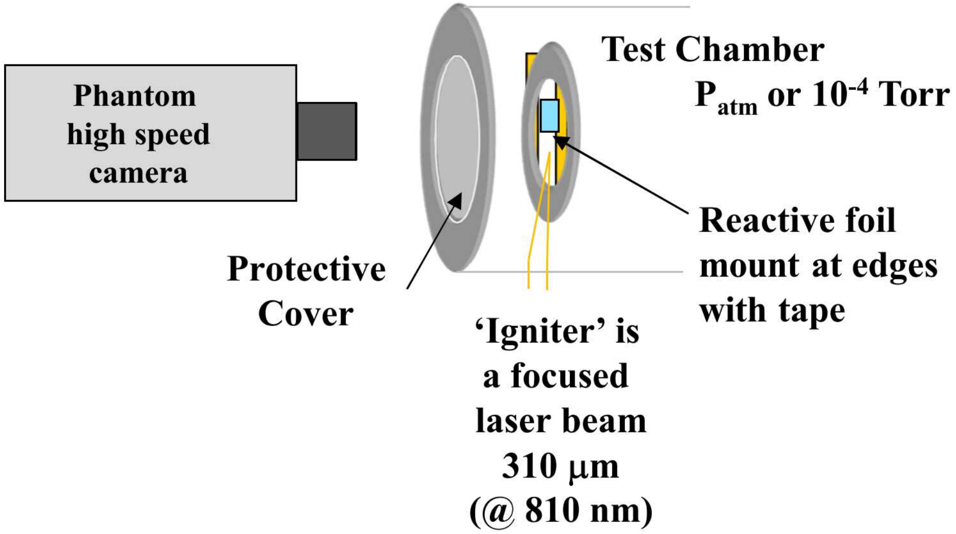
Point ignition in air

No preheat above room temperature

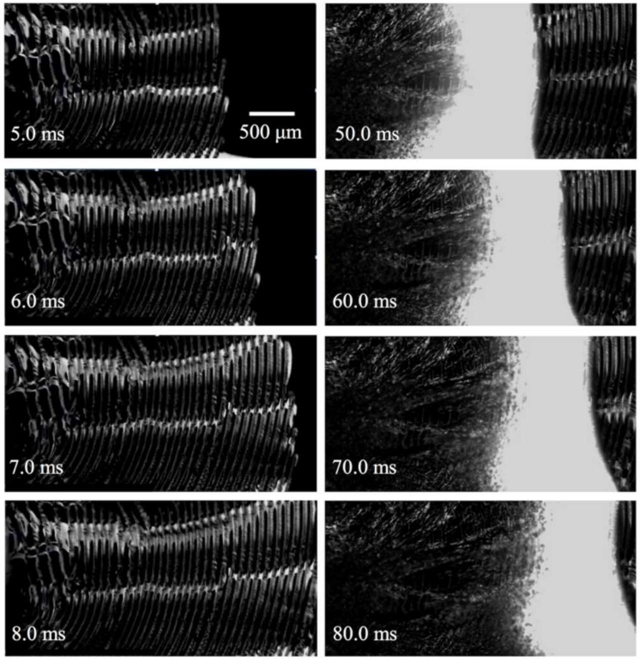
Evaluate front position outside ignition zone

Videographs are obtained in plan view

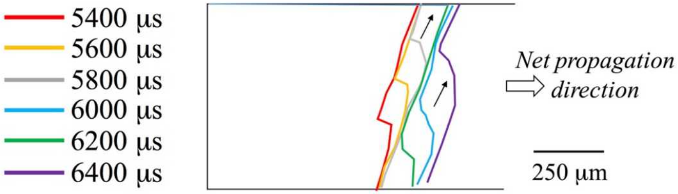
Position is plotted versus time to determine speed



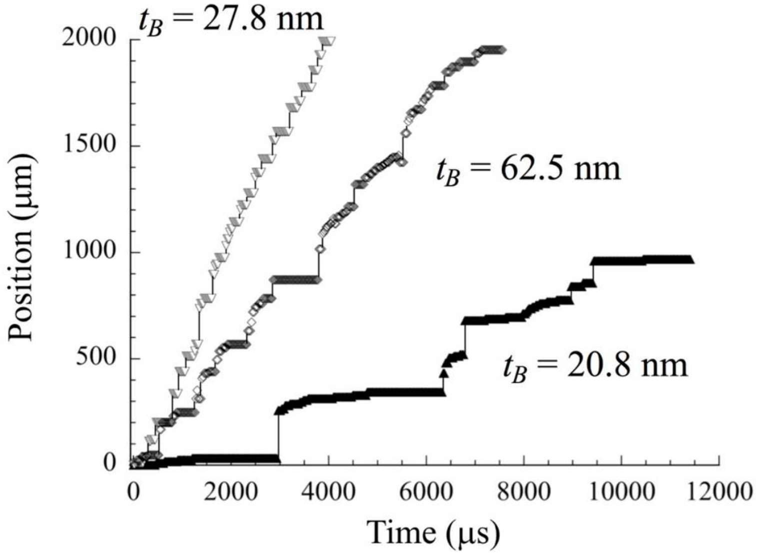
Propagating reactions in Sc/Ag multilayers ($20\ \text{nm} < t_B < 100\ \text{nm}$)



Intermetallic wave front positions



Plot of position versus time (3 multilayers)

