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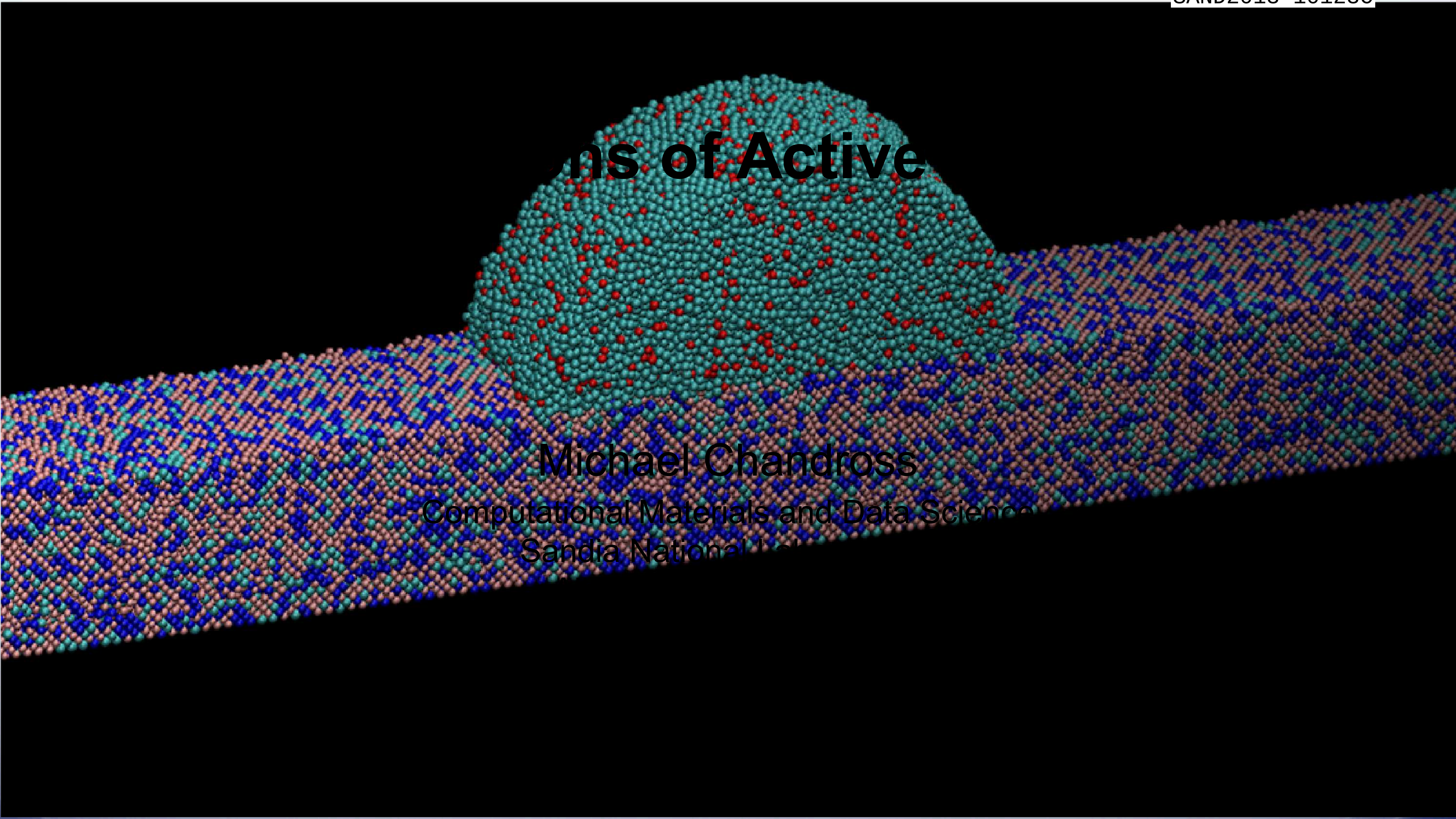

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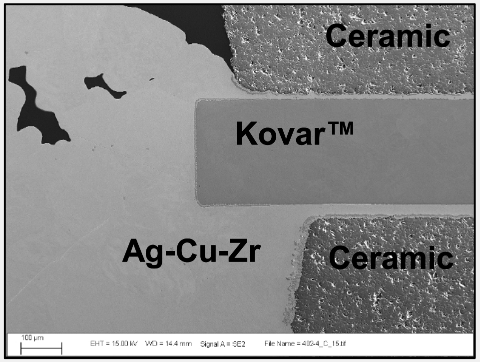
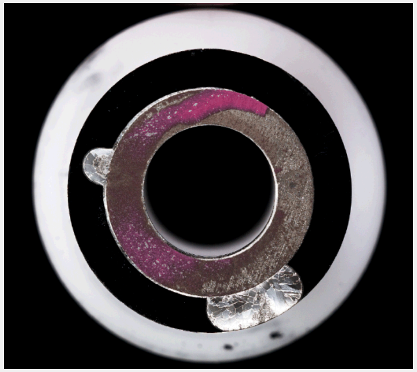
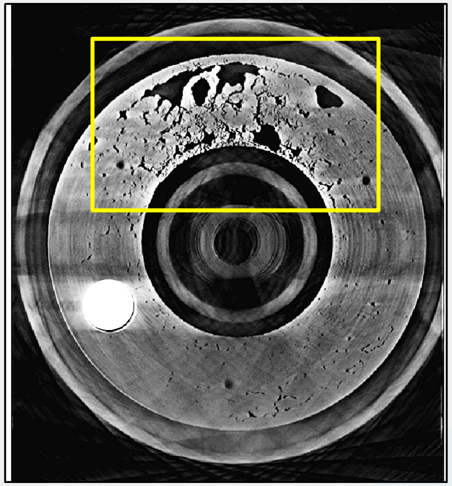
Introduction

