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Effects of Environment on the Self-Propagating High Temperature Synthesis of Reactive Ni/Ti Multilayers

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

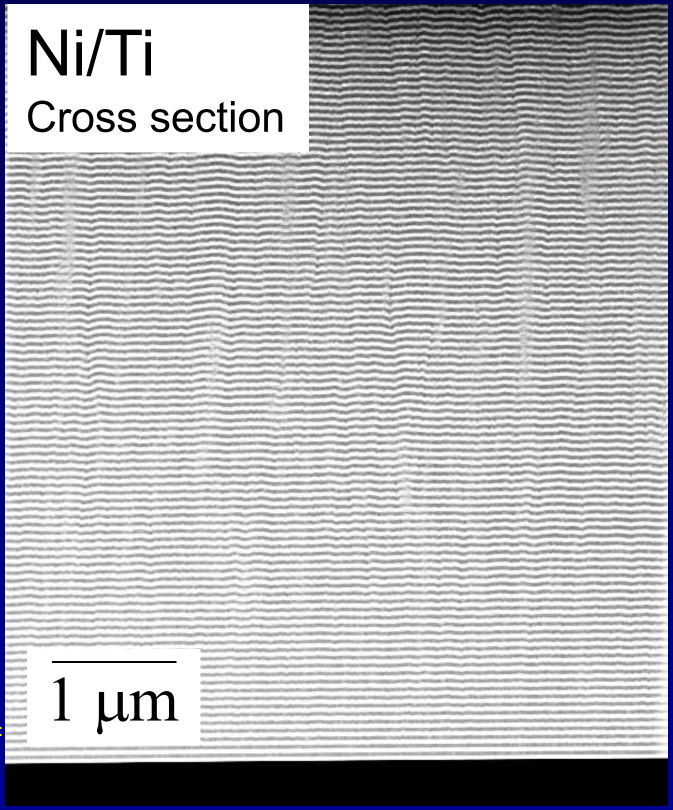
Appropriately-designed reactive multilayers exhibit self-propagating reactions.

- Heterostructures that consist of two or more reactants that, when mixed, generates heat

  ✓ $M_1 + M_2 \Rightarrow M_1M_2$

  $M_1 + M_2O \Rightarrow M_1O + M_2$

- 10's to 1000's of individual layers
- Typical design employs single periodicity
- Total thickness 0.15 -150 μm
- Exhibit Self-propagating Synthesis (SHS)
- Non-explosive and typically no gas
- Sputter deposited in 10^{-8} Torr base pressure system



Bilayer

Early references (vapor deposited reactive multilayers)

J. Prentice US Patent 4,158,084 (1979)
J. Floro J. Vac. Sci. Tech. A (1986).
D. Makowiecki US Patent 5,381,944 (1995).
Barbee and Weihs US Patent 5,547,715 (1996).

Nickel / titanium is of interest for its intriguing mechanical properties.

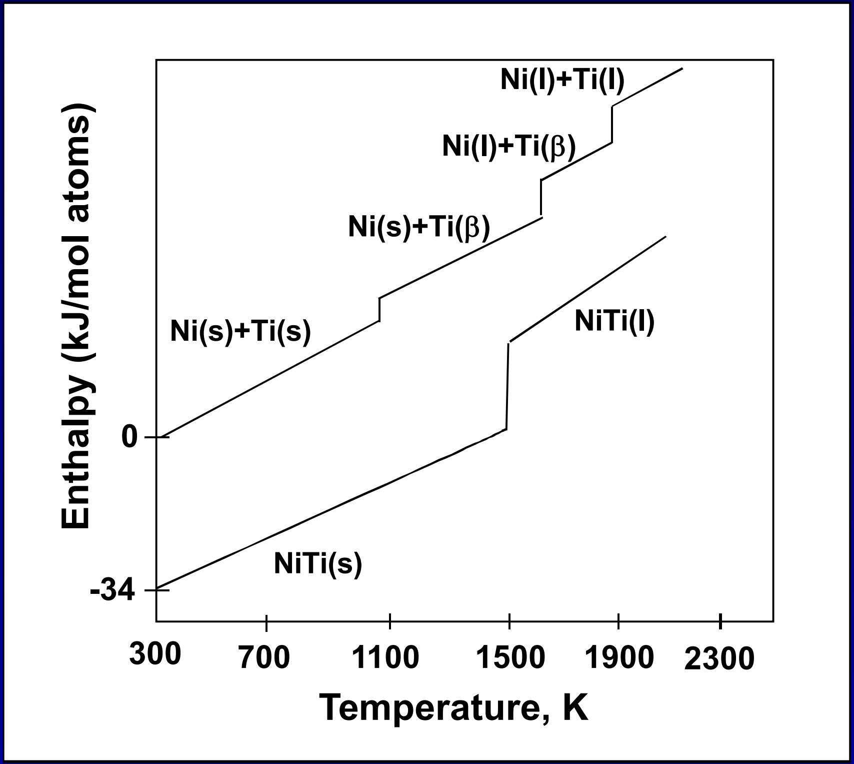
Applications:

- Shape memory for near equiatomic NiTi
- Superelastic, 8% recoverable strain T > T^{f}_{aus}

Reports on compacted powders

- Exhibit SHS and thermal explosion when particle size ~ 10 μm
- Require pre-heating (above room temperature) for SHS
- T_{ig} ~ 910 ± 10C for 10 μm particle size
  Yi, Moore Scr. Met.1988
- Reported that the oxidation of Ti subsequently triggered SHS of Ni-Ti
  Moore, Feng Prog. Mat. Sci. 1995, p. 286

E-T diagram from Moore et al. with updated properties



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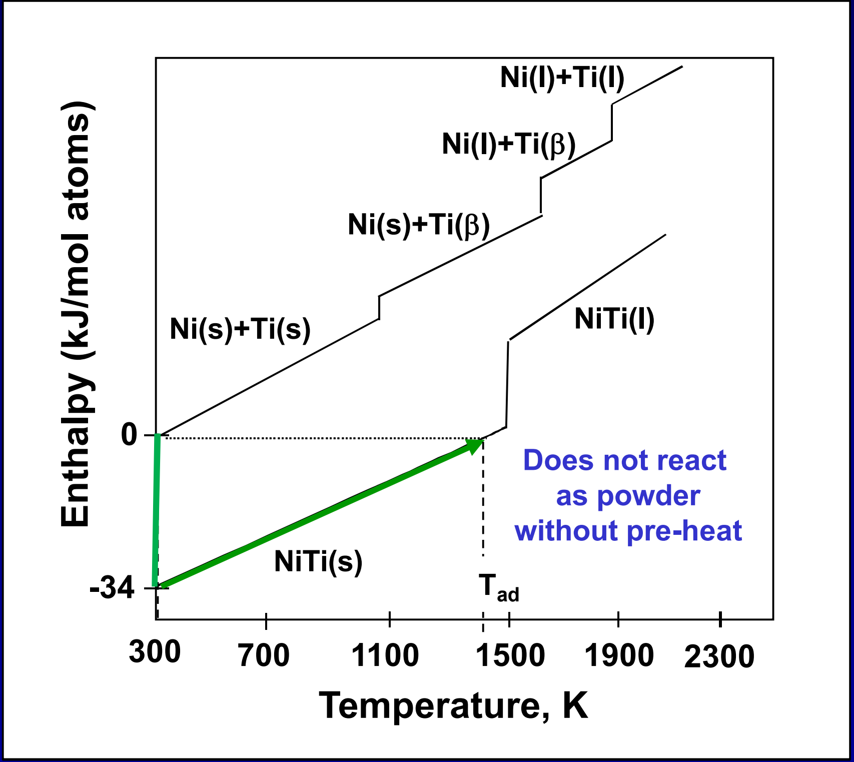