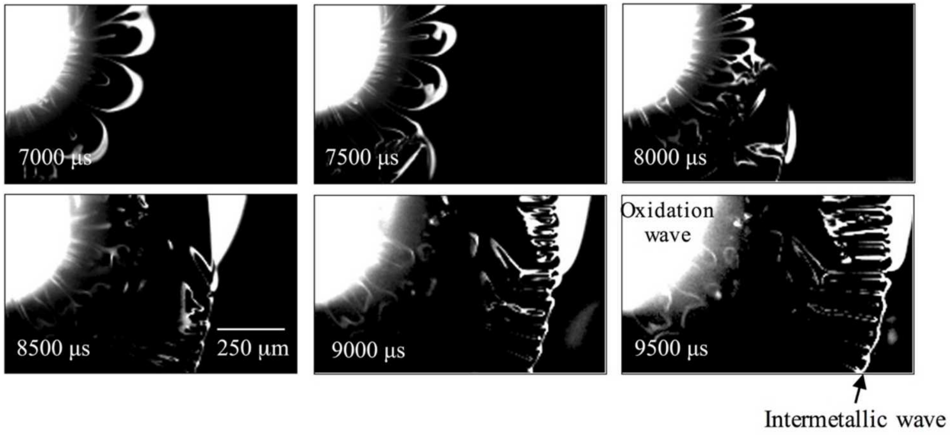


Total thickness of Sc/Ag = 5.0 µm

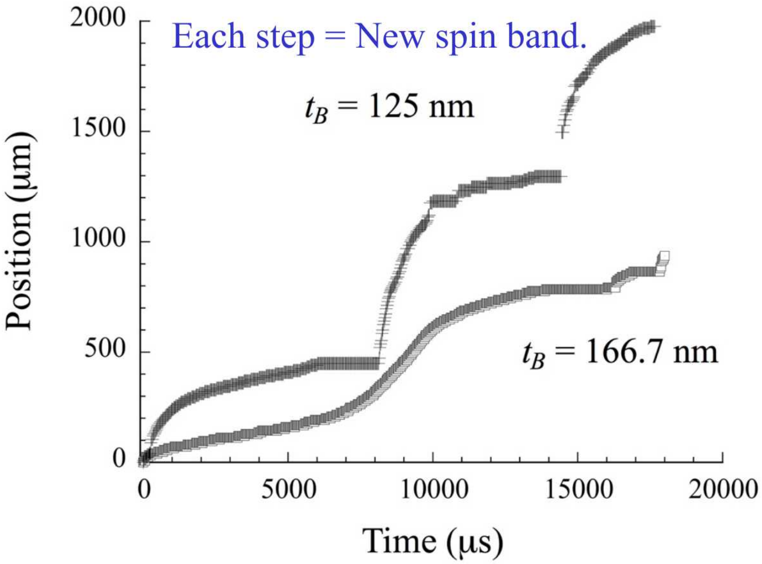
These particular multilayers exhibit self-propagating reactions in air.

Propagating reactions in Sc/Ag multilayers ($100\ nm < t_B < 200\ nm$)

Time lapse images in plan view



Plot of intermetallic wave front position versus time



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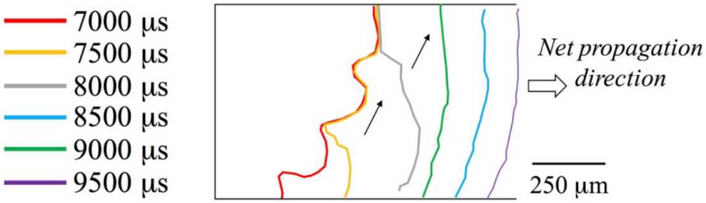
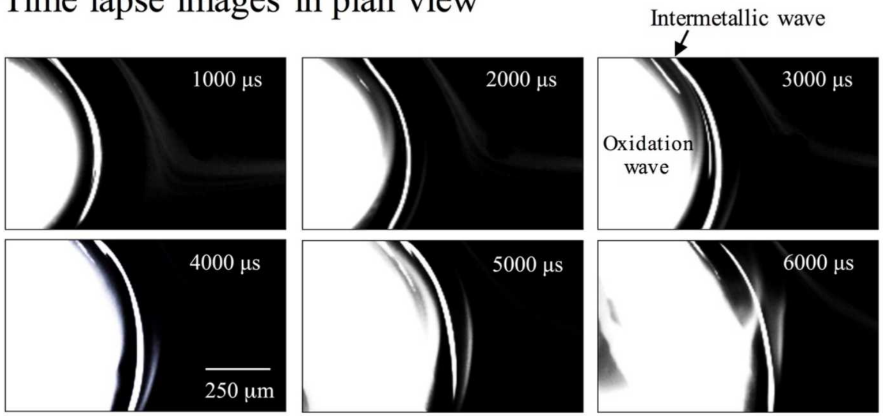
Intermetallic wave front positions



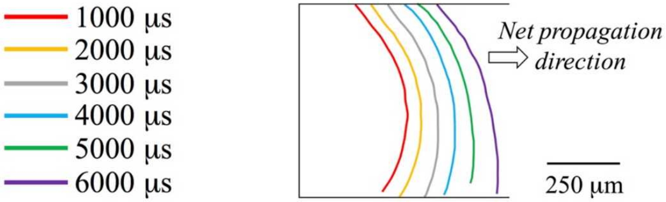
These particular multilayers do not exhibit self-propagating reactions in air.

Propagating reactions in Sc/Ag multilayers
($t_B > 200$ nm)

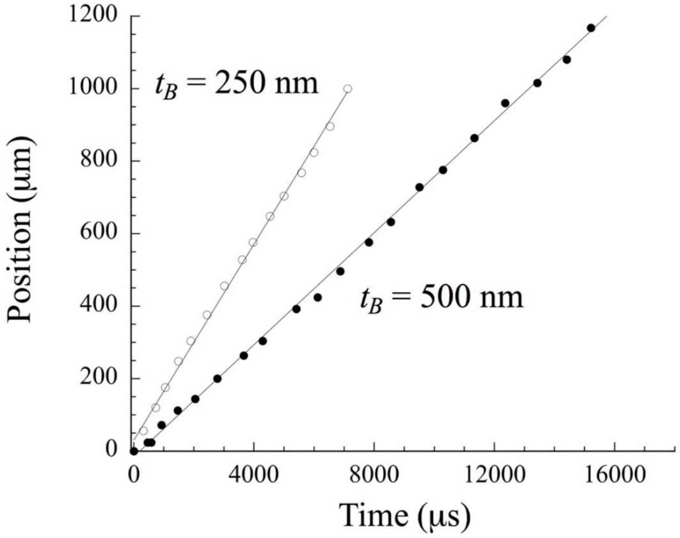
Time lapse images in plan view



Intermetallic wave front positions



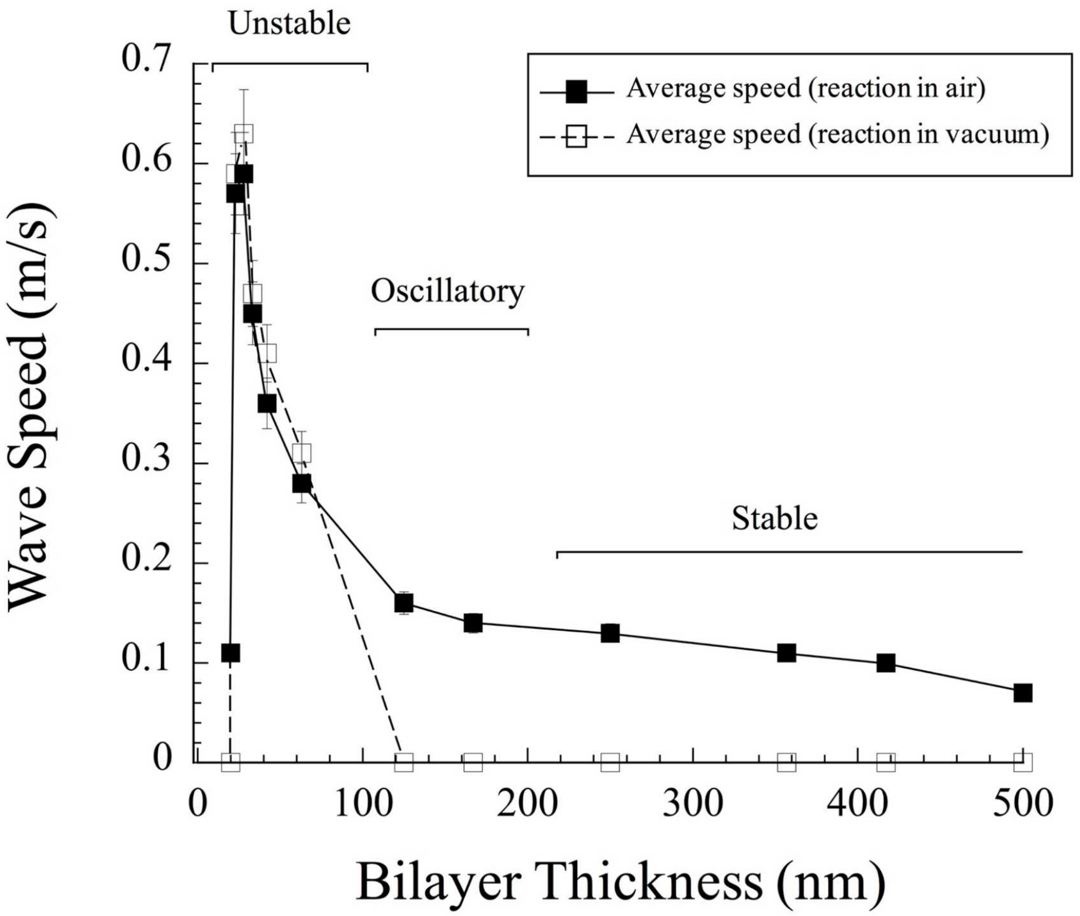
Plot of intermetallic wave front position versus time