- Brazing of ceramics to metals is a crucial bonding technology for many components
- Ceramics are highly desirable structural materials
  - Resistance to wear and corrosion
  - Can withstand high temperatures
- Ceramics have issues limiting applicability
  - Low fracture toughness
  - Lack of ductility
- High mechanical and thermal stresses can be alleviated with a ductile filler material
- Mechanics of joint formation poorly understood
- Wetting and spreading of filler material on metallic substrate is crucial component

Runout Affects Reliability

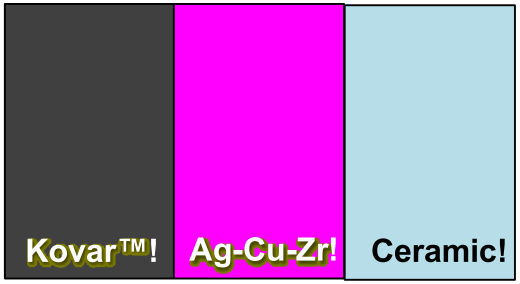




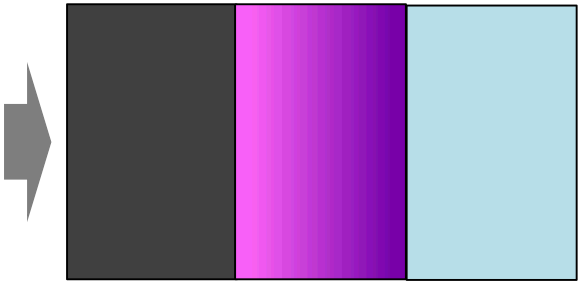


- Runout is a prevailing issue in metal-metal and metal-ceramic joints
  - Negatively impacts strength and hermiticity
  - Affects cosmetic requirements
  - Unfilled regions and solidification shrinkage
  - Local residual stresses, leading to cracking
- Efforts have been made to minimize runout
  - Increasing filler viscosity
    - Temperature
    - Alloying elements
  - Alter geometry or surface condition of the metals

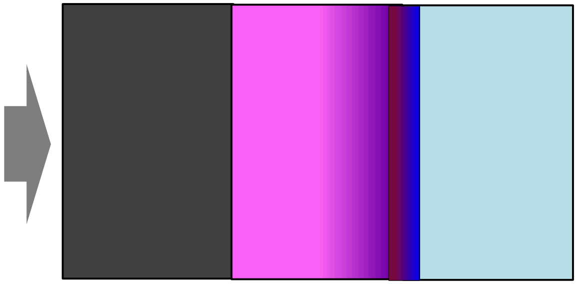
Multi-Step Reaction



Initial state of Kovar^{TM}, alumina and Ag-Cu-Zr braze alloy



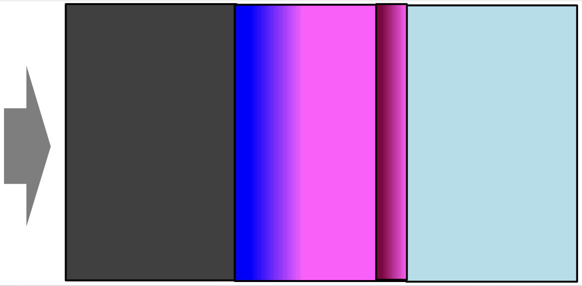
Zr diffuses to alumina through oxidation/reduction reaction



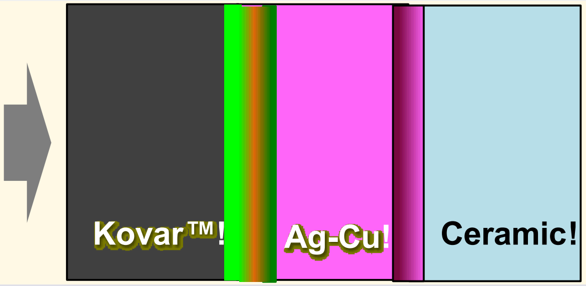
Reduction/oxidation reaction at alumina interface