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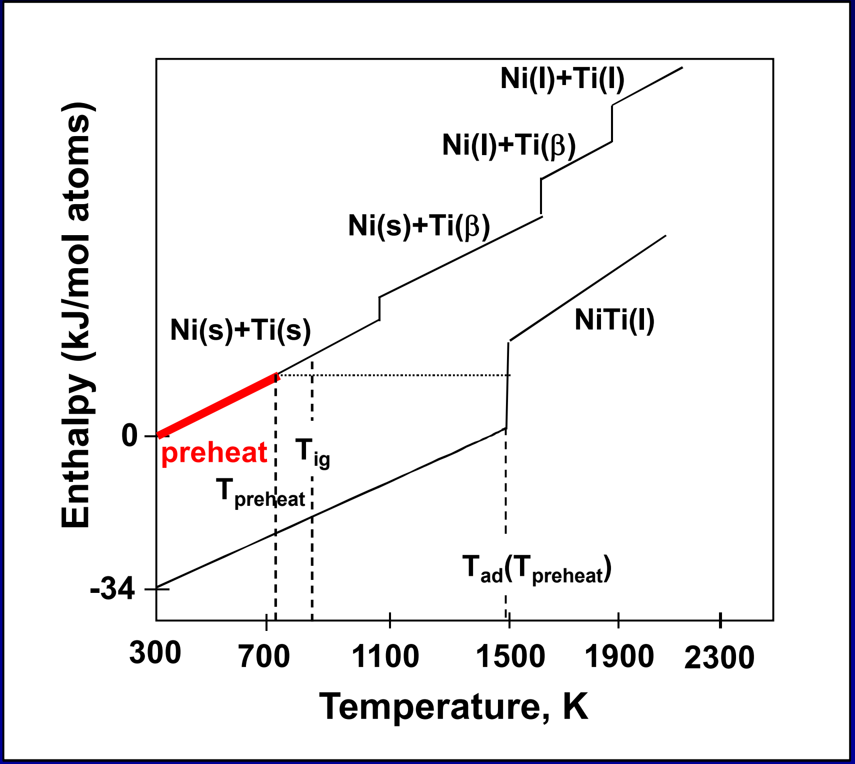

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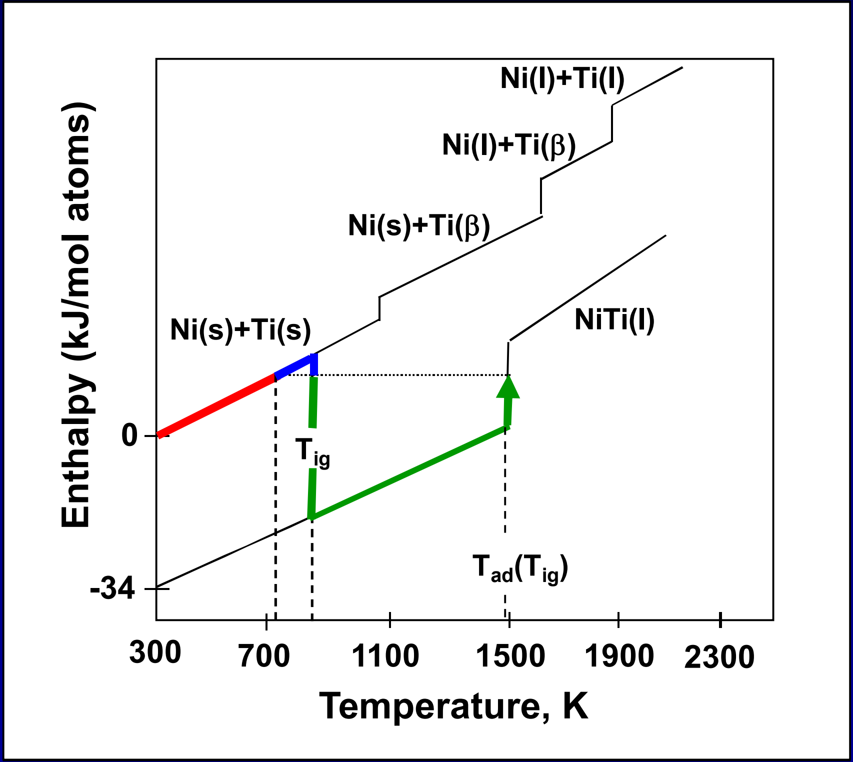

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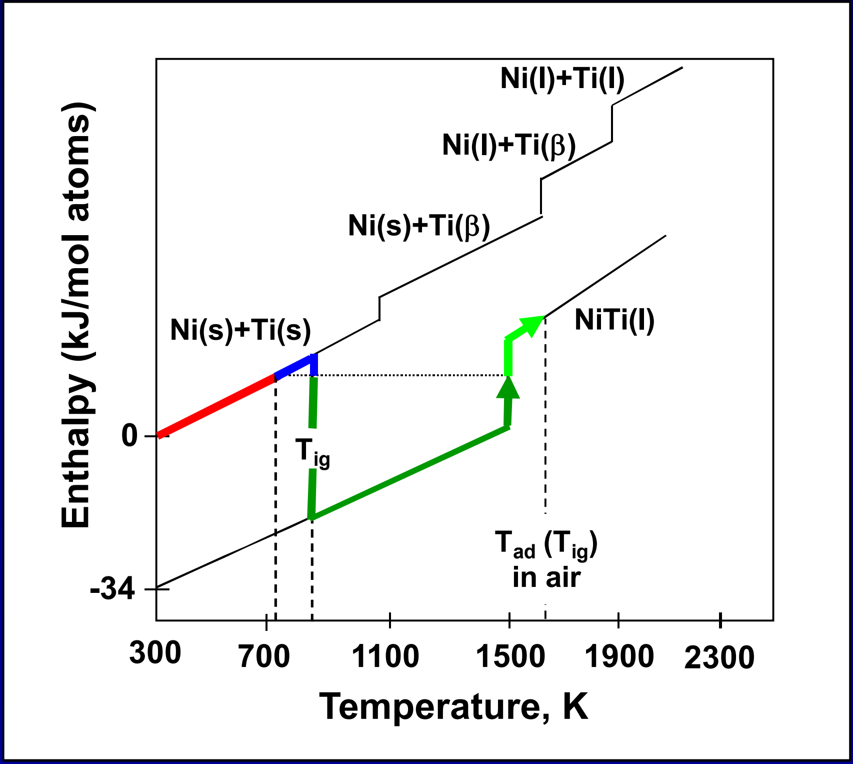

ΔH_o (rutile TiO_2) = -912 kJ/mol

ΔH_o (TiO) = -515 kJ/mol

ΔH_o (NiO) = -239 kJ/mol

Tasks of this research

High level: Determine if vapor-deposited, equiatomic Ni/Ti multilayers exhibit self-propagating reactions with no pre-heating (above room temperature)

Focus: examine how the surrounding gaseous environment affects

- propagation speed
- reaction mode
- final phase

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)