Total thickness of Sc/Ag = 5.0 µm

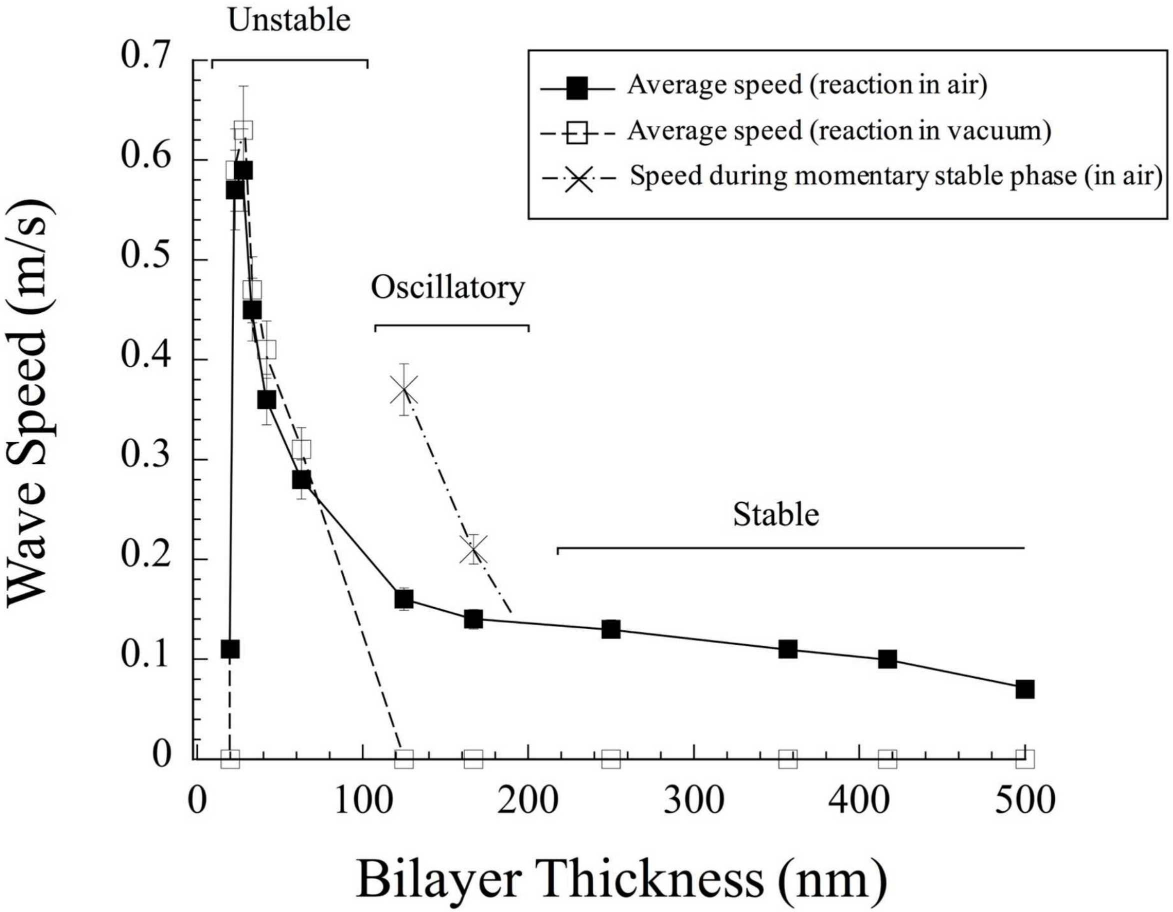
These particular multilayers do not exhibit self-propagating reactions in air.

Wavefront speed varies with bilayer thickness and gaseous environment.



- Zero speed means multilayer could not be ignited (multiple attempts).

Wavefront speed varies with bilayer thickness and gaseous environment.



- Zero speed means multilayer could not be ignited (multiple attempts).

Summary

- Gaseous environment affects the stability of propagating waves in this particular rare earth – transition metal system (via secondary reaction with air)

- Multilayers composed of Sc/Ag exhibit three unique behaviors when reacted in air

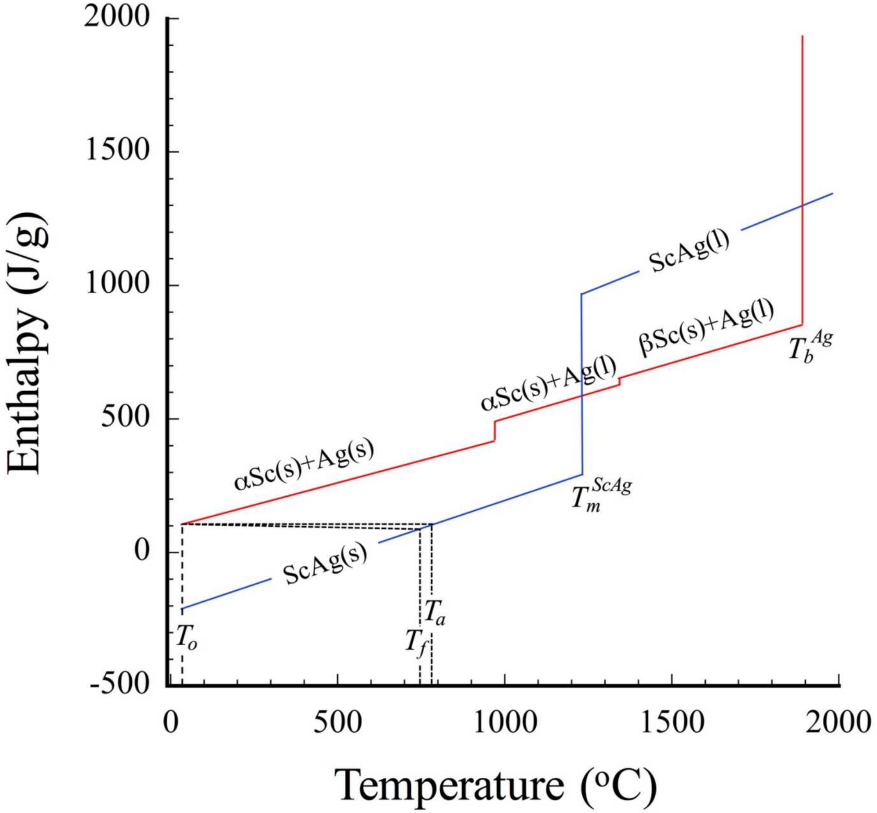
  - Unstable (2D spin) intermetallic reaction wave which outpaces oxidation wave (when $t_B < 100$ nm)