$3Zr + 2Al_2O_3 = 3ZrO_2 + 4Al$

$Zr + SiO_2 = ZrO_2 + Si$



Elemental Al and small amount of Si driven to Kovar by aluminide/silicide reaction



Final state of braze joint

- Entire process is too complicated to model
- Break down to components essential for runout

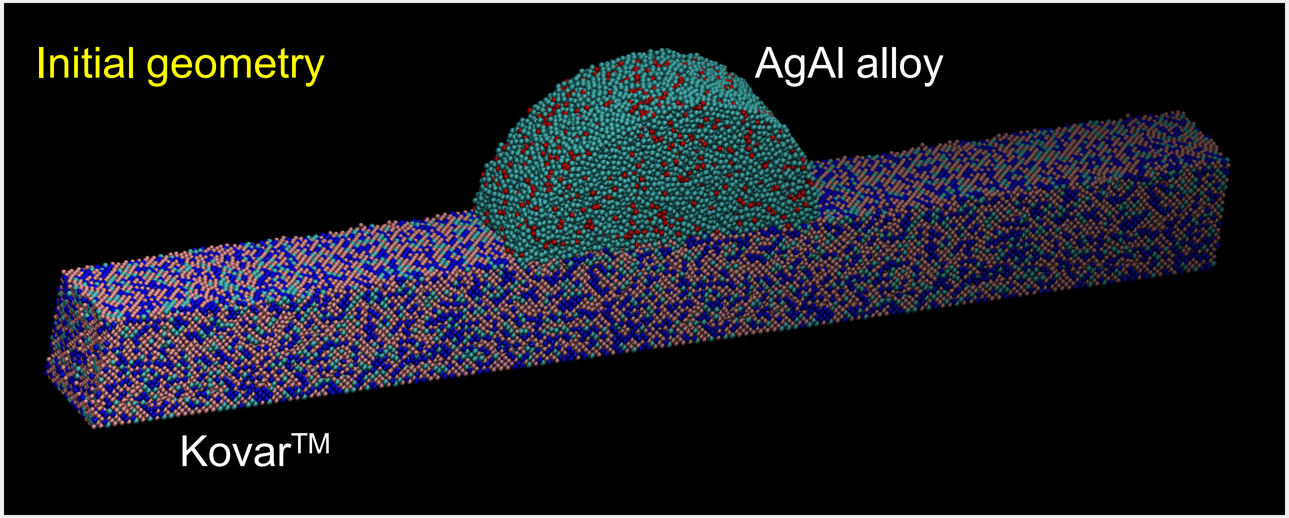
Kovar is the Key to Runout

		Buttons	
		Kovar™	**Alumina**
Washer	**Kovar™**	*None*	*Run-out* *(baseline)*
	Alumina	*None*	*None*

Sandwich sample

- Kovar^{TM}/Kovar^{TM} joints did not result in runout
- *But*, Kovar^{TM}/Kovar^{TM} joints with Al did…
- Study AgAl alloy on Kovar^{TM} substrate to understand chemical aspects

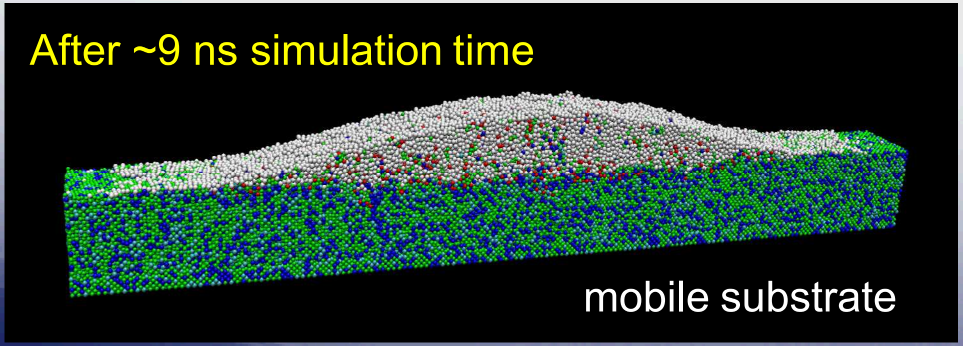
Simulation Methods



- Large-scale Molecular Dynamics simulations
- Embedded Atom potentials
- Half cylinder of metals on Fe with 16.5% (at) Co, 28.2% (at) Ni (pseudo-2D)
  - Pure Al or pure Ag
  - Alloy with 85% (at) Ag, 15% (at) Al
- Variety of spreading conditions
  - Fixed (nonreactive) or mobile (reactive) substrate
  - Prewet with Al or Ag