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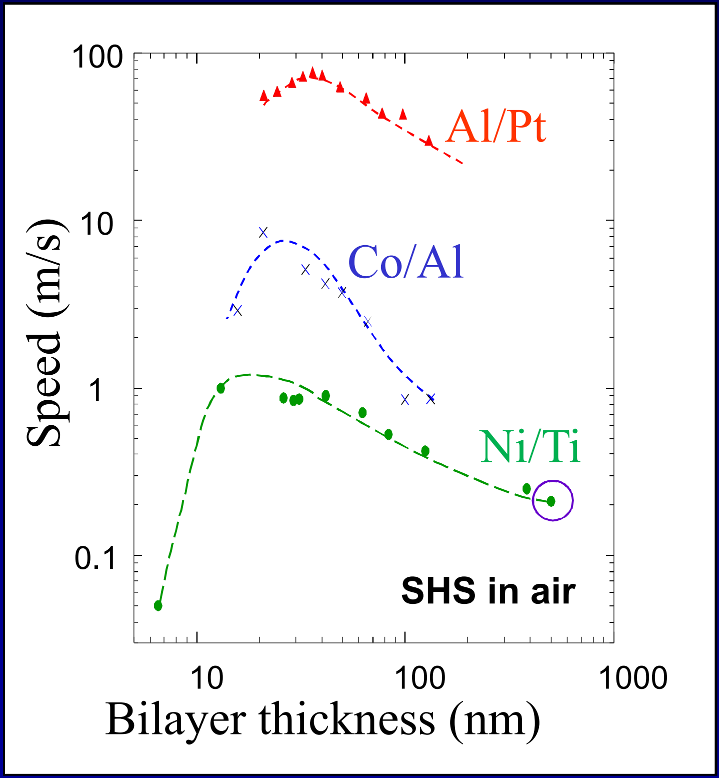
- Maximum propagation speed of ~ 1 m/s for 5 μm thick foils (equiatomic).



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

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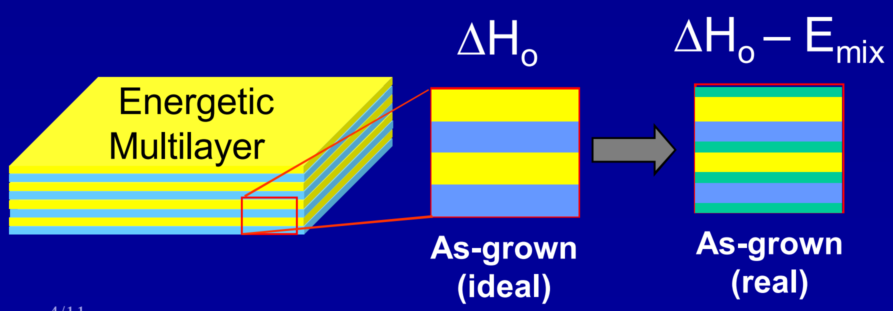
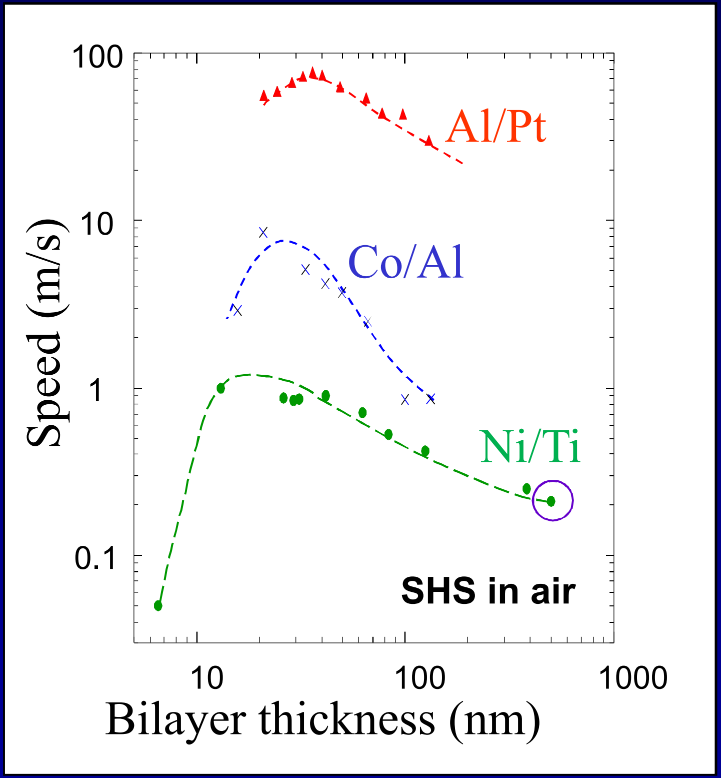
- Decreased speed at small bilayer thickness due to premixed reactants.

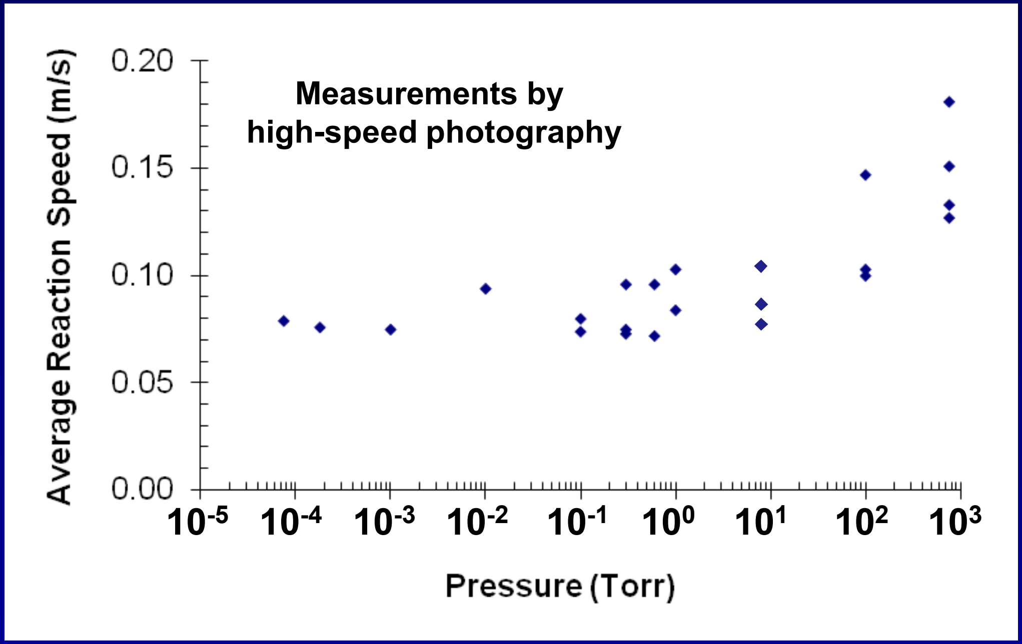




Y. Picard, J. Mcdonald, S.M. Yalisove, D.P. Adams, Appl. Phys. Lett. 93 (2008).

Nickel / titanium foils exhibit SHS in vacuum.

- Average propagation speed of Ni/Ti is affected by reaction environment.
- Maximum average propagation speed at atmospheric pressure (for our tests).
- Average propagation speed appears to be constant for pressure < 1 Torr.