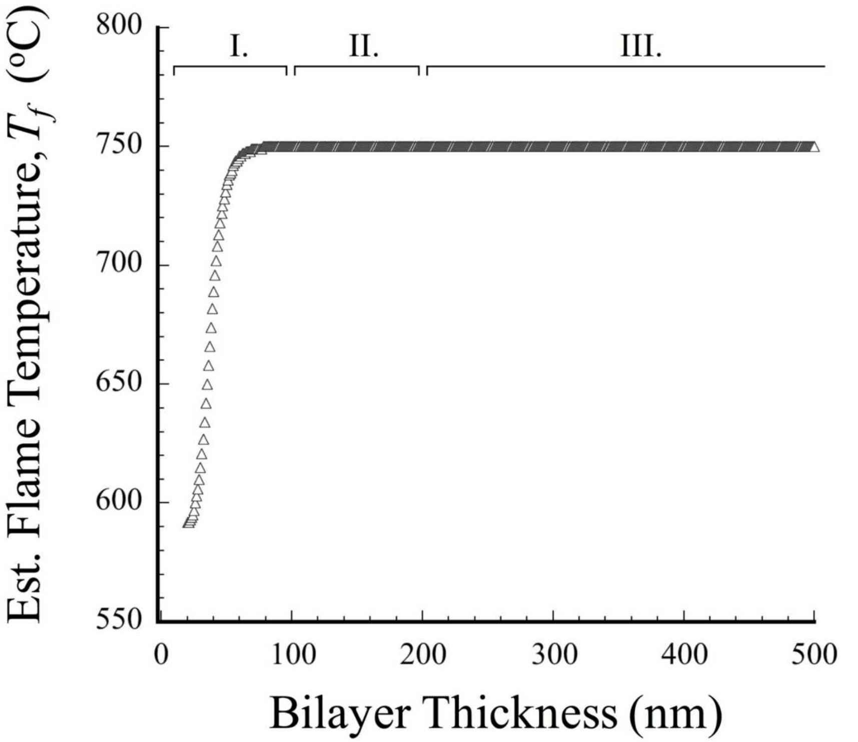
  - Oscillatory stable + unstable reaction wave (when $100 \text{ nm} < t_B < 200$ nm)

  - Stable reaction wave when oxidation occurs promptly (when $t_B > 200$ nm)

EXTRA SLIDES

Enthalpy-Temperature diagram for equimolar Sc + Ag-> ScAg and predicted flame temperatures (T_f)





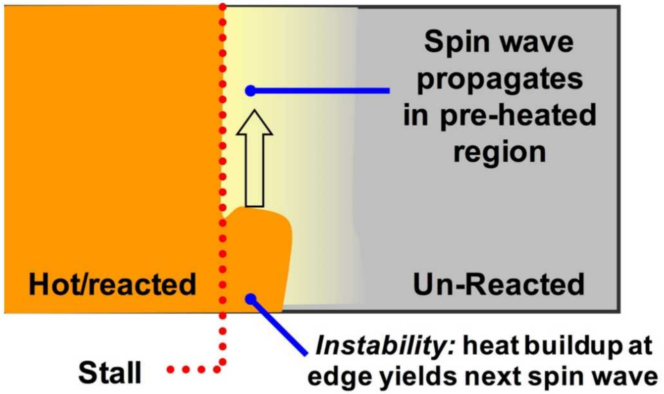
Compare with key temperatures:

T_{melt} (Ag): 62°C

T_{melt} (Sc): 1230°C

T_{melt} (ScAg): 1155°C

Enthalpy-temperature diagram for equimolar Sc + Ag-> ScAg with preheating



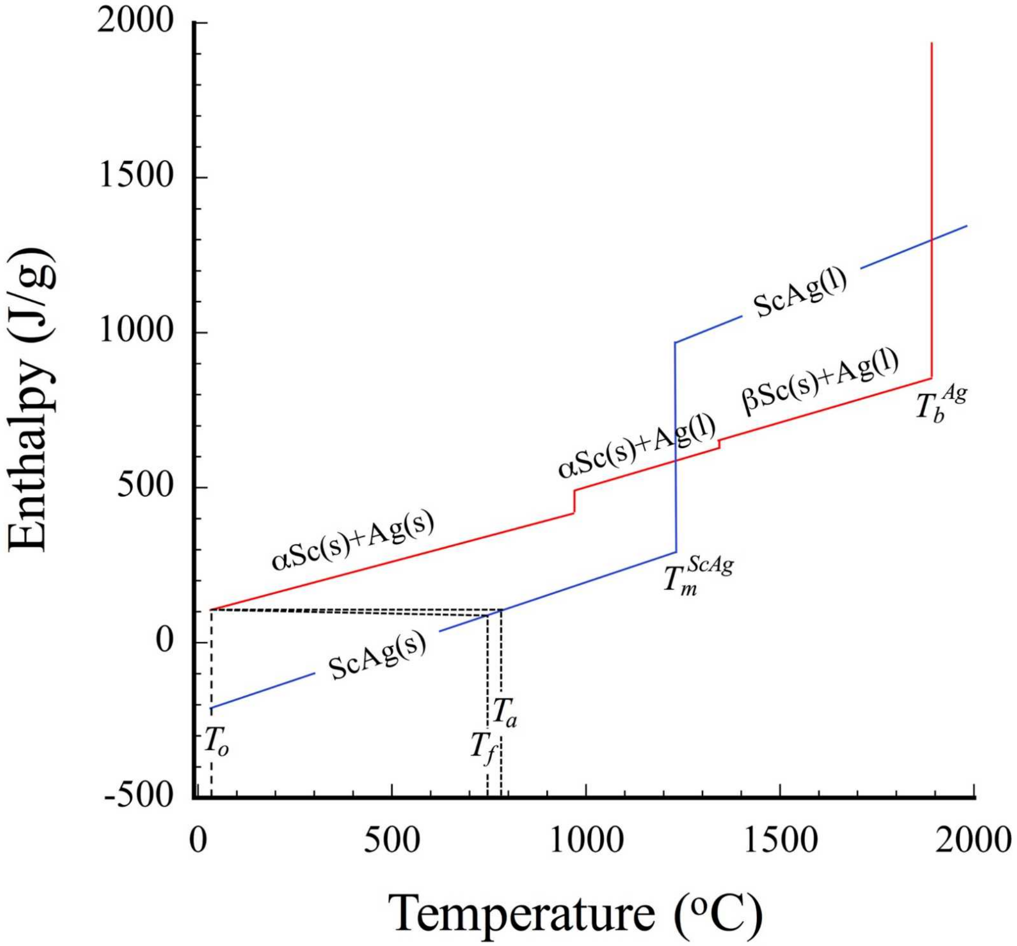
Spin wave propagates in pre-heated region