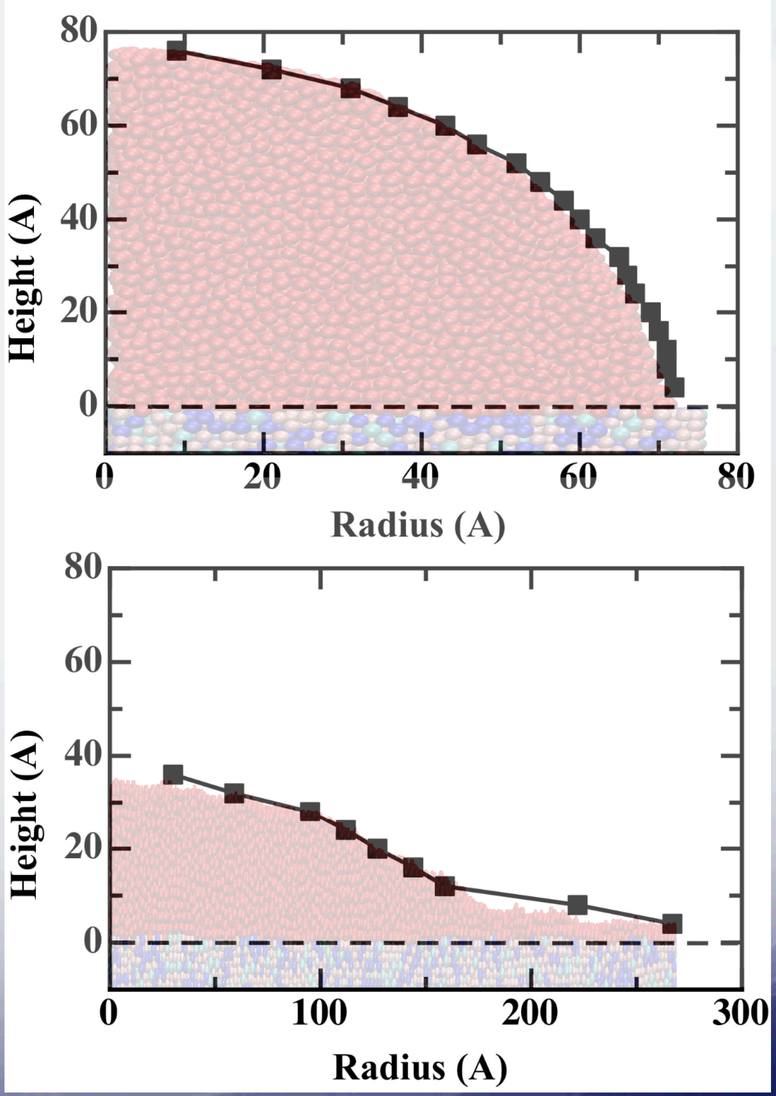
Analysis Techniques

- Interested in spreading of drops vs. t
- Analyze drop profiles
- Create histograms
  - 4A high bins
  - Fit each bin to circle
    - Contains 95% of atoms
    - Returns drop “radius”
- Plot radius of each bin vs. t