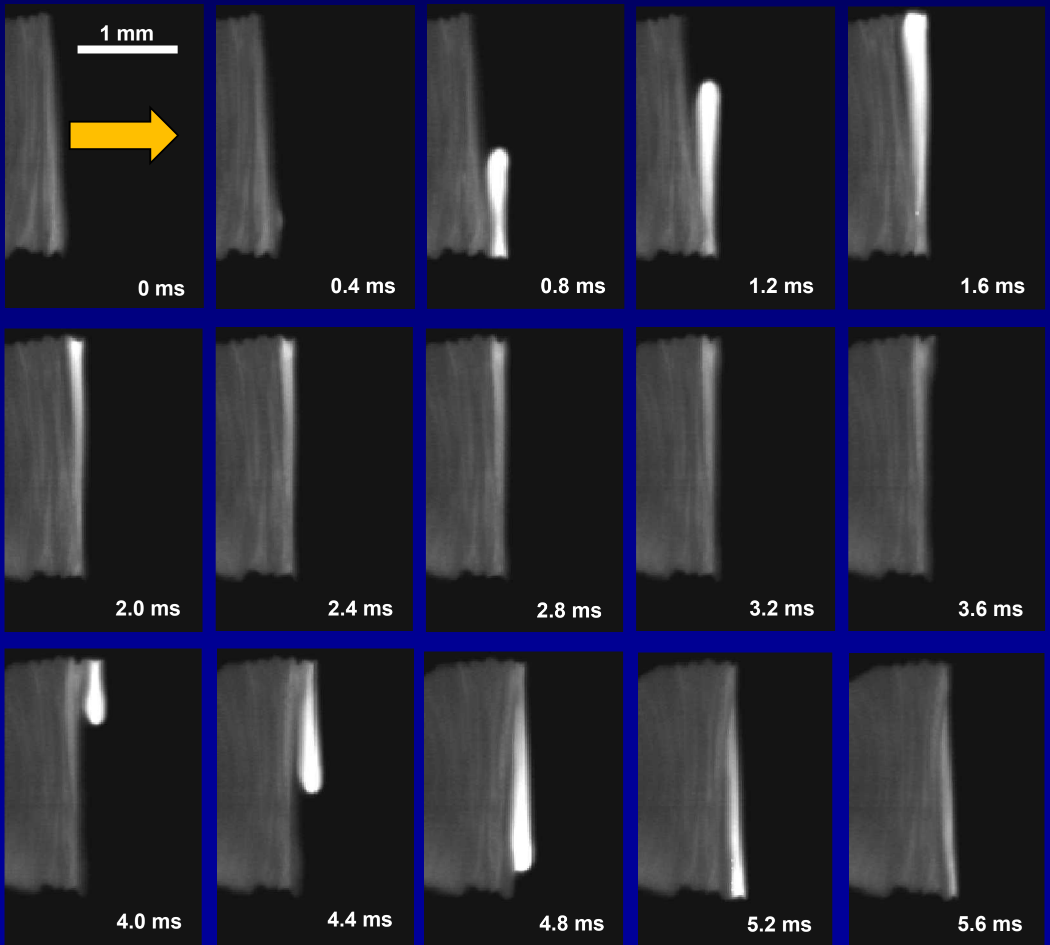
Single foil design evaluated (above):
Bilayer thickness = 4730 Å
Total thickness = ~ 5.0 μm
Ti capped (two sides)

High-speed photography reveals that Ni/Ti exhibits an unstable propagation mode (when tested in vacuo)

Ni/Ti foil (equiatomic)

Bilayer thickness = 4730 Å; Total thickness = ~ 5.0 μm

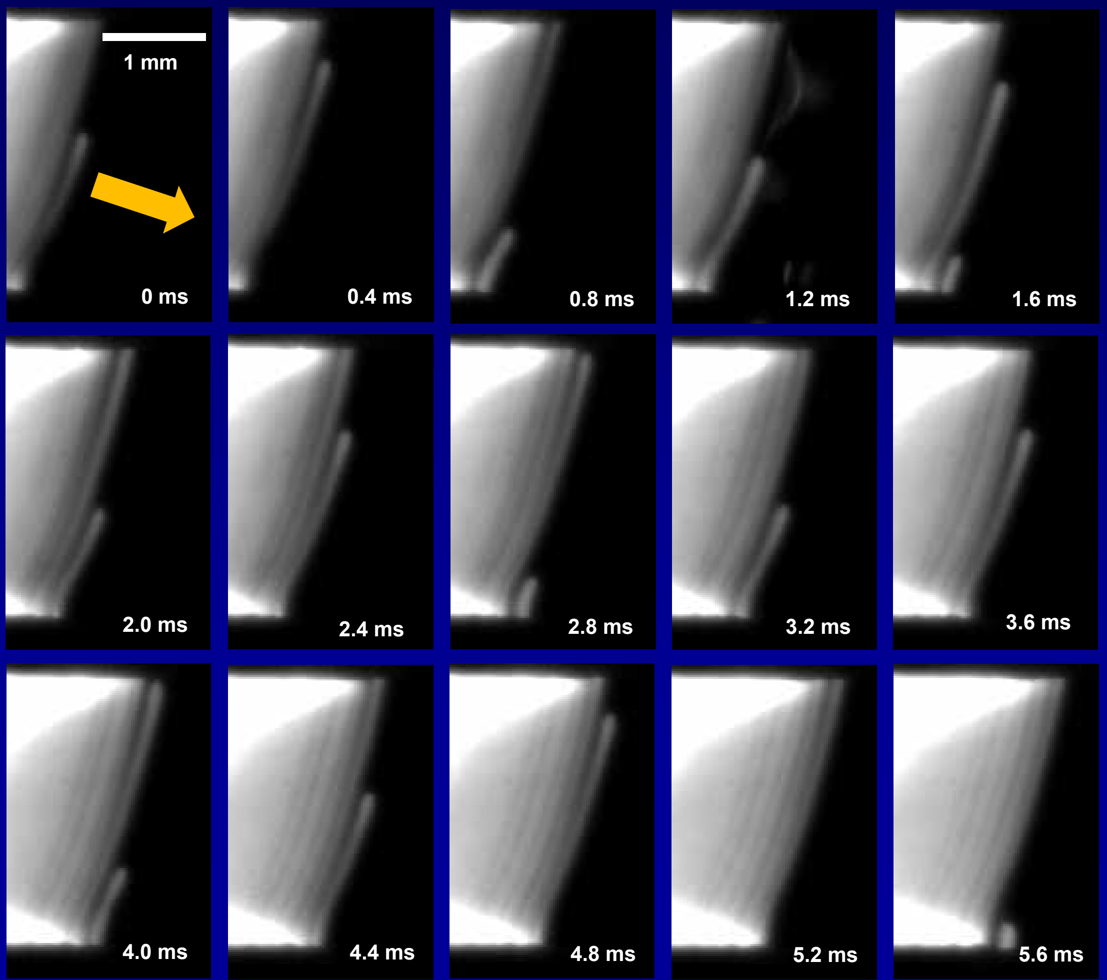
Ti capped (two sides); P = 300 mTorr



- Reactions occur by the propagation of transverse reaction bands (this resembles spin modes in cylindrical compacted powder samples).
- Transverse reaction bands nucleate at foil edges and, occasionally, via the ‘collision’ of bands.
- Transverse band speed exceeds average propagation speed.

