SAND2008-4656P

57th Annual Denver X-ray Conference

Denver, Colorado

DETERMINATION OF ACTIVATION ENERGY IN TEXTURED METAL-METAL MULTILAYER FILMS VIA 2D XRD

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6 August 2008

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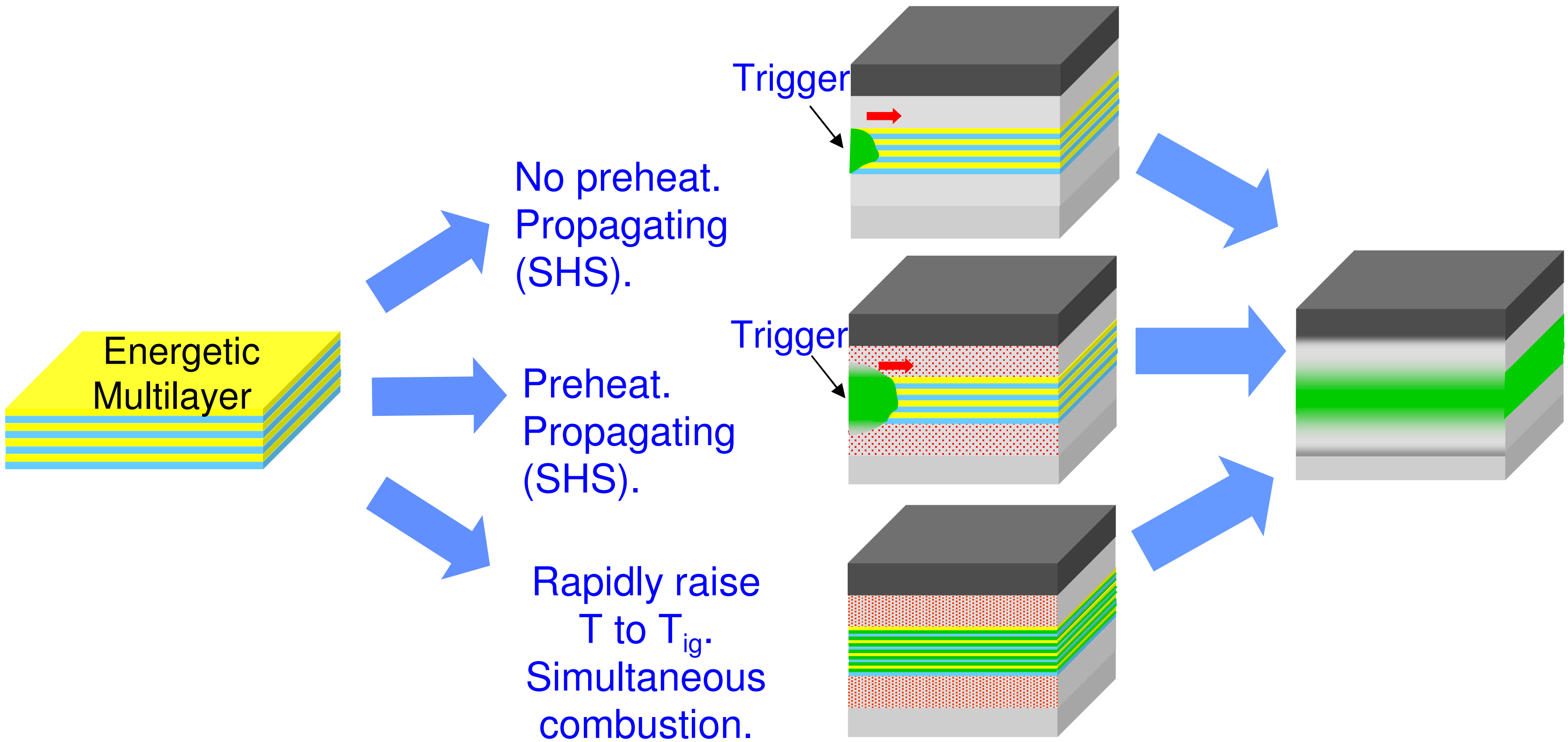
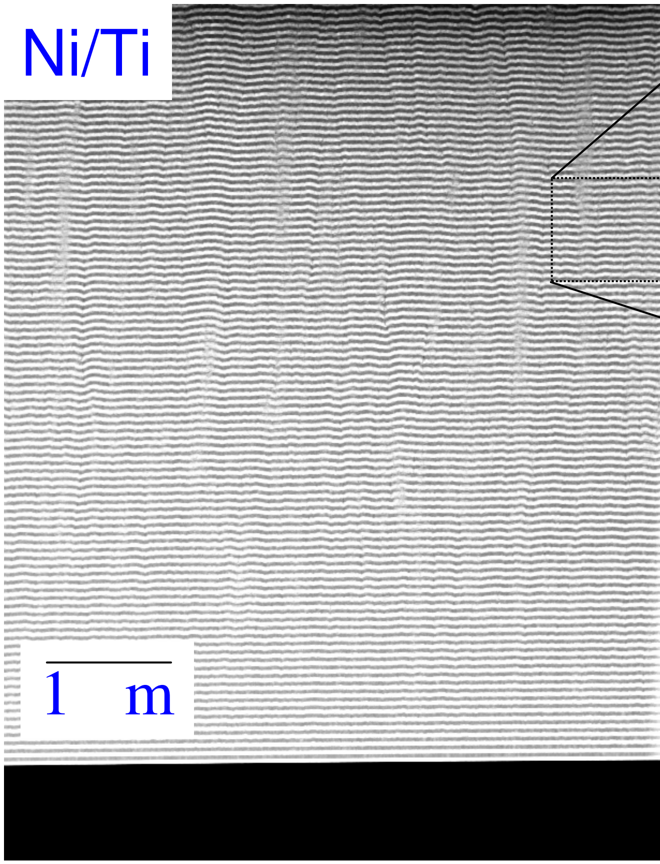
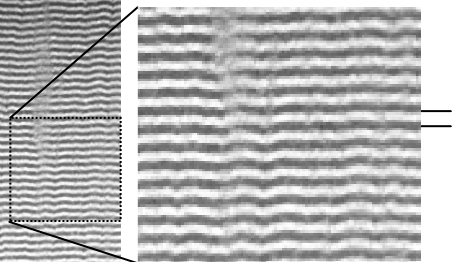
Metal-Metal thin film multilayers store significant energy which can be employed for materials joining