Hot/reacted

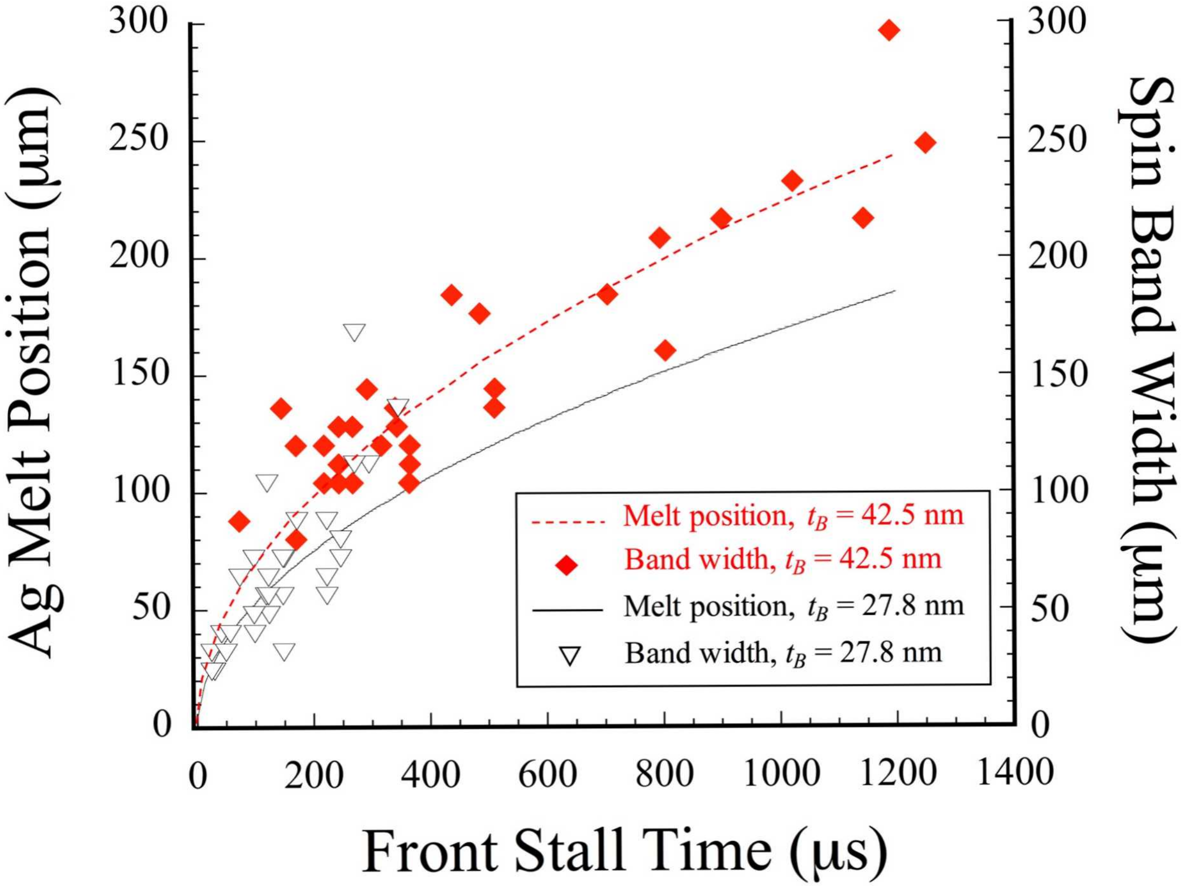
Un-Reacted

Stall

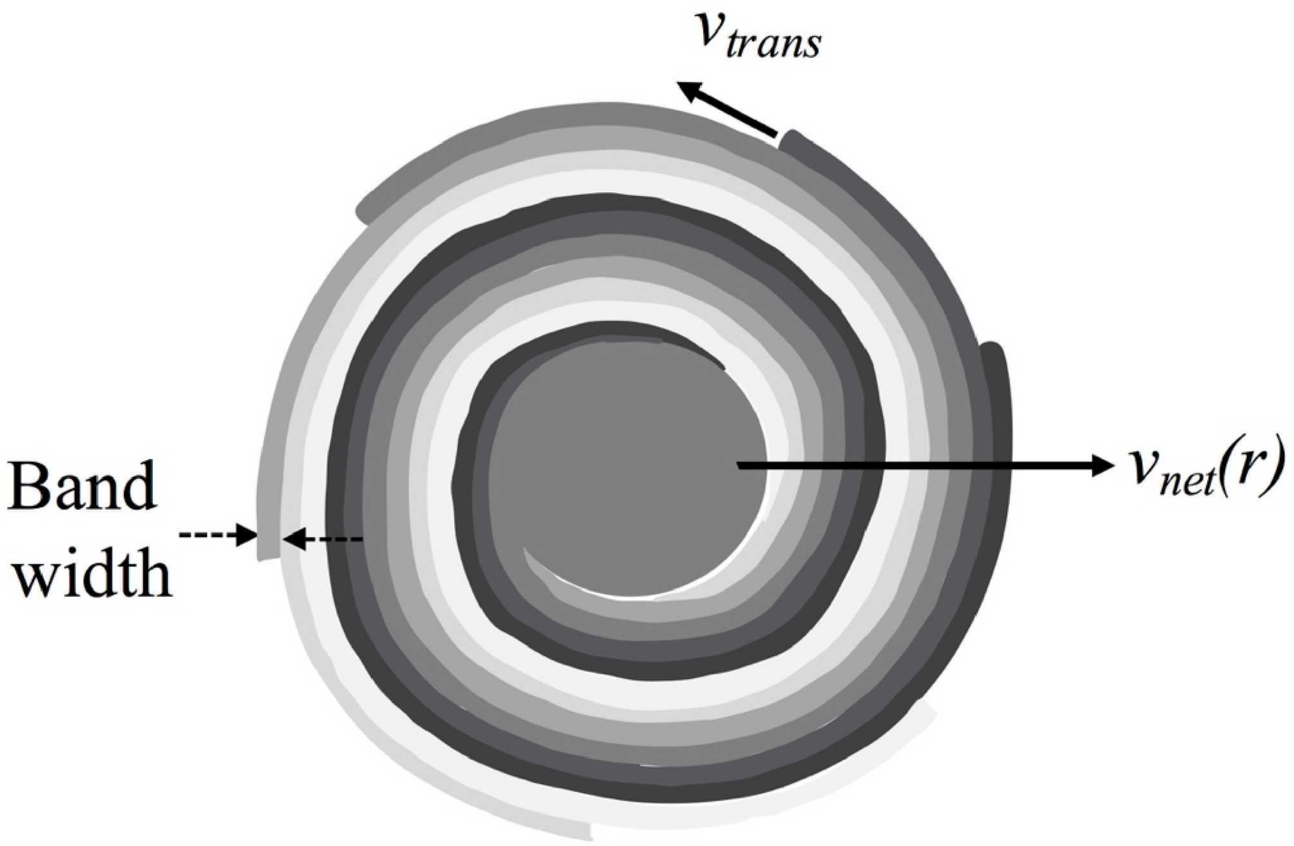
***Instability:* heat buildup at edge yields next spin wave**