High-speed photography shows that Ni/Ti exhibits unstable reaction modes when reacted in air

Ni/Ti foil (equiatomic)
Bilayer thickness = 4730 Å; Total thickness = ~ 5.0 μm
Ti capped (two sides); P = 670 Torr



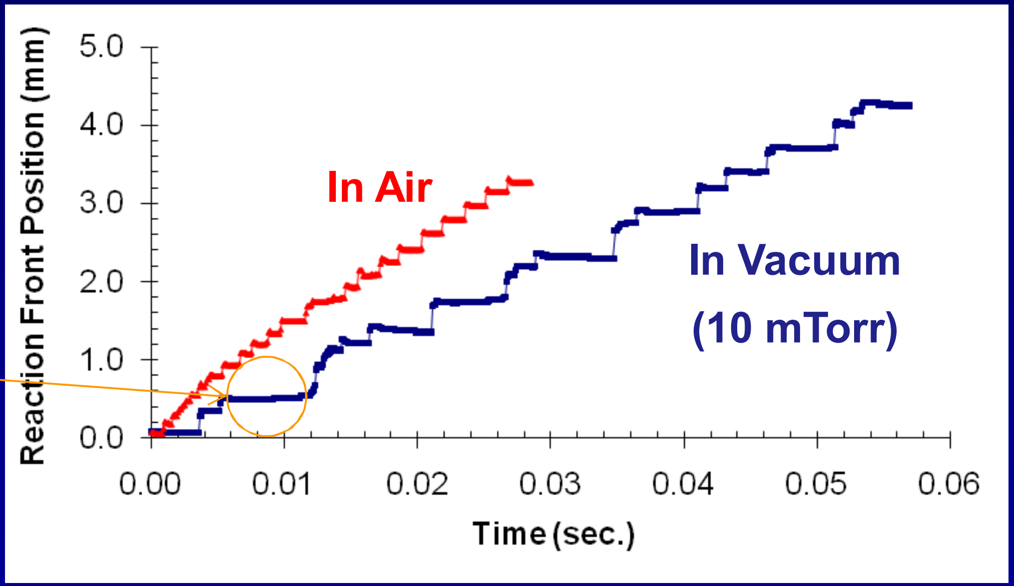
- Similar to reactions in vacuum, reaction bands propagate transversely.
- A second reaction ‘wave’ appears behind the intermetallic reaction front.
- Frequency of transverse bands is increased when air is present.

Plan view images

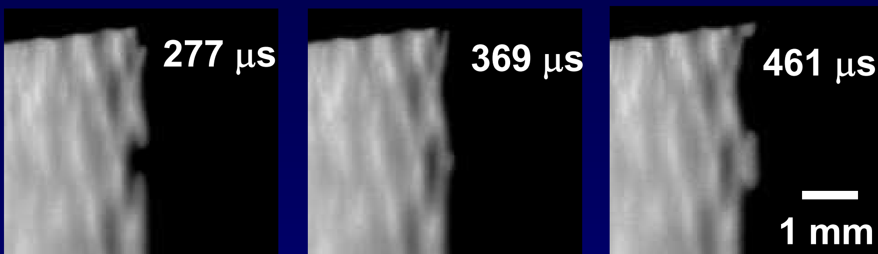
High-speed photography shows how air increases the average propagation speed of Ni/Ti

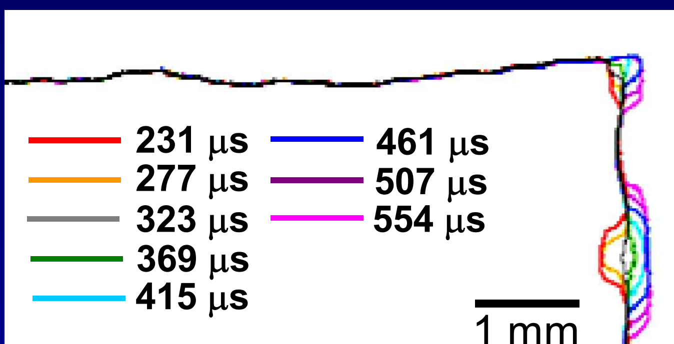
- Frequency of transverse bands is increased when air is present.
- Detailed measurements suggest that reaction advances solely by propagation of transverse bands.
- Other Ni/Ti multilayer designs exhibit similar behavior.

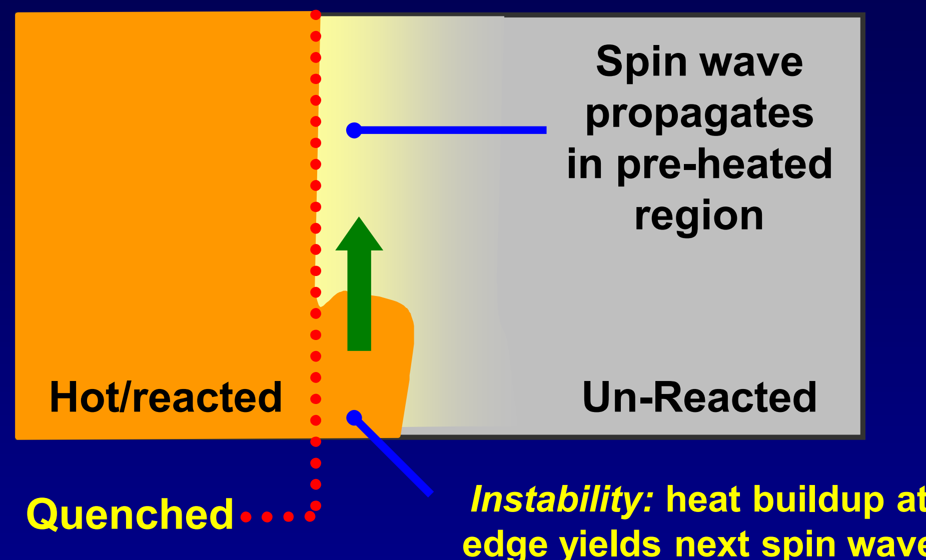
Ni/Ti foil (equiatomic)
Bilayer thickness = 4730 Å; Total thickness = ~ 5.0 μm
Ti capped (two sides)



Reaction front morphology: evidence of instabilities and colliding reaction fronts