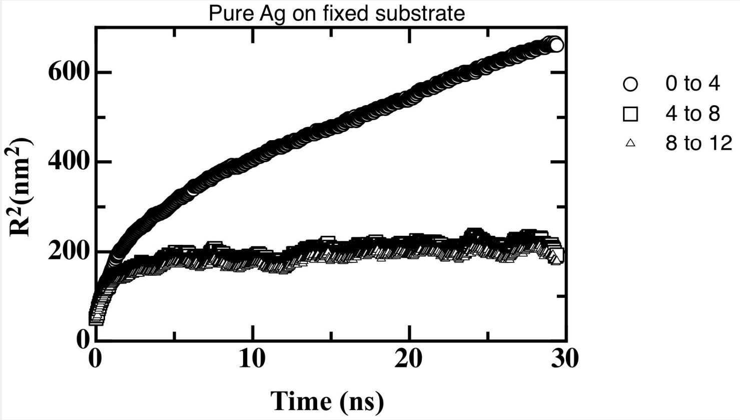


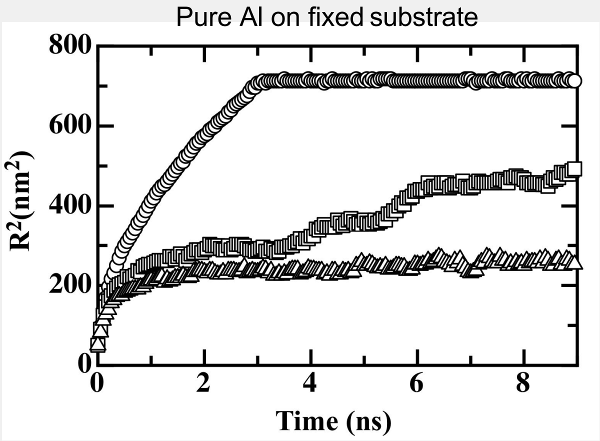
After ~9 ns simulation time

mobile substrate



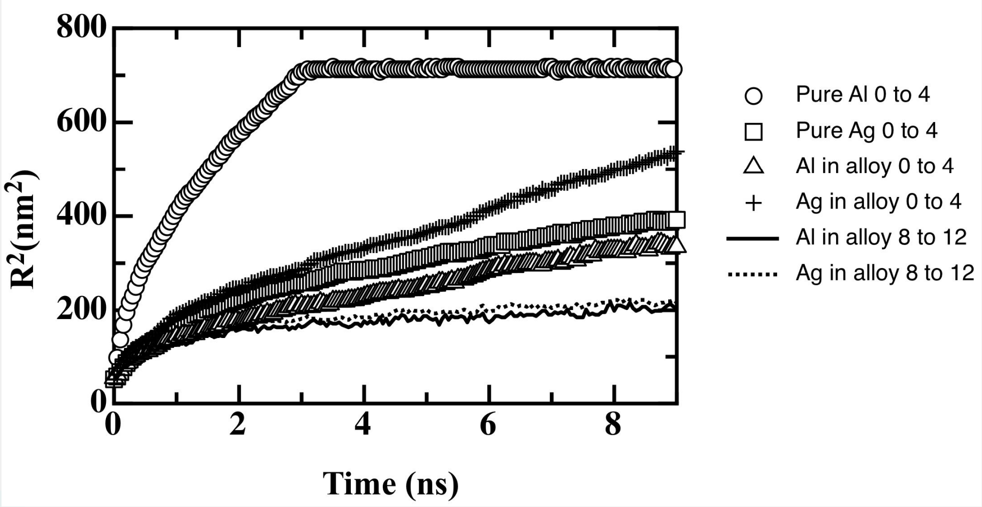
Results – Pure Metals on Fixed Substrate

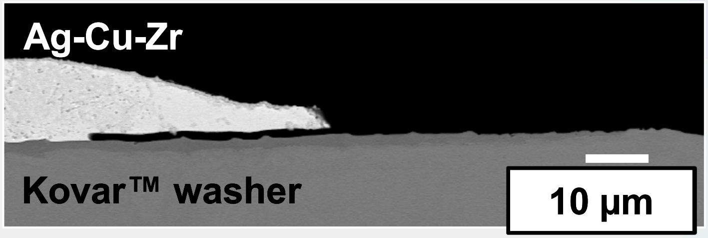


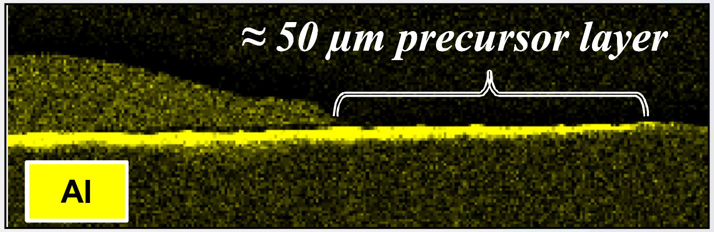


- Pure Ag
  - Precursor foot spreads quickly
  - Bulk of drop spreads much more slowly
- Pure Al
  - Still has precursor foot
  - Spreads much more quickly than pure Ag – *note differing axes on plots*