SHS = Self-propagating High-temperature Synthesis
- combustion synthesis



Exothermic thin-film multilayers are heterostructures that consist of two or more species that react.



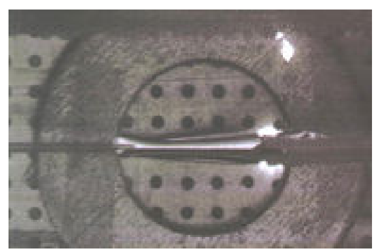


BL = Ni layer + Ti layer = 670 Å

e.g. Ni + Ti → NiTi

Typical design:

- Large negative H_f
- Can exhibit high-T combustion synthesis (self-propagating)



NiTi

AlPt

[1] J.A. Floro, J. Vac. Sci. Technol. A, 1986.
[2] L.A. Clevenger, C.V. Thompson and K.N. Tu, J. App. Phys. 1990.
[3] T.W. Barbee, T. Weihs, US Patents 5,538,795 5,547,715, 1995.
[4] C. Suryanarayana, J.J. Moore, R. Radtke, Adv. Mat. and Proc. (2001).

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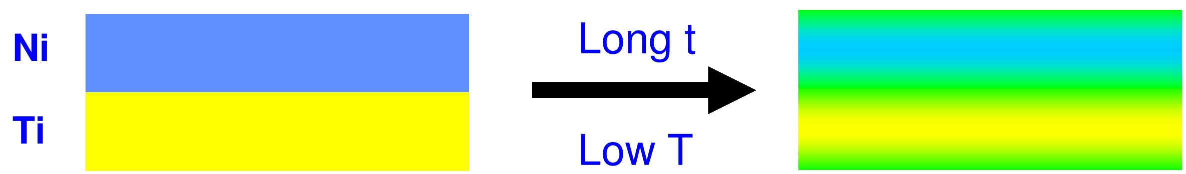
We desired to evaluate not the fast Rx during SHS, but the slower "intermixing" Rx for shelf-life prediction

Slow diffusion of reactants at relatively low temperature (T) over a long time (t) could significantly reduce the stored energy for SHS