Enthalpy-temperature diagram for equimolar Sc + Ag-> ScAg with preheating

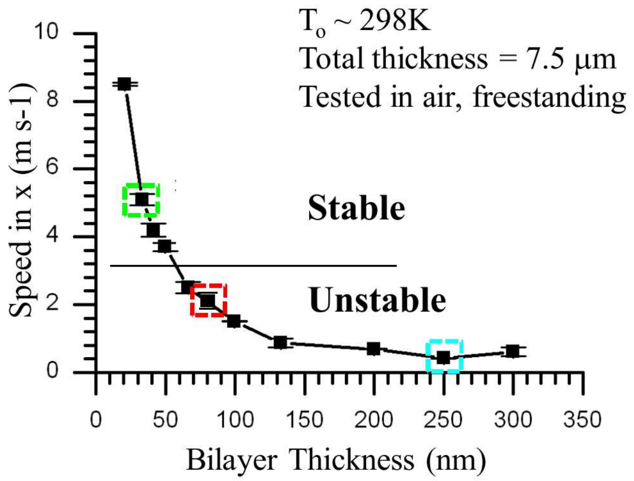


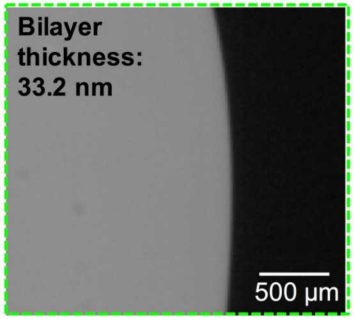
2D (spin) instability nomenclature

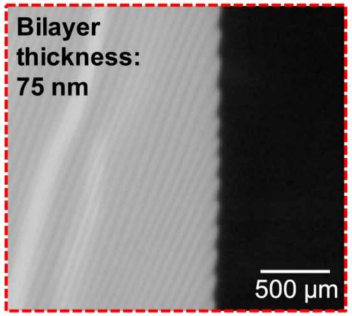


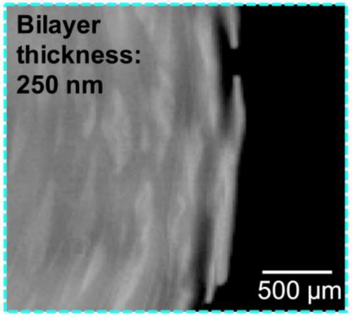
A few reactive multilayers ignite and undergo unstable propagating reactions.

Example: Co/Al



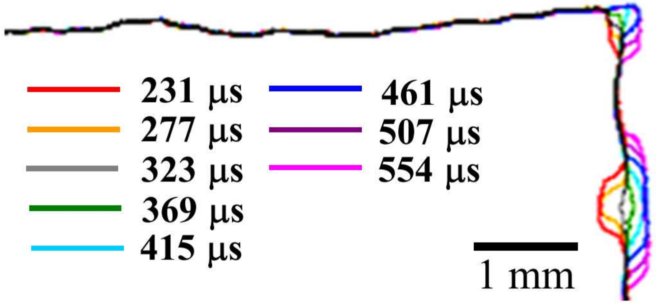


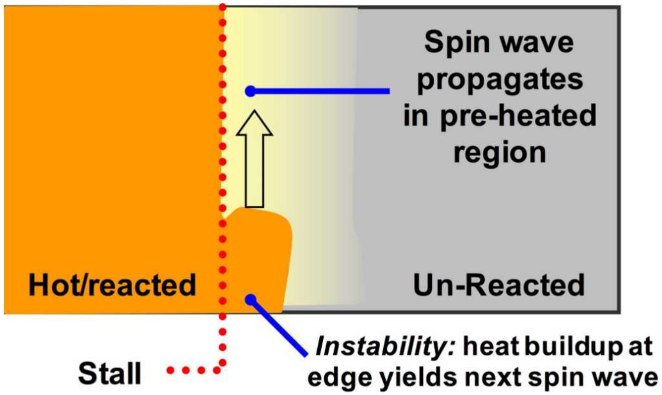




Unstable (2D) reactions exhibit:

- Rough reaction front morphology
- Momentarily-stalled fronts
- Non-uniform velocity