Results – Alloy on Fixed Substrate

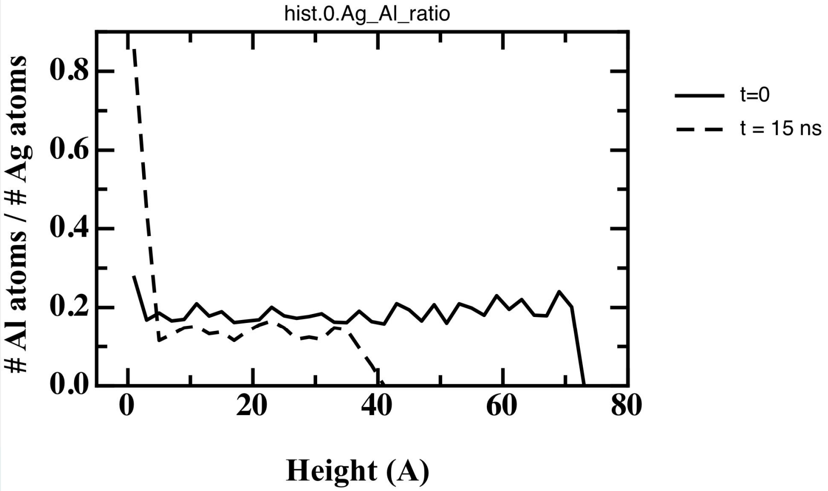


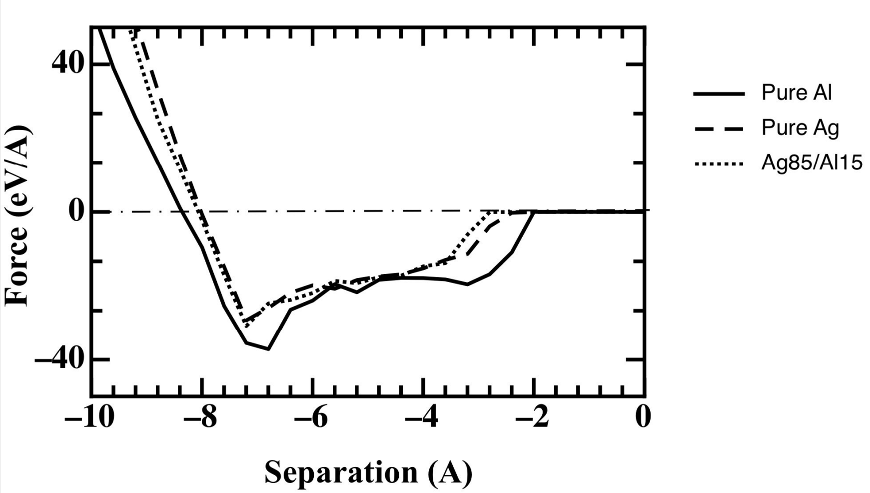




- In the alloy
  - Ag spreads faster than pure Ag
  - Al spreads more slowly than pure Al
  - Alloy has less of a dominant foot
- Competitive wetting
  - Ag inhibits the spreading of Al
  - Al enhances the spreading of Ag
  - Qualitatively similar to experiments
  - Is this a potential cause of runout?

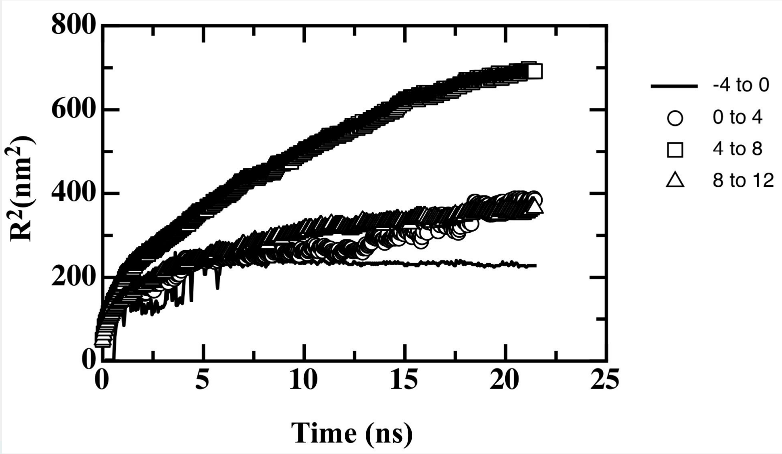
Why is the Alloy Different?

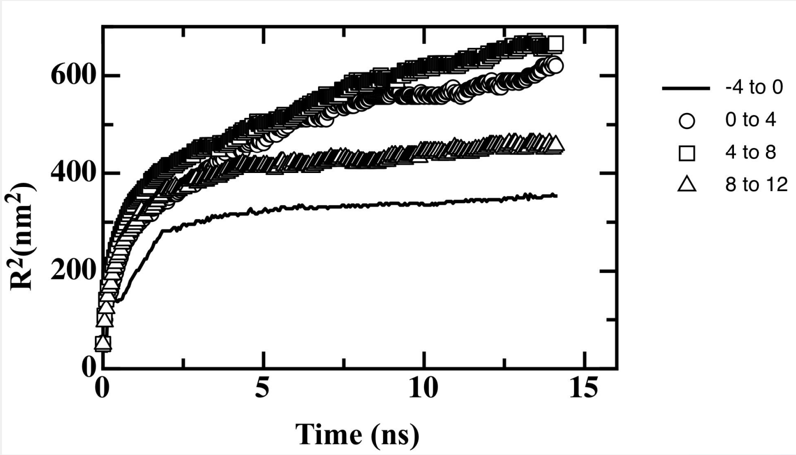




- Al moves quickly to substrate
- Surface tensions could be the cause
  - Surface tension is known to be incorrectly predicted with EAM
    - Experiments: Al lower than Ag
    - Simulations: Ag lower than Al
    - Close in both cases…
  - Difficult calculation when considering a solid/liquid interface
- Instead, look at force vs. separation
  - Al shows significantly more adhesion
  - Adhesion/depletion leads to increased Al at substrate

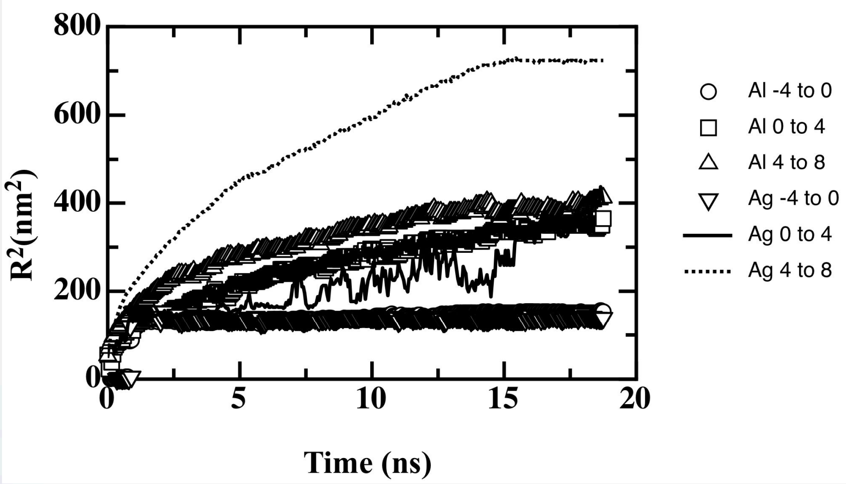
Results – Pure Metals on Mobile Substrate