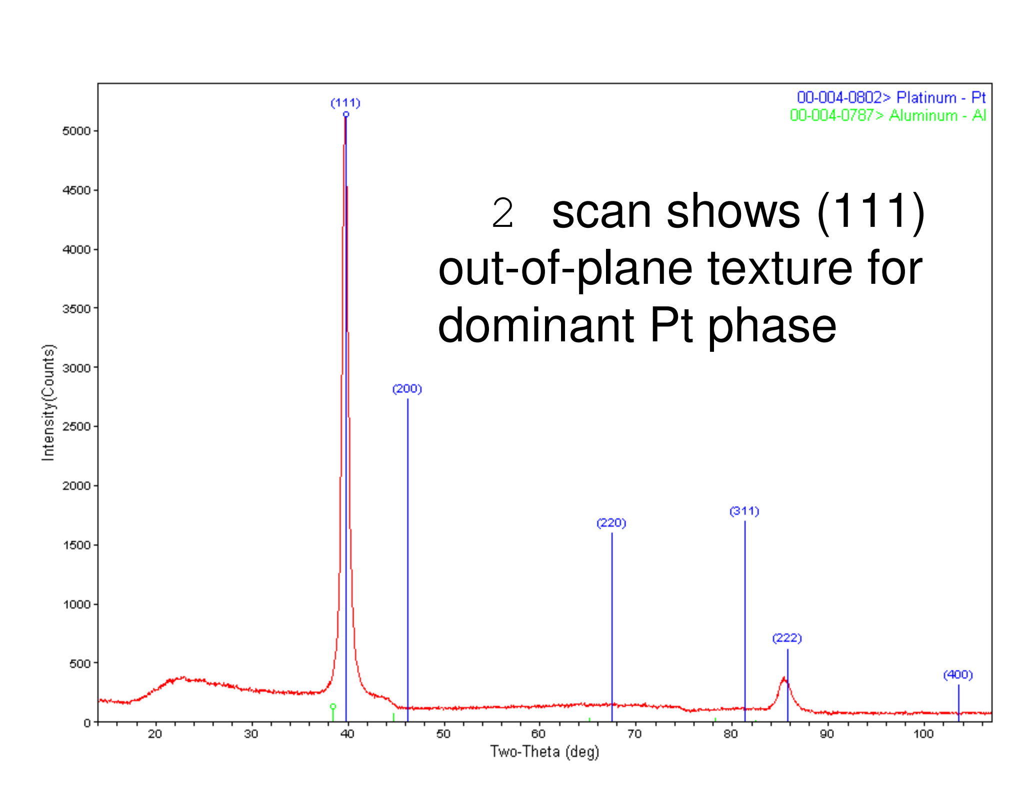
Intermixed film

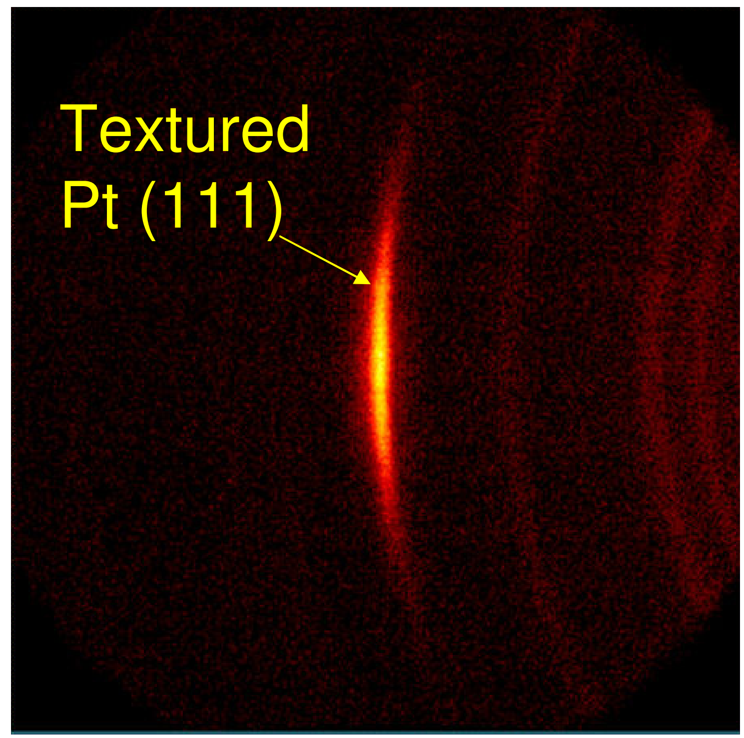
Our approach:

- monitor one film constituent as a fn(t) at various temperature values.
- assume pseudo-first-order behavior for Rx.
- determine rate constants for decay of Intensity of reactant as Fn(T).
- calculate activation energy for intermixing Rx by Arrhenius relationship.

Problem: Multilayer films are often textured. What if texture decreases as sample reacts?

If we measure standard 2 scans we could be assigning intensity loss from peak assuming loss of constituent concentration and not decay of texture.





Al/Pt multilayer, $_{BL}$ = 400 Å, total thickness = 0.2 m

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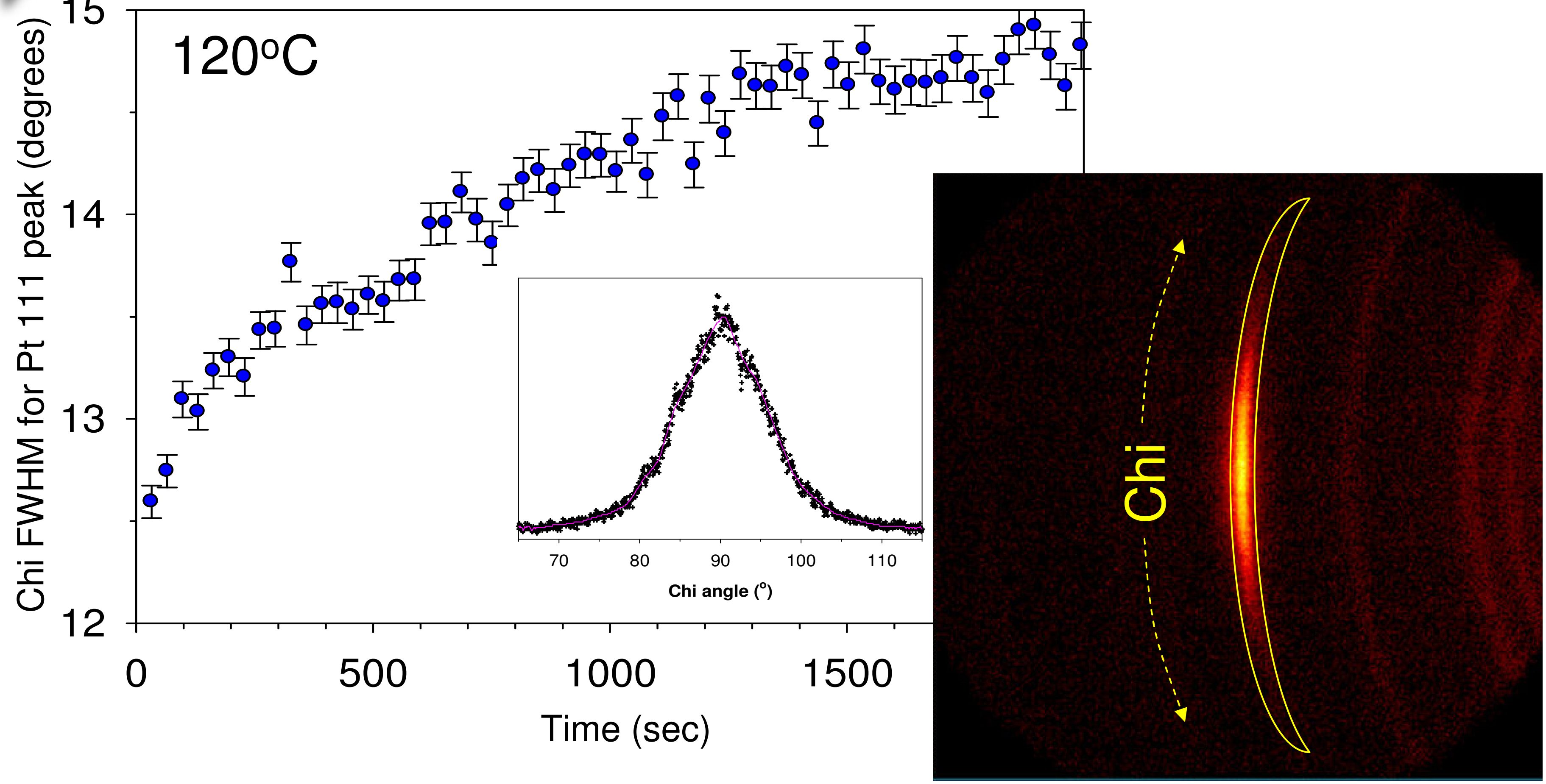
Integration along Chi indicates Pt (111) peak FWHM is increasing during intermixing Rx