J. Mcdonald, D.P. Adams, Appl. Phys. Lett. 94 (2009).

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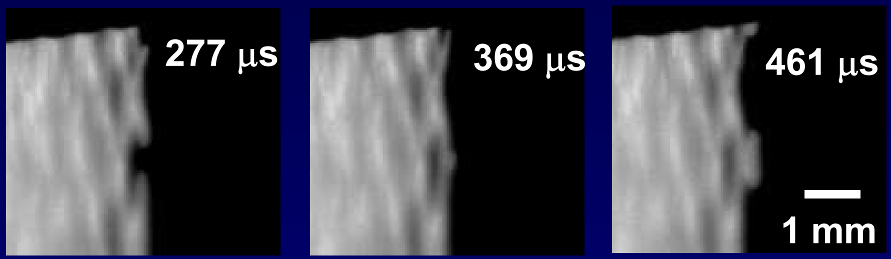
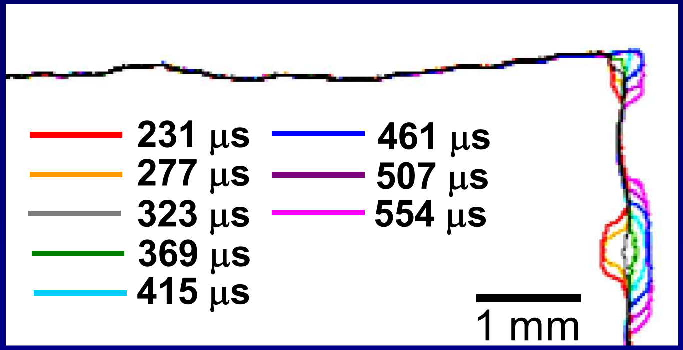
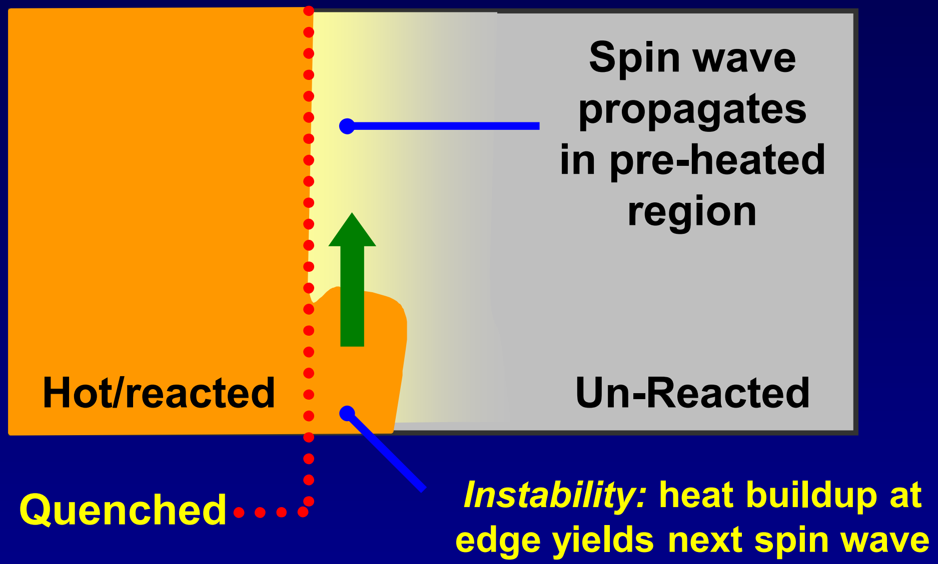
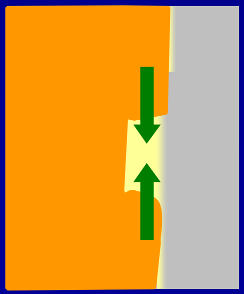


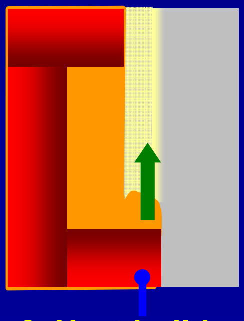




Observed origins



1. Collision of spin waves



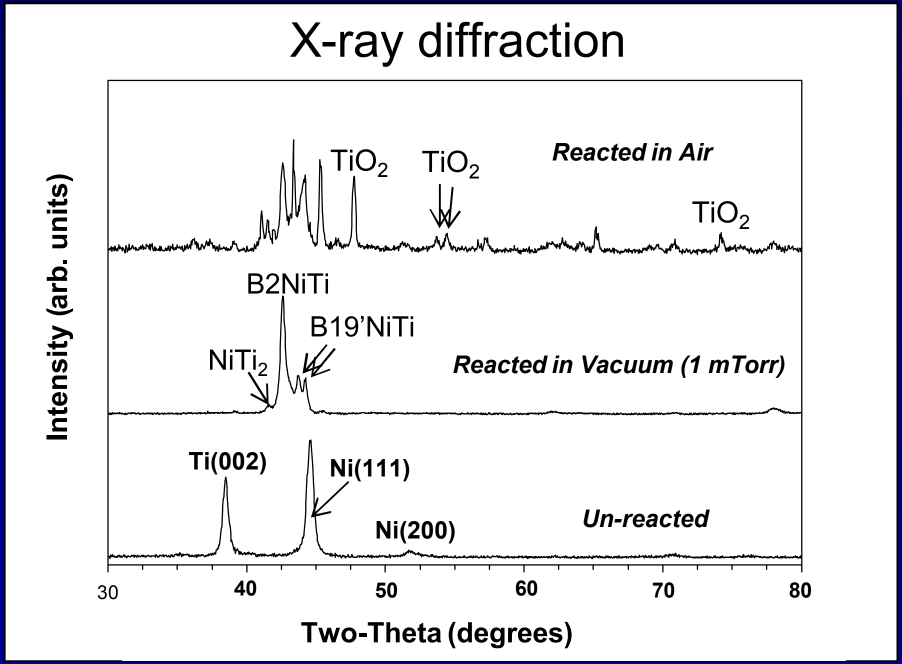
2. Heat buildup at foil edge

J. Mcdonald, D.P. Adams, Appl. Phys. Lett. 94 (2009).

Final phases of Ni/Ti are affected by reaction environment.

Single foil design evaluated (above):
Bilayer thickness = 625 Å
Total thickness = ~ 5.0 μm

- As-deposited multilayers are composed of elemental Ni and Ti.
- Foils reacted in vacuum generally form a mixture of B2 NiTi (or hexagonal NiTi) and B19' NiTi with evidence for other intermetallic compounds Ni_3Ti, $NiTi_2$).
- Foils reacted in air form a mixture of Ni-Ti intermetallic compounds and crystalline TiO_2 (rutile and anatase).

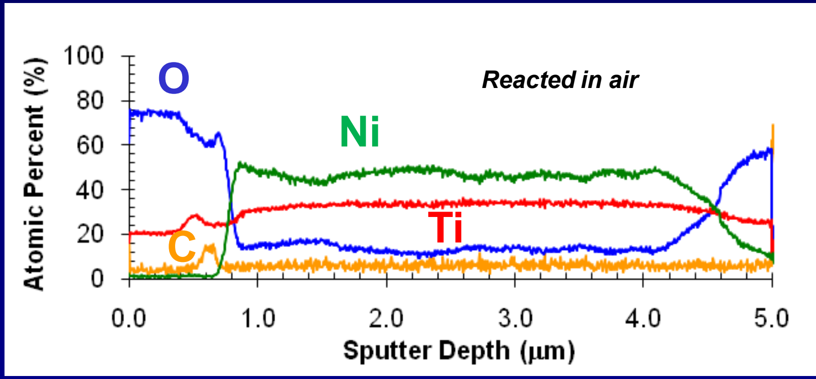


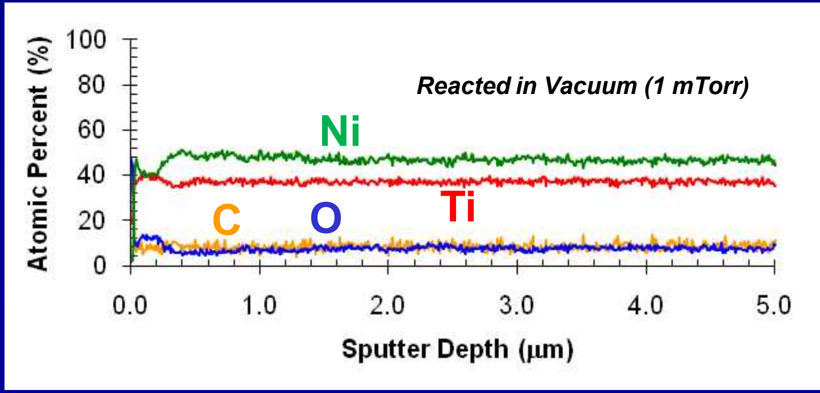
D.P. Adams, M.A. Rodriguez, J. Appl. Phys. (2009).