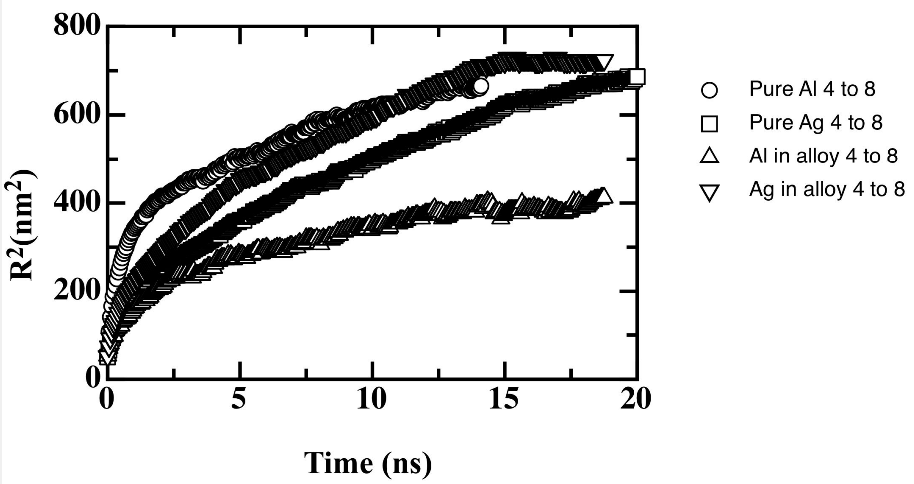

Pure Ag


Pure Al

- Reactions with substrate allowed – need to consider “subsurface” bin
- Pure Ag
  - Very small subsurface layer
  - 1st layer is not foot – almost pinned to substrate
  - Precursor foot from 4 to 8 A
- Pure Al
  - Larger reaction zone than pure Ag
  - Precursor foot is both 0 to 4 *and* 4 to 8 A