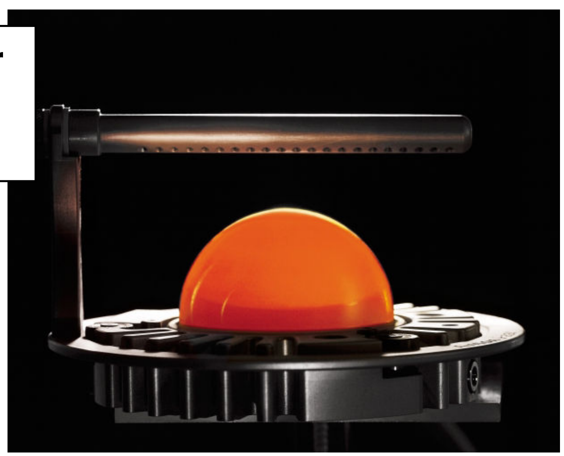
To account for change in texture during Rx we integrate intensity as a window of 2 and Chi

Metal-Metal multilayer films were made using an in-house sputter system.

- Films were deposited by direct-current sputtering
  - cryopumped vacuum system (Unifilm, Boulder CO)
  - base pressure = $8x10^{-8}$ Torr
  - Argon sputtering gas (10 mTorr)
- high purity elemental targets employed
  - Al (99.995%), Pt (99.95%)
  - Ni (99.99%), Ti (99.99%)
  - Co (99.99%), Al (99.995%)
- Deposited on 0.5mm thick fused Silica substrates
  - Substrate temperature < 50^{o}C

Data collection employed a Bruker D8 system equipped with a Anton-Paar stage

Anton-Paar DHS 900 hot stage



Courtesy Anton-Paar GmbH

- Temperature calibrated via alumina thermal expansion
- Films heated 10°C/min to various hold temperatures
  - Vacuum (~10^{-2} Torr)
- Data collected using Hi-Star area detector
  - 120 frames @ 30 sec/frame
  - 1 hr total collection time/film
  - 1 mm incident beam snout
- Data integrated in GADDS
- Peak profile fitting performed using JADE 8.5

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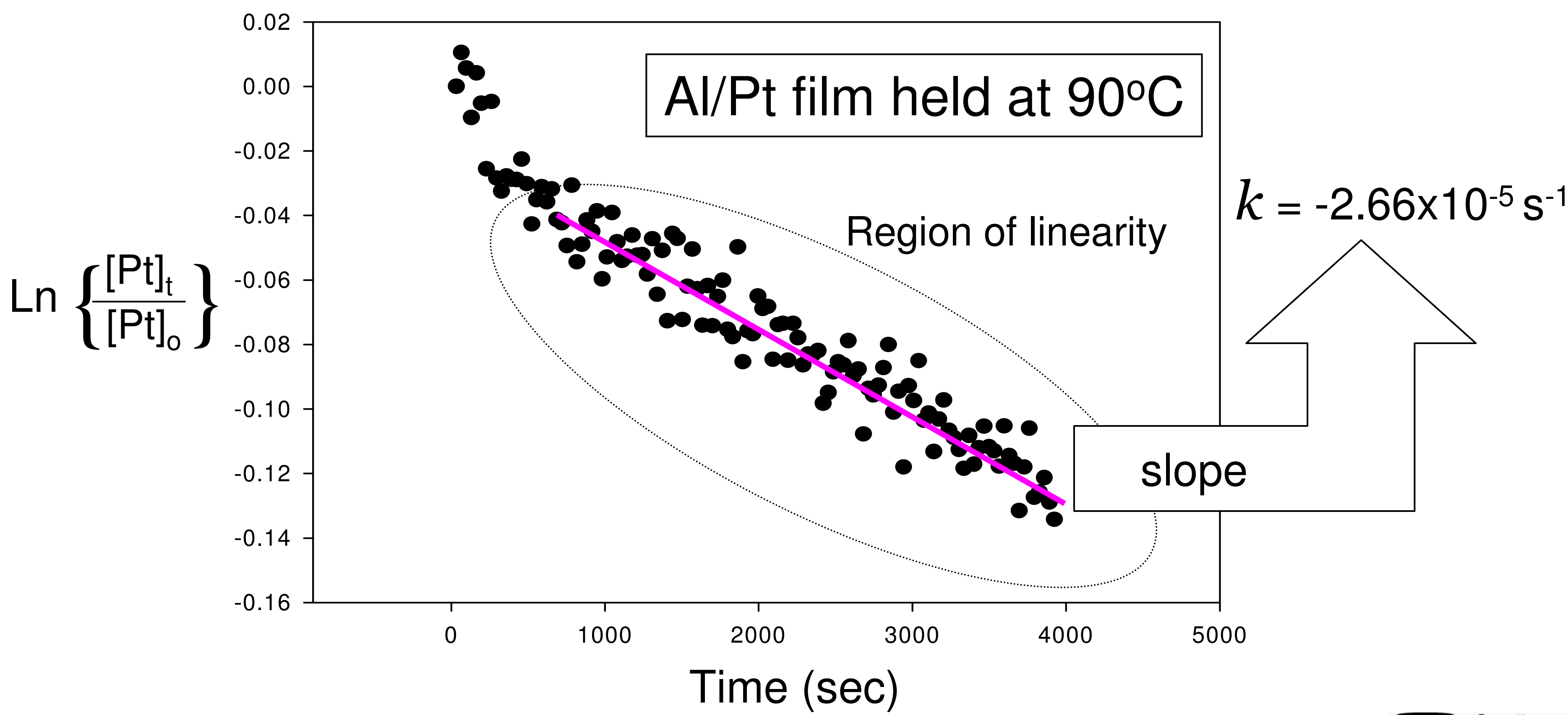
To generate a rate constant for a given (T) we plot the natural log of concentration vs. time