Reacted Ni/Ti foil composition is affected by reaction environment

- Ti_xO_y forms to a depth of approx. 800 nm on both sides when reacted in air.
- Minimal amounts of oxygen are present within foils reacted at 1 mTorr.
- Similar behavior is observed regardless of capping layer (Ni or Ti).

Single foil design evaluated (above):
Bilayer thickness = 4730 Å
Total thickness = ~ 5.0 µm
Ti capped (two sides) initially





Auger electron spectroscopy

Summary

- Sputter-deposited, reactive Ni/Ti multilayer foils exhibit self-propagating, high temperature synthesis (SHS) reactions in air and in vacuum. Oxidation of Ti is not necessary for stimulating / triggering Ni-Ti reactions !!

- Nickel / titanium SHS reactions are characterized by moderate average propagation speeds and unstable (spin-like) modes (reactions in air, vacuum).

- The gaseous environment affects several characteristics of Ni/Ti multilayers and their reactions including

  - average propagation speed

  - reaction mode (frequency of spin waves)

  - final phase

- We speculate that an increased average propagation speed in air is due to an increased frequency of spin waves nucleated at a foil edge.

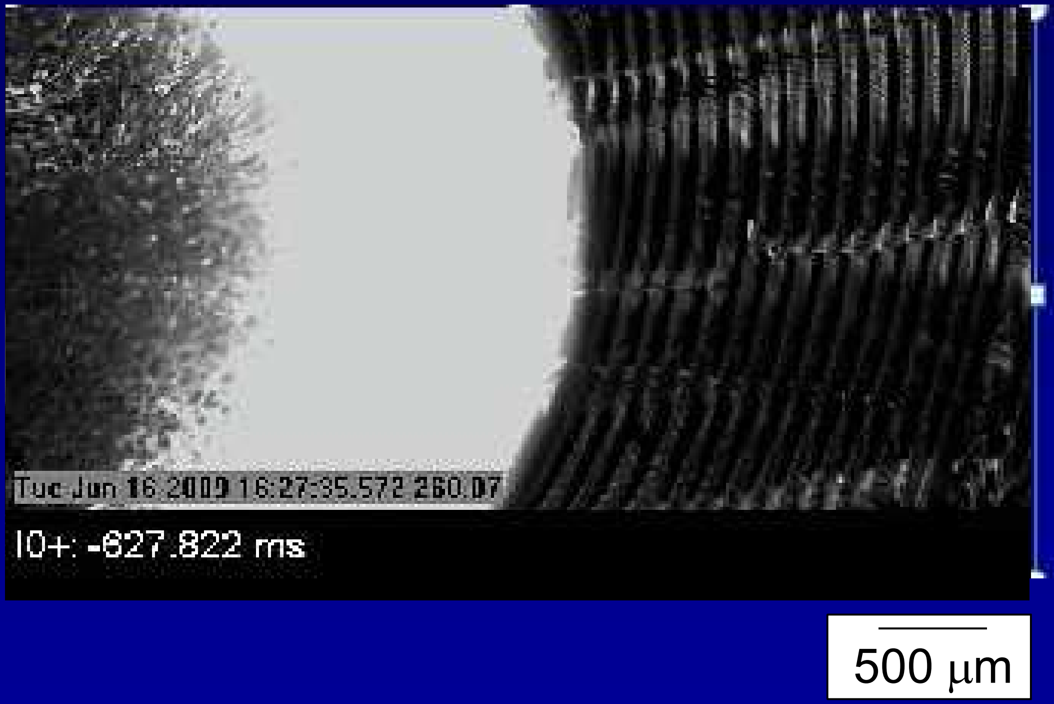
- Additional reactive multilayer systems are similarly affected by environment.

EXTRA SLIDES

Interactions with gaseous environments: Evidence of trailing combustion waves

Example: Sc/Cu multilayer – shown in plan view

- Second reaction wave is an oxidation reaction
  - crystalline Sc_2O_3 phases observed when reacted in air
- Second reaction wave is not observed when reacted in vacuum.



J. Mcdonald, D.P. Adams, J. Mater. Res. (2010).

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

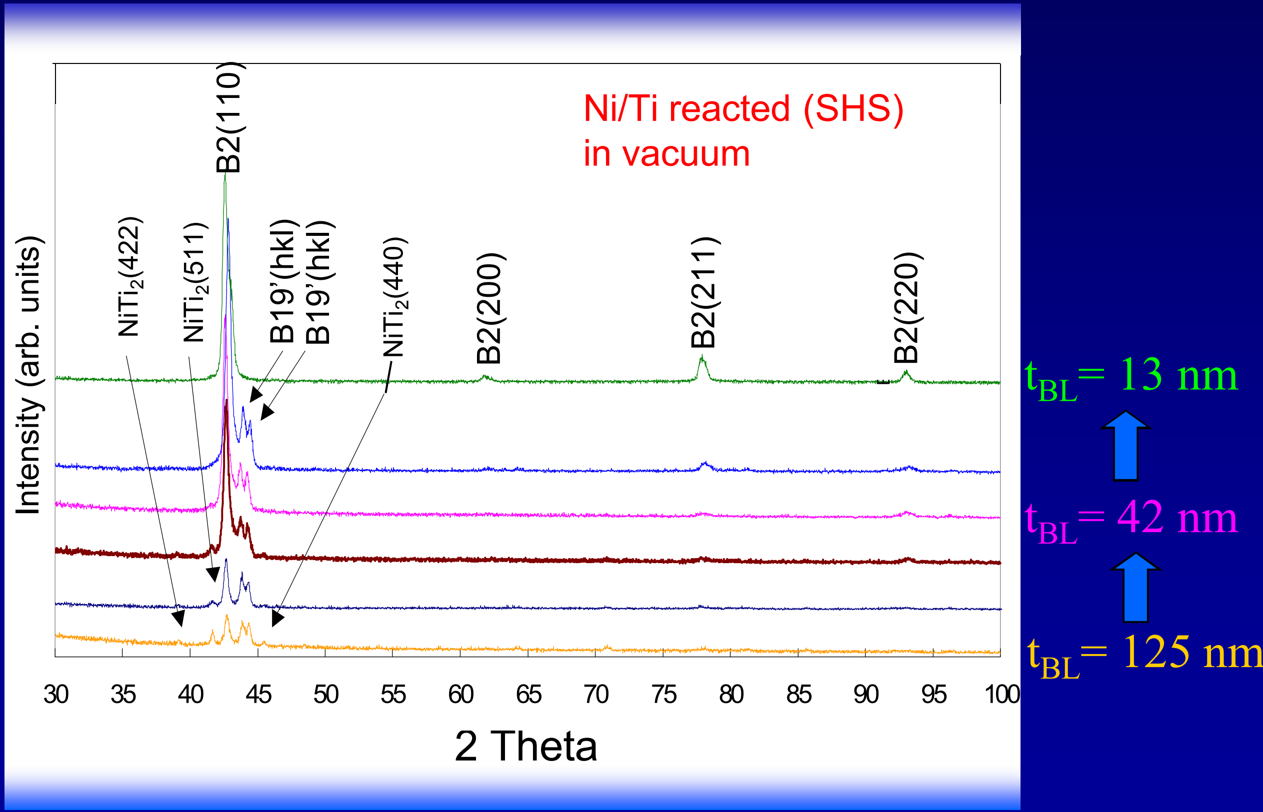
Other:

Adjust film thicknesses to
compensate for densities

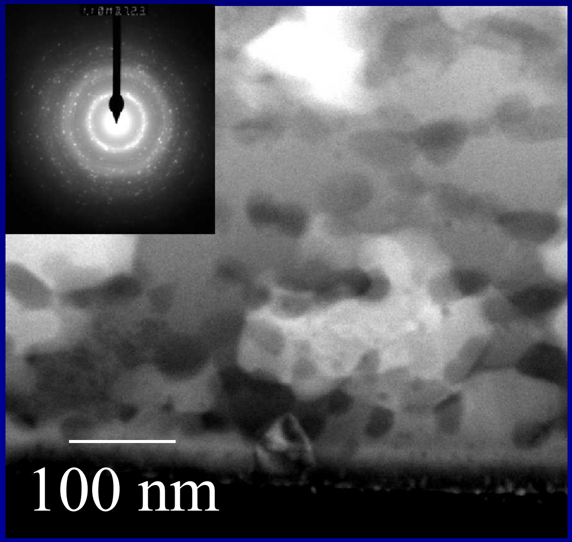
Generally, multilayer is peeled off to ‘create’ a foil for testing.

Single phase B2 NiTi forms when bilayer thickness is made small (~ 10 nm)

We expect that the small spacing promotes mixing and homogeneity



'Slow' film having $NiTi_2$ ppts.
t_{BL}= 83 nm



D.P. Adams, et al.
J. Appl. Phys. 106 (2009)

Global annealing leads to high-temperature reaction (potentially thermal explosion)

- Reactive foils ignite at temperatures far below the melting point of their constituents.

  compare with bulk Ni - Ti powder (with μm periodicity) $T_{ig} \sim 910 \pm 10^oC$
  - *reference Yi and Moore Scr. Met. 1988*

- Ignition temperatures vary with bilayer thickness (i.e., periodicity) with more coarse multilayers having higher T_{ig}.

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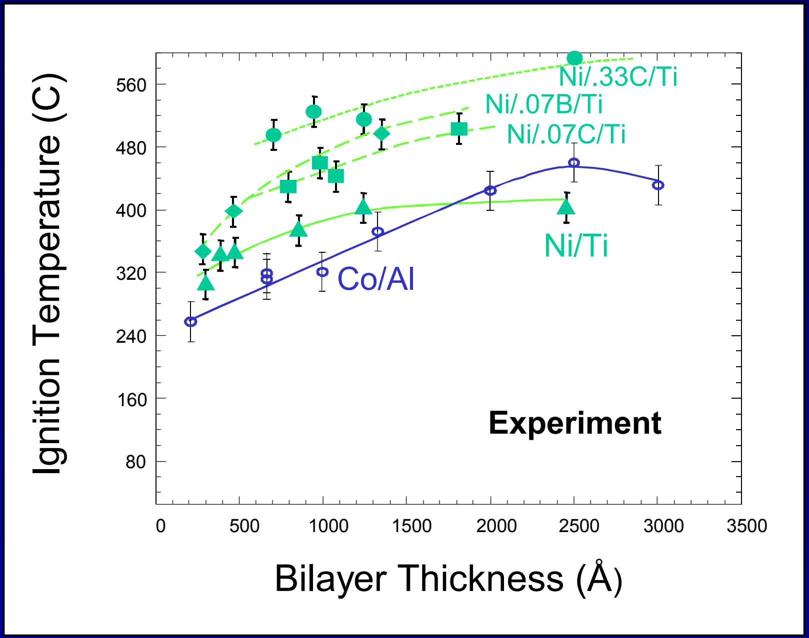


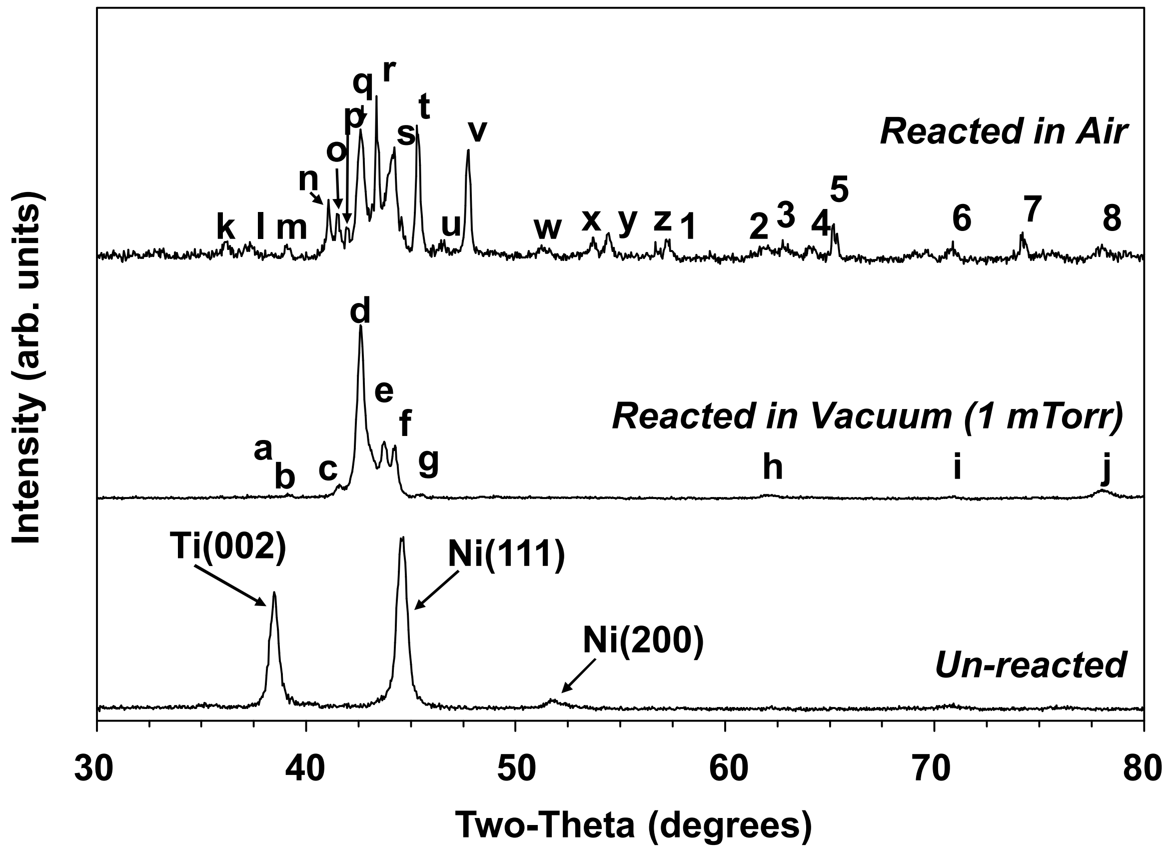
Estimated heating rate ~ 1-10 deg./ms

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)
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



Phase	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x	y	z	1	2	3	4	5	6	7	8
B2 NiTi				X				X									X											X						X
Hex NiTi				X						X						X	X						X											X
B19' NiTi	X	X			X	X				X			X	X				X	X								X				X			X
Ni_3Ti				X	X				X							X		X														X	X	
Ni_4Ti_3								X		X								X			X							X						X
$NiTi_2$		X	X				X		X				X		X					X												X		
TiO_2 Rutile											X		X	X					X						X	X			X	X	X		X	
TiO_2 Anatase													X									X		X					X					
NiO Bunsenite												X						X											X					