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

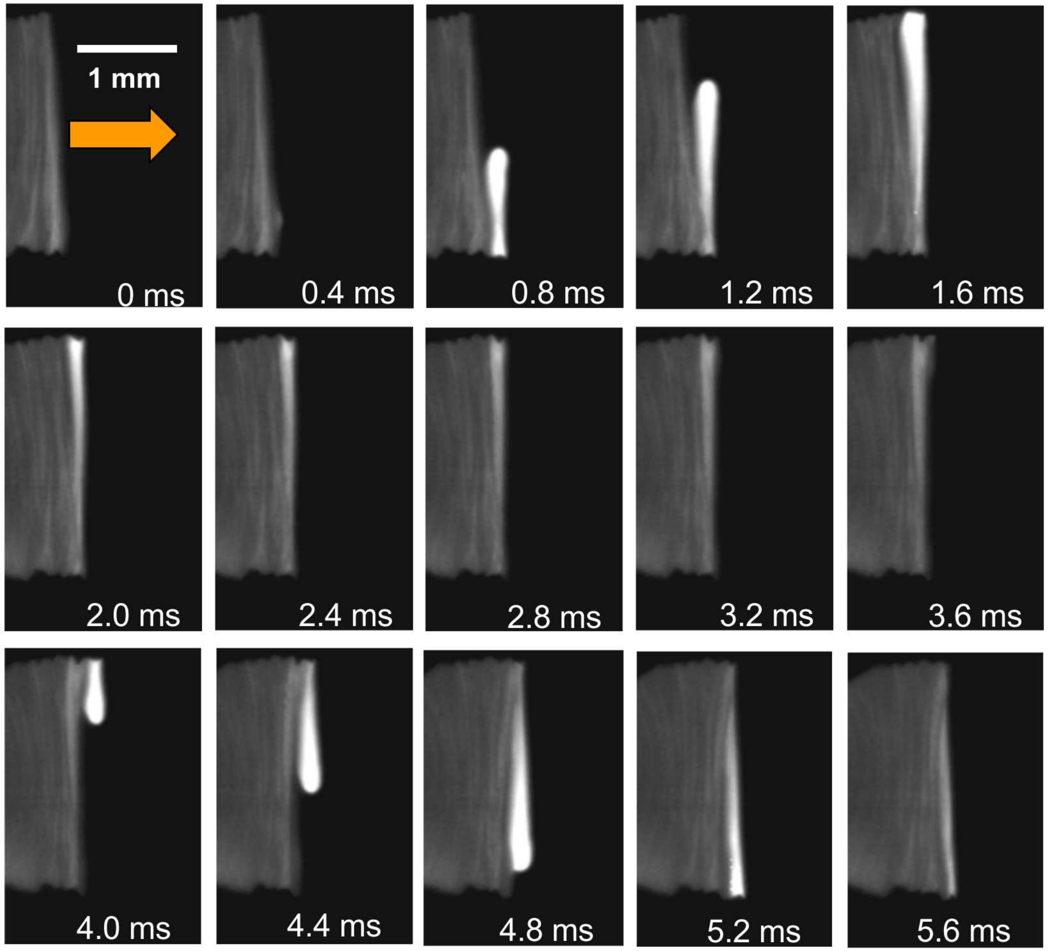
Transverse reaction bands nucleate at foil edges and, on occasion, at the point of intersection of colliding bands.

Transverse band speed exceeds average propagation speed.

Band widths are similar to those exhibited by Co/Al and other systems.

Plan view images

Nickel / Titanium



Bilayer thickness = 473 nm; Total thickness = ~ 5.0 mm
Ti capped (two sides); P = 300 mTorr

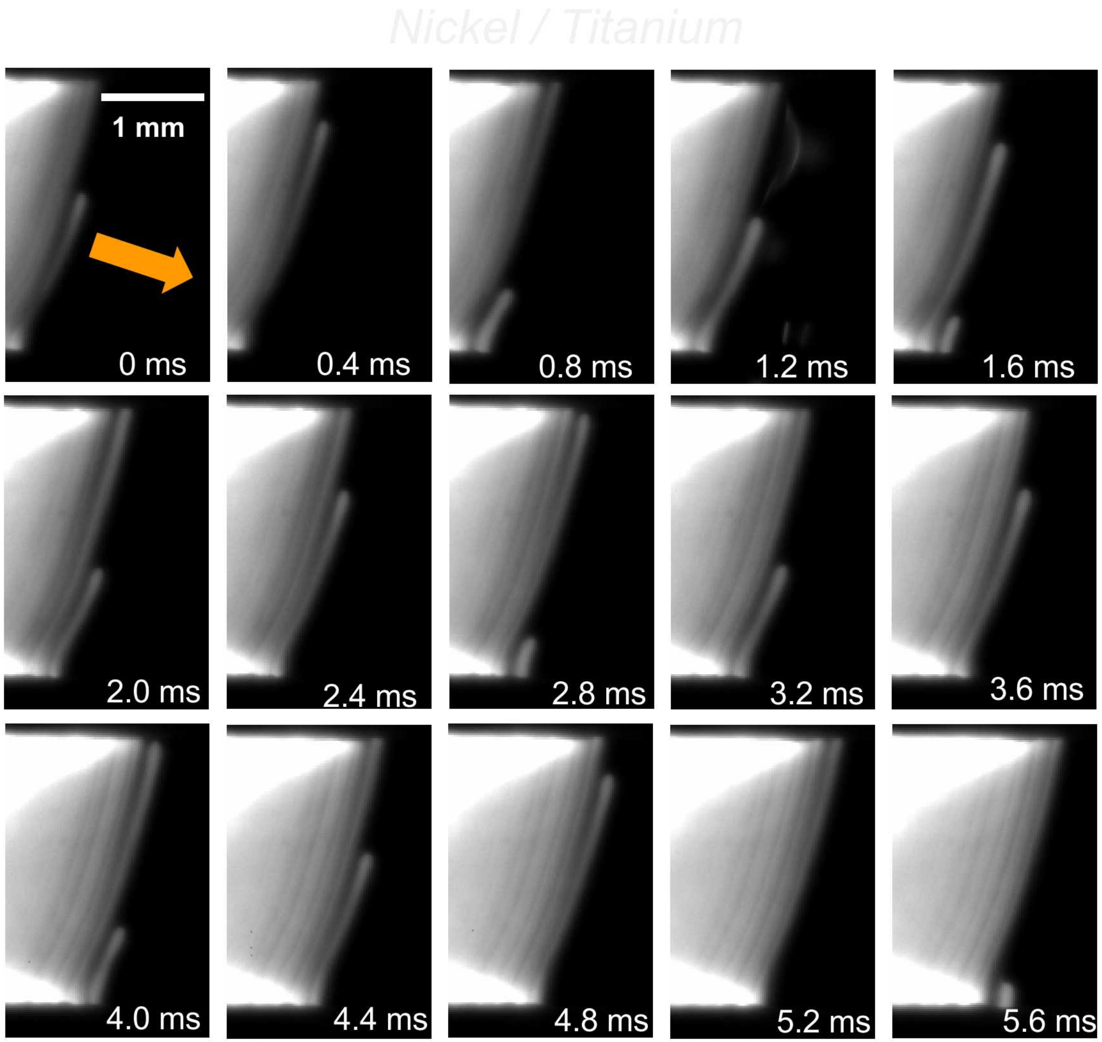
Ni/Ti exhibits a 2-D reaction front instability and undergoes secondary combustion when reacted in air.

- Similar to reactions in vacuum, reaction bands propagate transversely.

- A second reaction ‘wave appears behind the intermetallic reaction front.