We assume that the intensity of the Pt (111) is $\propto$ to [Pt]



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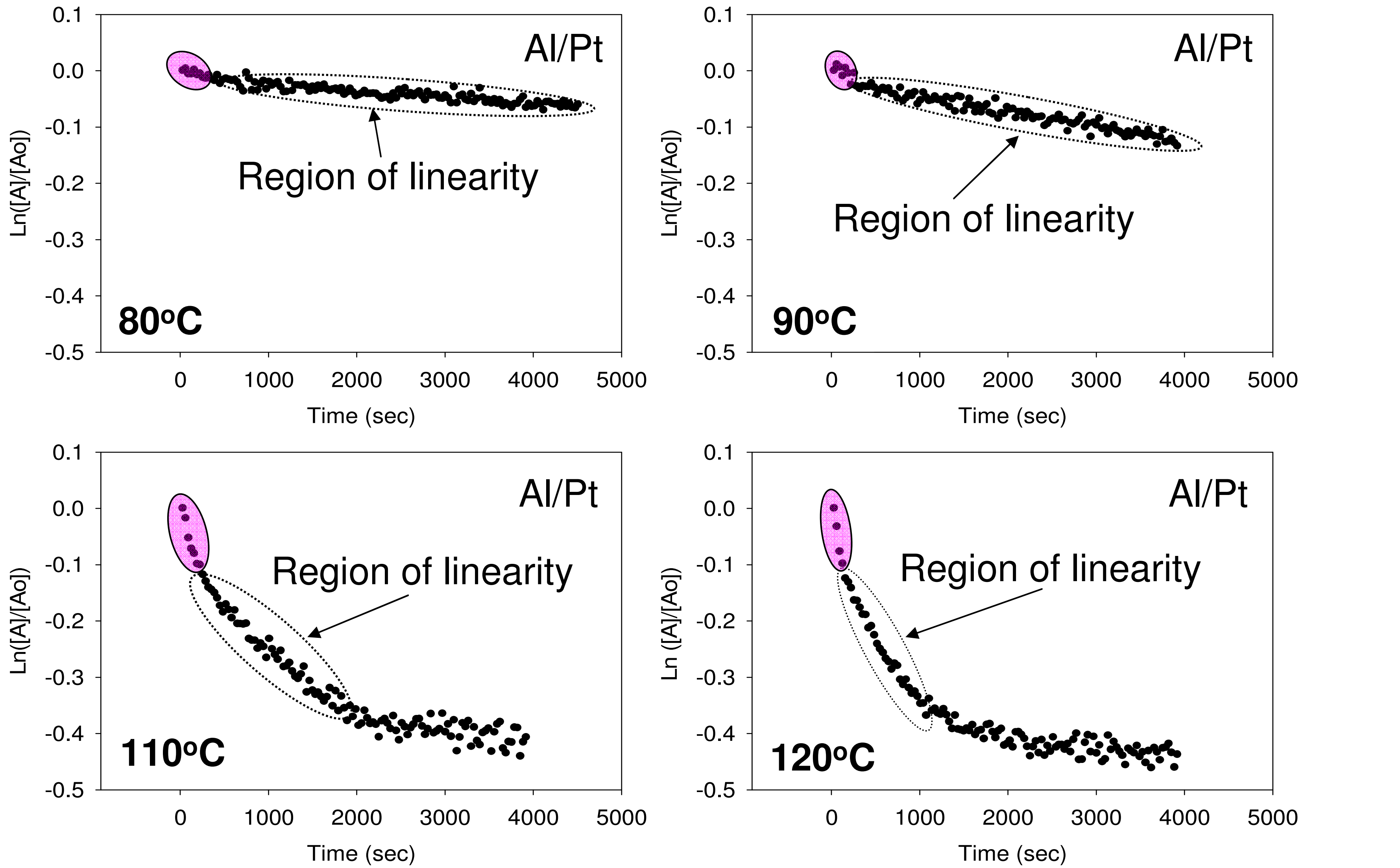
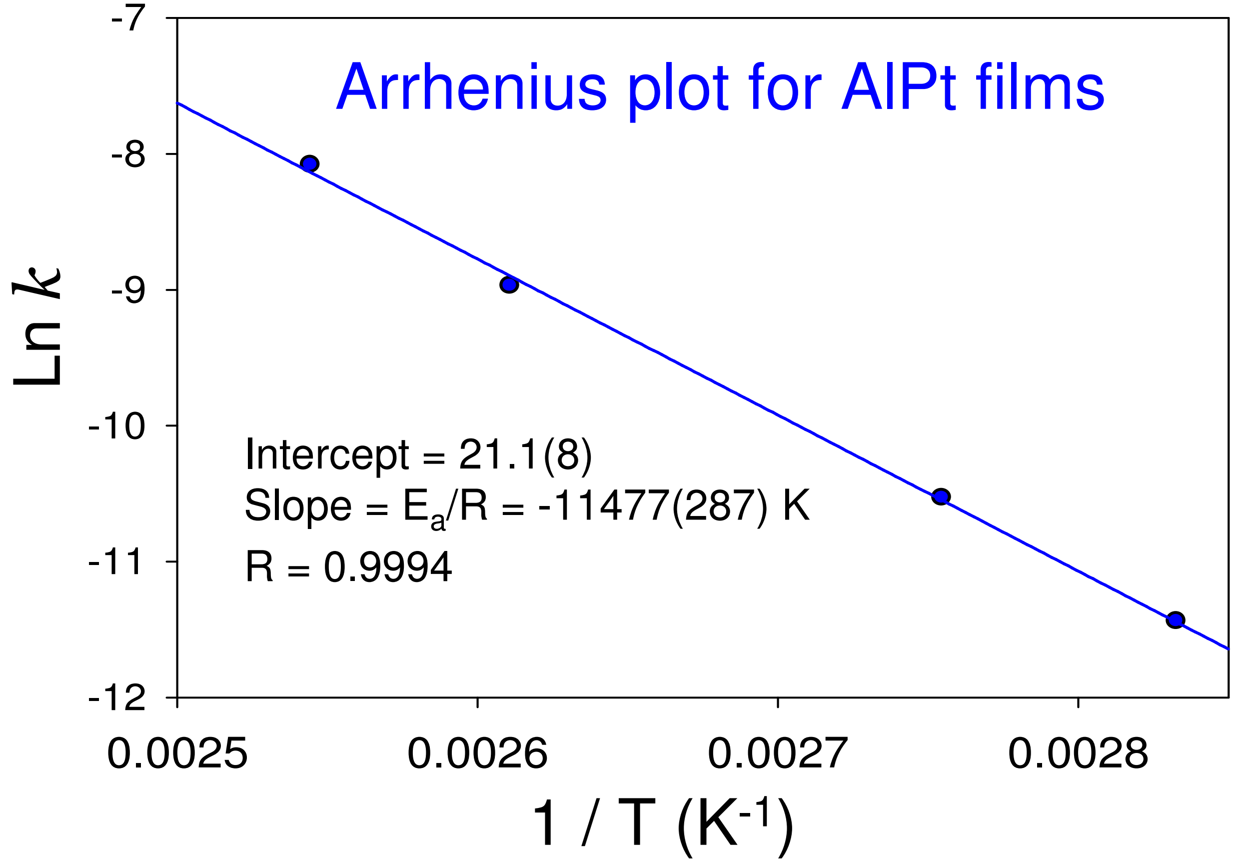
Increased reaction rate in first few minutes attributed to temperature overshoot of controller