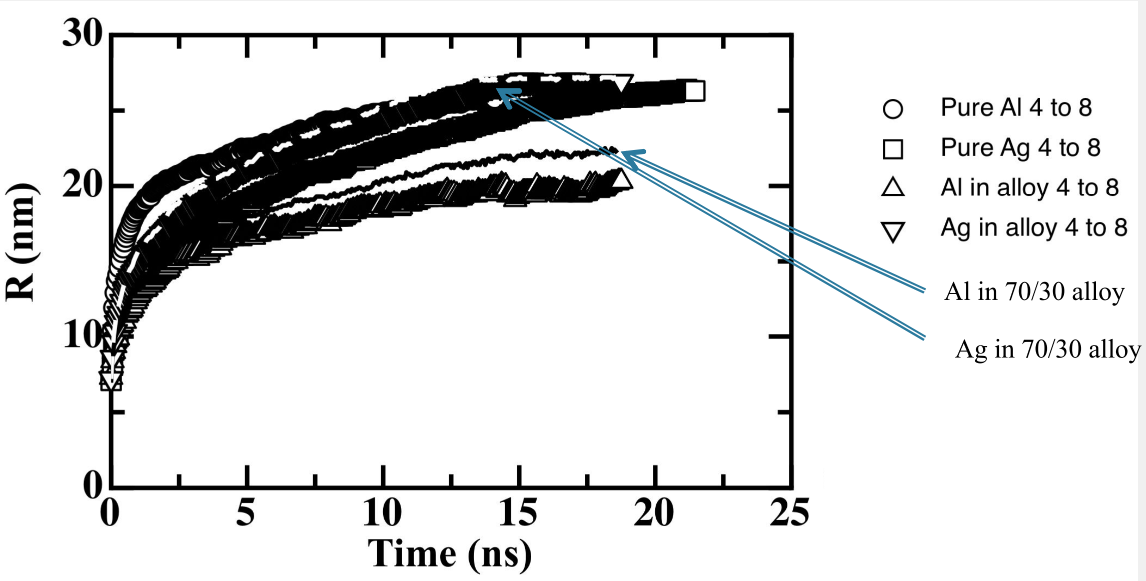
Results – Alloy on Mobile Substrate





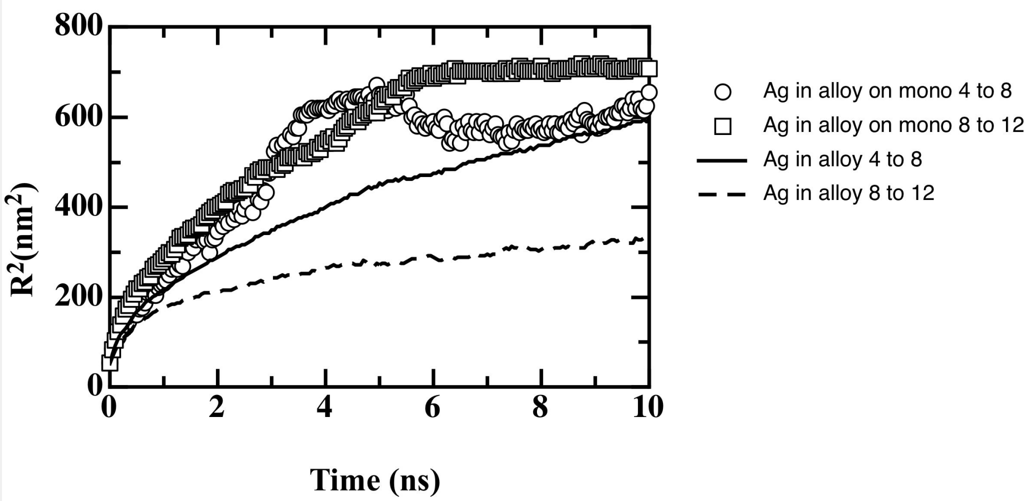
- Very little subsurface spreading (Al circles, Ag down triangles)
- 1st bin (Al squares, Ag solid line) shows slow spreading – reactions slow the first layer
- Precursor foot is from 4 to 8 A (Al up triangles, Ag dotted line)
- Comparing feet
  - Al enhances spreading of Ag
  - Ag inhibits spreading of Al

Increase the Al Content



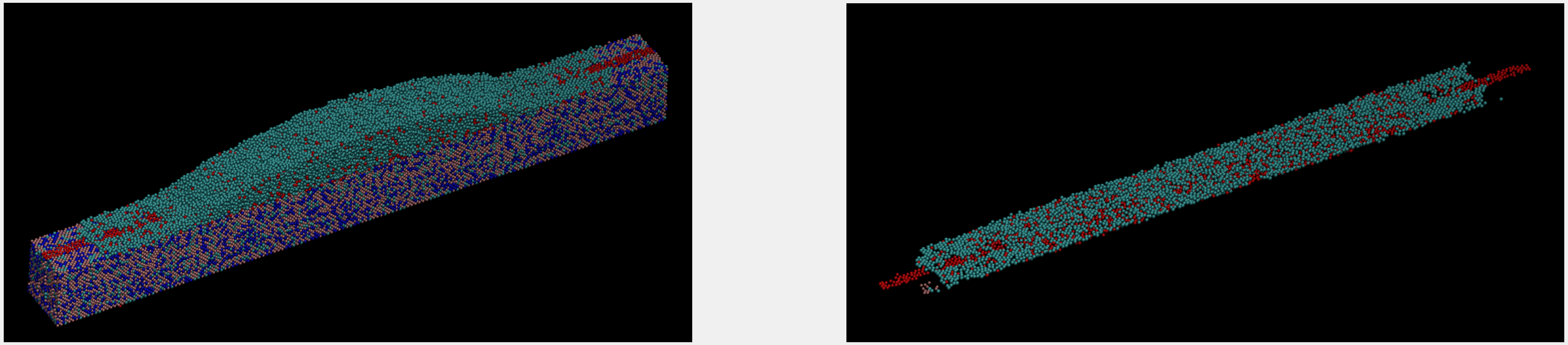
- Examine effects of Al
- Increase alloy content to 70% Ag and 30% Al
- Ag foot shows little change from increase
- Al shows slight increase
- Further increase should result in Al rates approaching pure results

Al is a Troublemaker



- Put down a “prewet” layer of Al
  - Allow pure Al to completely spread on fixed substrate
  - Remove all Al atoms from 0 to 4 A
  - Put on mobile substrate & equilibrate
- Only look at effects on Ag
  - Irregularities in 4 to 8 A bin, so also showing 8 to 12
  - Presence of Al prewetting layer greatly enhances spreading of Al

Discussion



- Al moves quickly to Kovar$^{\mathrm{TM}}$ substrate
  - Seen in experiments and simulations
  - Due partially to surface energy and adhesion

- In all cases, Al enhances spreading of Ag

- Lubrication effect (Popescu, *J. Phys. Condens. Matter* 2012)
  - Unlikely in our case
  - Prewet “stripe” of Al shows no enhancement
  - Ag moves along sides of stripe, implying an interstitial diffusion mechanism

- Comparison between mobile and fixed substrates
  - Pure metals show differences (Ag faster, Al slower on mobile)
  - No change in alloys
  - Contrasts with previous works (Webb, *Scripta Mater.* 2002, *Acta Mater.* 2005)
  - Effects of reactions are system dependent