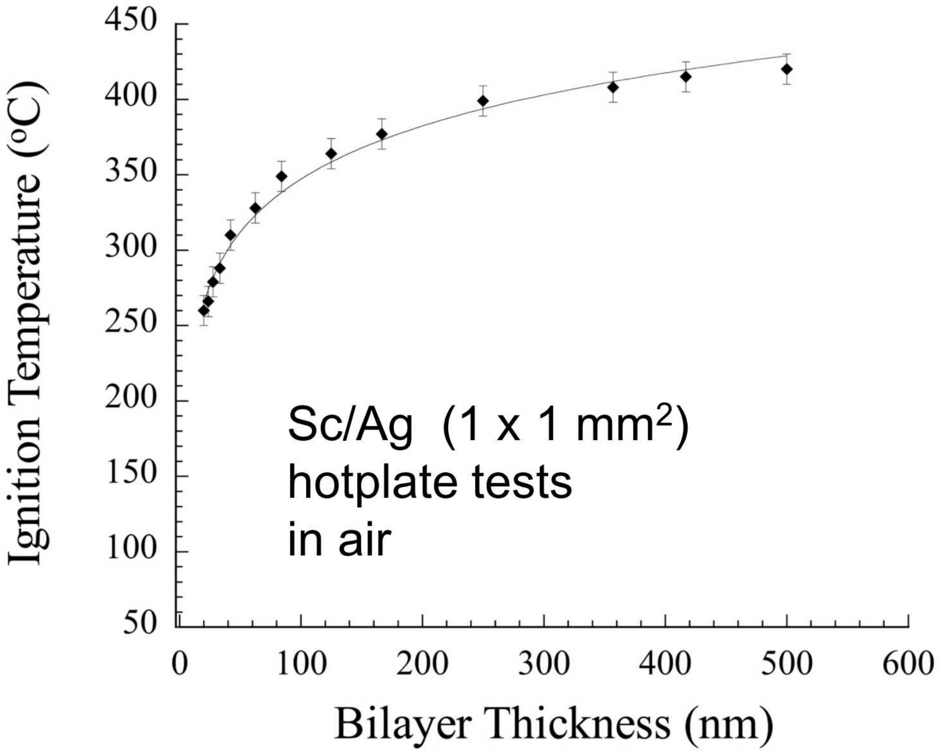
- Second reaction front is faster along the edges of foils.

Plan view images

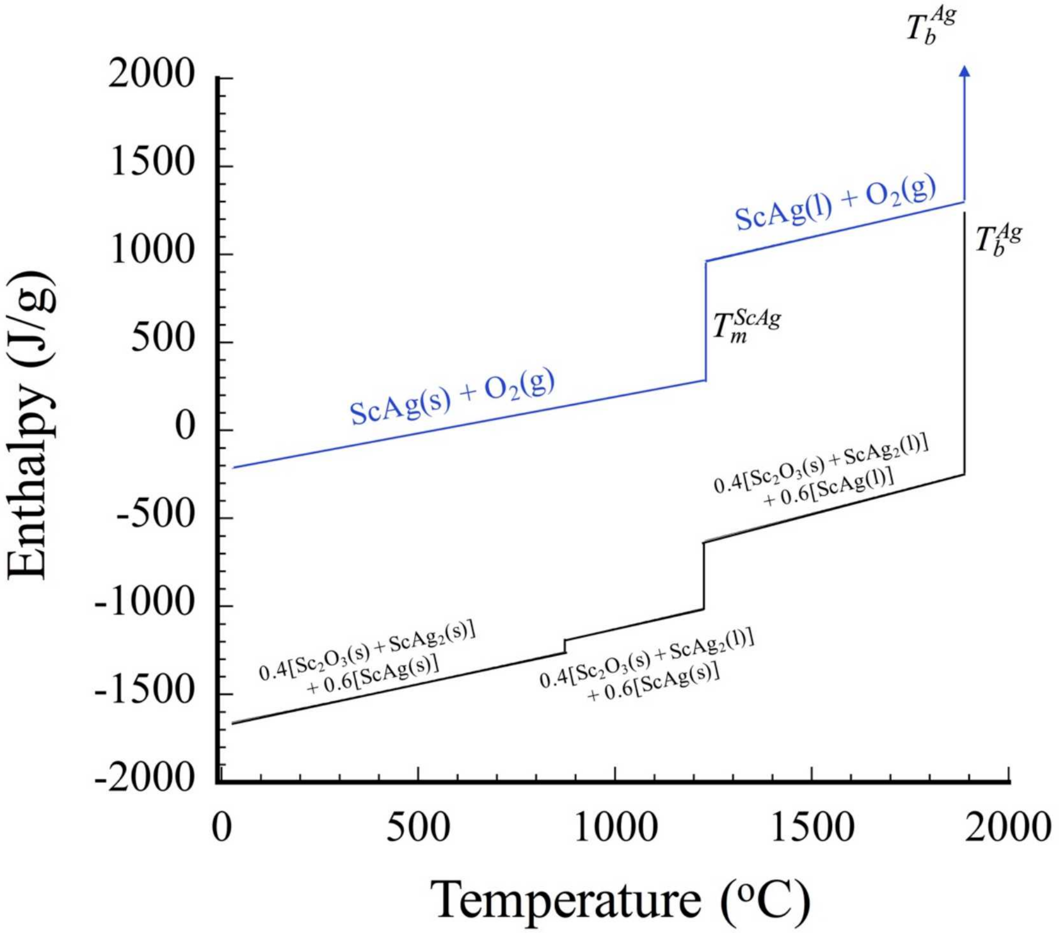


Bilayer thickness = 473 nm; Total thickness = ~ 5.0 μm
Ti capped (two sides); P = 670 mTorr air

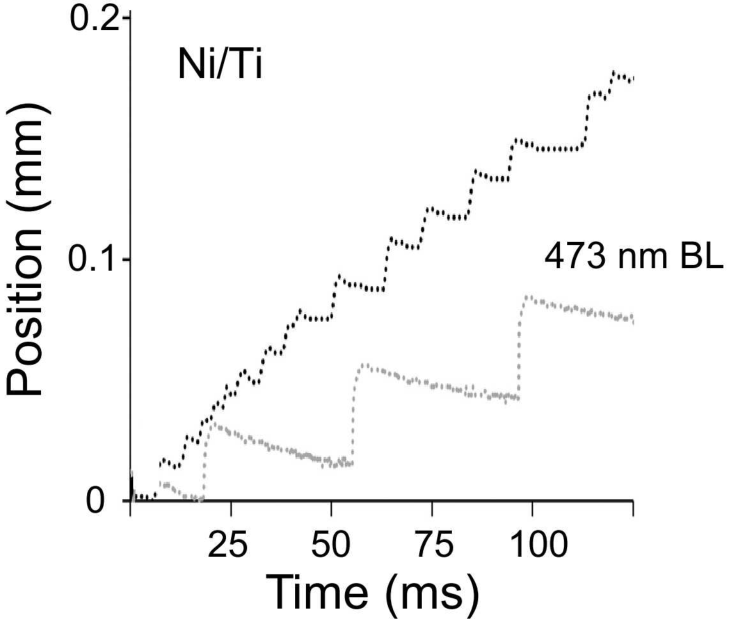
Reactive Sc/Ag multilayers having nanometer periods exhibit low ignition temperatures that are less than the T_{melt} of its constituents.



Enthalpy-temperature diagram for equimolar Sc + Ag-> ScAg



D.P. Adams, 4/19



Ni/Ti
473 nm BL
Position (mm)
0.2
0.1
0
25
50
75
100
Time (ms)