Plot of Ln(rate constants) vs. 1/T generates line by which activation energy may be calculated

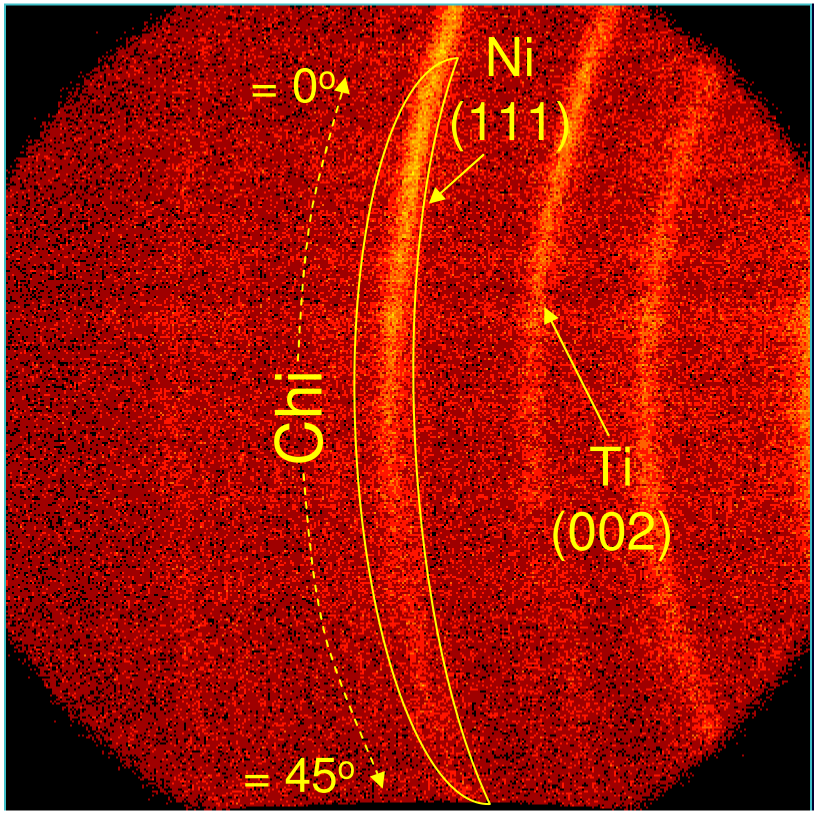


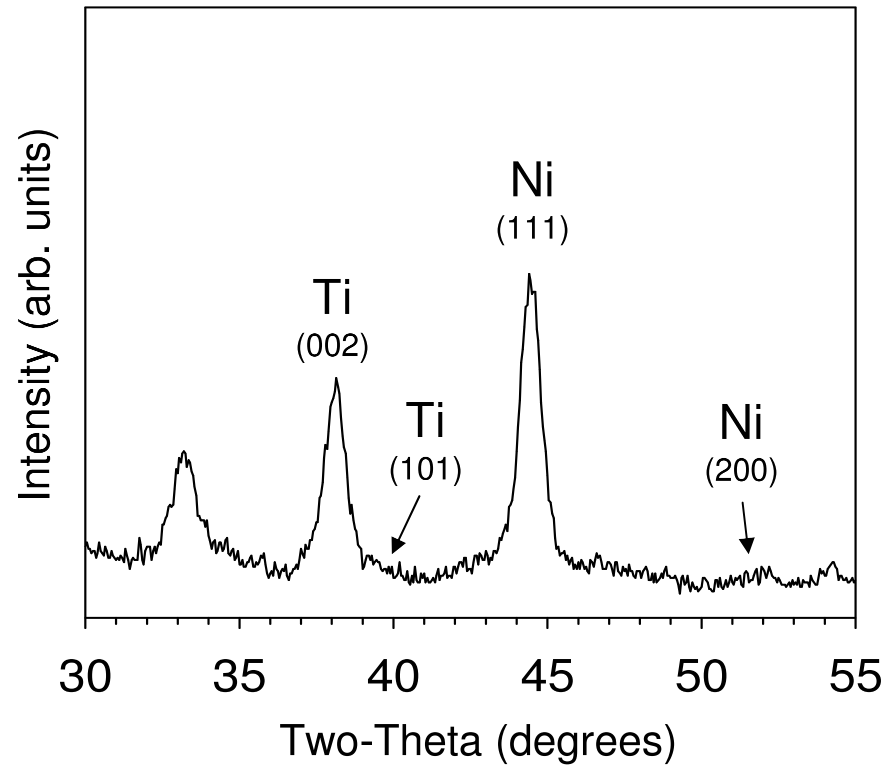
AlPt $\mathbf{E_a}$ = 1.1477x10^4 (K) * 8.314 (J K^{-1}mol^{-1}) = **95.4 ±0.2 kJ/mol**

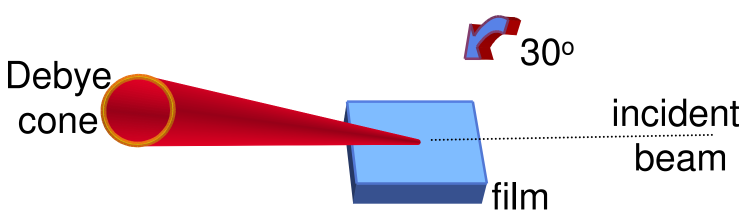
We have performed the same analysis for NiTi and CoAl Metal-Metal Multilayer films

- Lower scattering from lighter elements
- Needed to improve signal from film layers
- Bilayer thickness for Ni/Ti and Co/Al increased to 500 Å
- Increased total thickness for Ni/Ti and Co/Al to ~1 m (20 Bilayers)
- Films tended to be less oriented

Ni/Ti shows out-of-plane texture of Ni (111) and Ti (002) but with larger variability in Chi angle

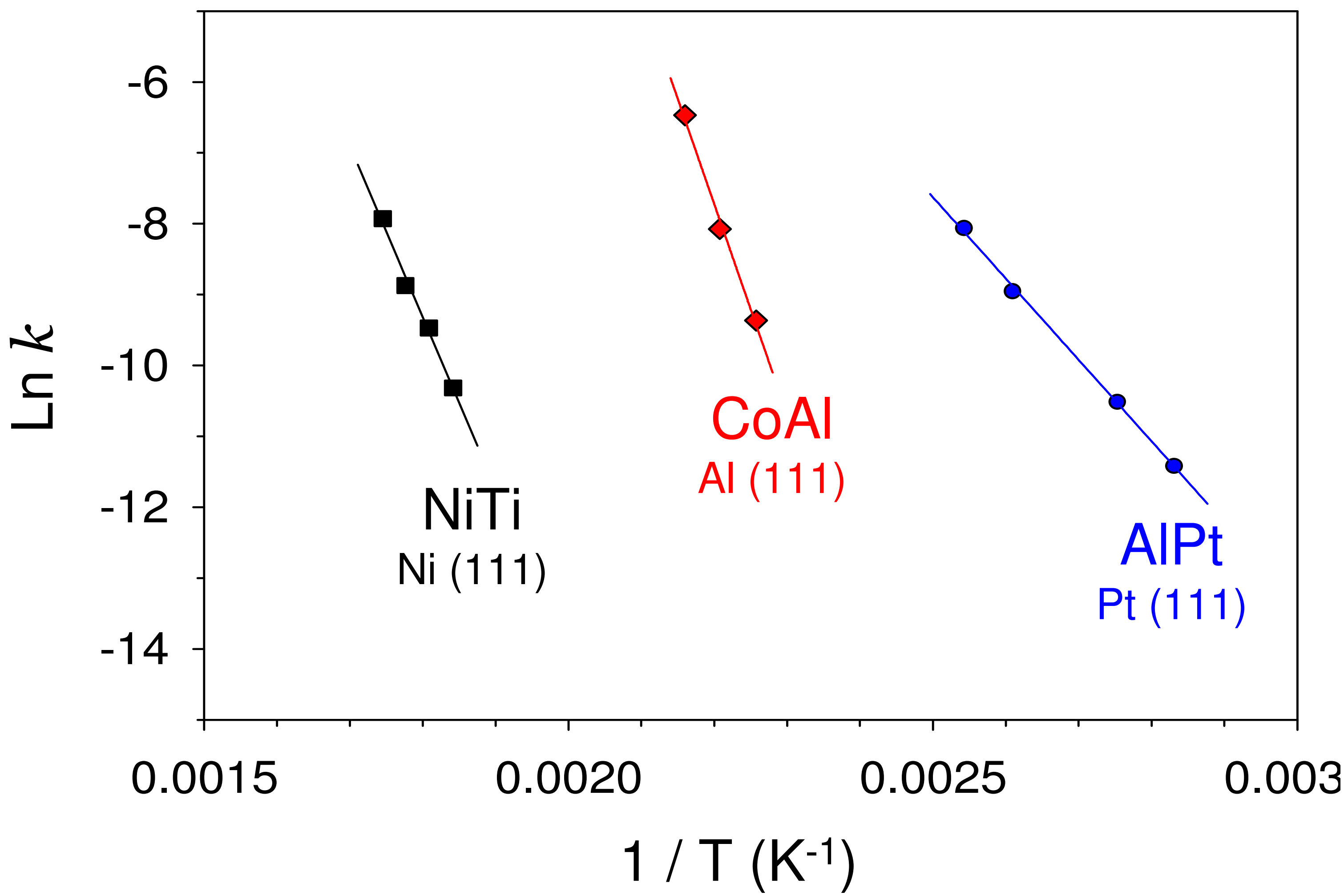






Film tilted 30° in Chi angle from normal to get at least **half** of intensity distributed along Chi

Ni/Ti and Co/Al films show higher E_a for intermixing as compared to Al/Pt



Analysis of reaction results for different film systems shows Al/Pt is most susceptible to the intermixing behavior

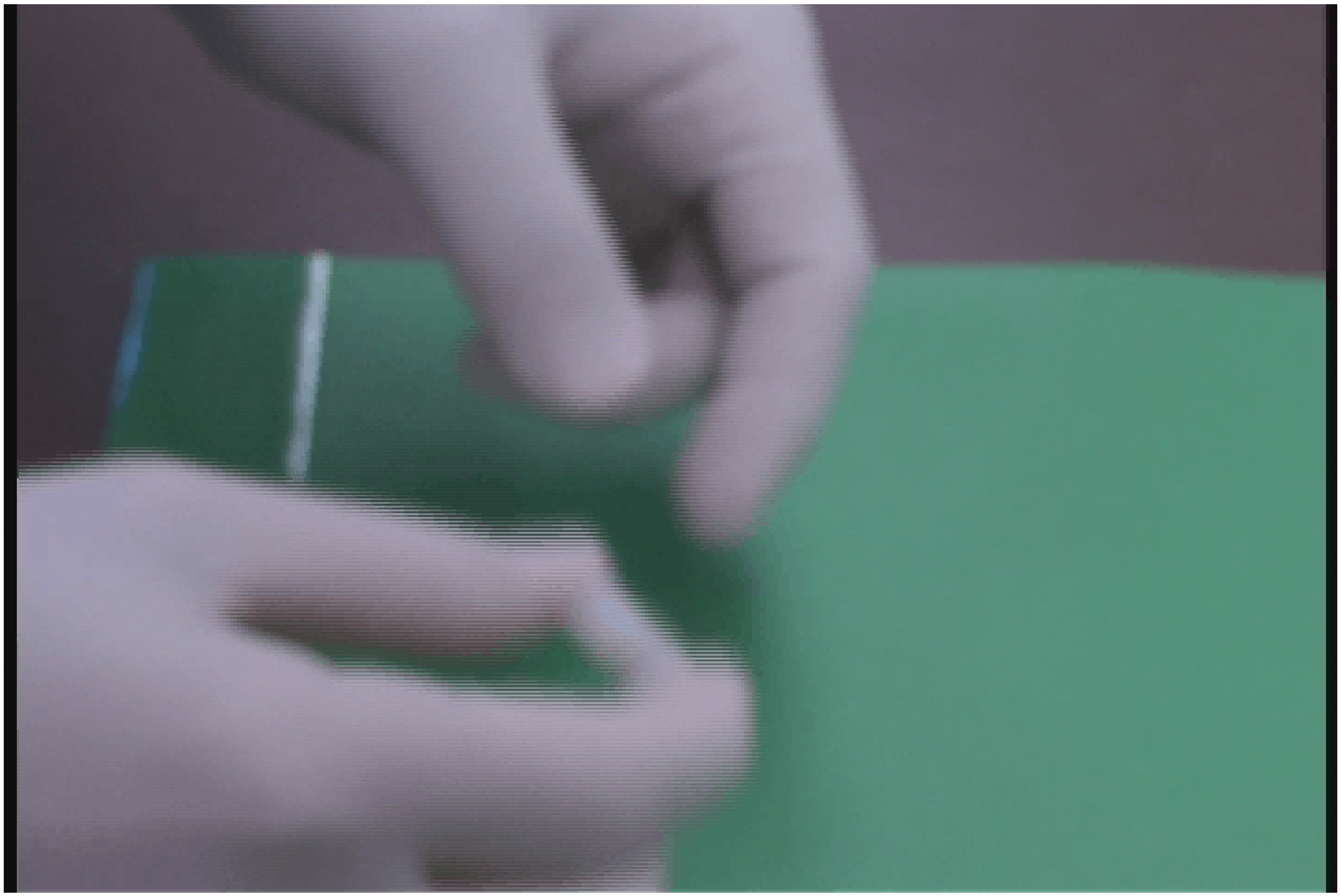
Film	Bilayer Thickness (Å)	Number Bilayers	Total Thickness (m)	Observed *hkl*	E_a (kJ/mol)	Rx Temp. range (°C)
Al/Pt	400	5	0.20	Pt (111)	95.4(2)	80-120
Co/Al	500	20	1.00	Al (111)	247(19)	170-190
Ni/Ti	522	20	1.04	Ni (111)	201(13)	270-300

Conclusions

- Use of a 2D area detector facilitates collection of Rx kinetics data from textured films.
- Reactions can be monitored for both texture decay and intensity decay simultaneously.
- Al/Pt films show more susceptibility to intermixing reaction than Co/Al or Ni/Ti film systems.

Fun movie

Joining plastic via Ni/Al Exothermic Metal-Metal Multilayer films



Acknowledgments

- **Malisu Bai (Co. School of Mines) for fun movie.**
- **Luke Brewer and Michael Rye for FIB and TEM data.**

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