Center for Advanced
Non-Ferrous Structural Alloys
An Industry/University Cooperative Research Center

Project 22: Formation, High Temperature Stability and Mechanical Properties of Microeutectics in Bulk Solidified Al-Fe-Si-V and Related Alloys

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Project 22: Formation, High Temperature Stability and Mechanical Properties of Microeutectics in Bulk Solidified Al-Fe-Si-V and Related Alloys

- Student: Joe Jankowski (Mines)
- Advisor(s): Michael Kaufman, Amy Clarke (Mines)

Project Duration
PhD: June 2015 to August 2019

Problem

Aluminum alloys with acceptable high temperature structural properties are expensive and difficult to produce.

Objective

Develop high-temperature, high-strength Al alloys without use of rapid solidification by forming stable microeutectic.

Benefit

Reduce production cost and increase selection of high performance high-temperature Al alloys.

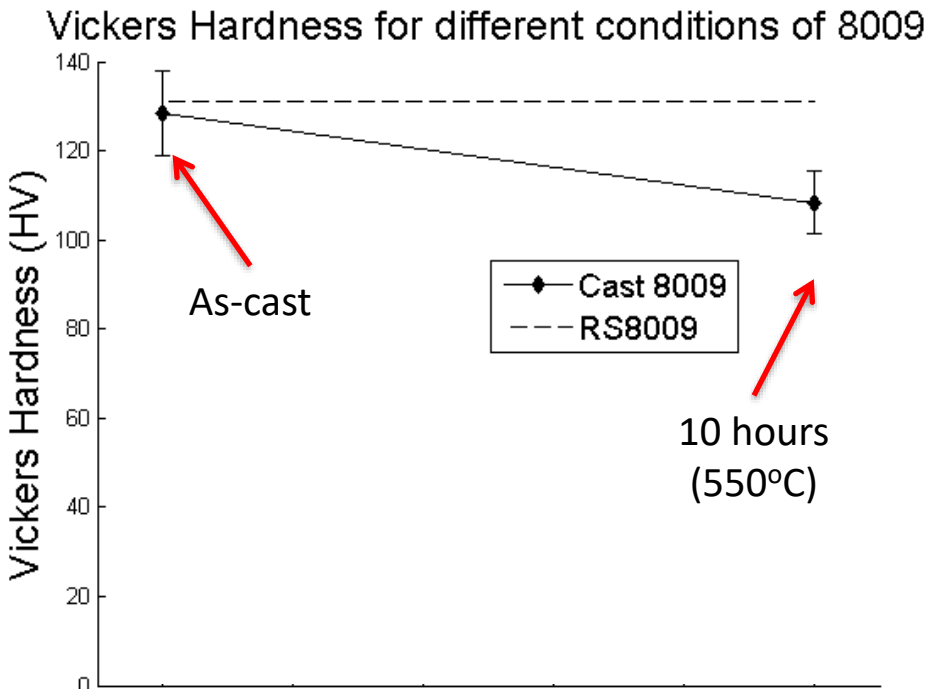
Recent Progress

- Began cooling rate / repeatability analysis
- DSC analysis of Al-Fe-Mn-Cr-Si alloys
- Charge density determination using MEM/Rietveld method

Metrics		
Description	**% Complete**	**Status**
1. Develop experimental protocols for reproducible castings	90%	●
2. Make castings from baseline material to identify key research questions	100%	●
3. Develop crystallography / phase stability knowledge of α-phase	50%	●
4. Assess ability to produce microeutectic in chill castings	50%	●
5. Determine how fundamental solidification parameters affect microeutectic formation	5%	●

Project Motivation

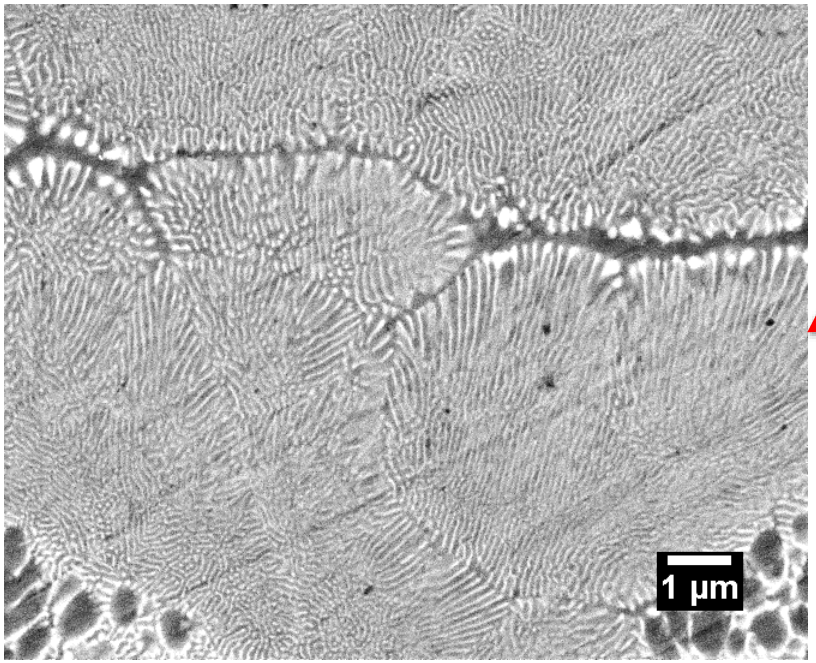
- Microeutectic between Al and α-$Al_{13}(Fe,V)_3Si$ in chill castings
- Hardness of microeutectic similar to RS8009
- Lower cooling rate than rapidly solidified alloys
  - Lower cost of production
- Potential high-temperature Al structural alloy

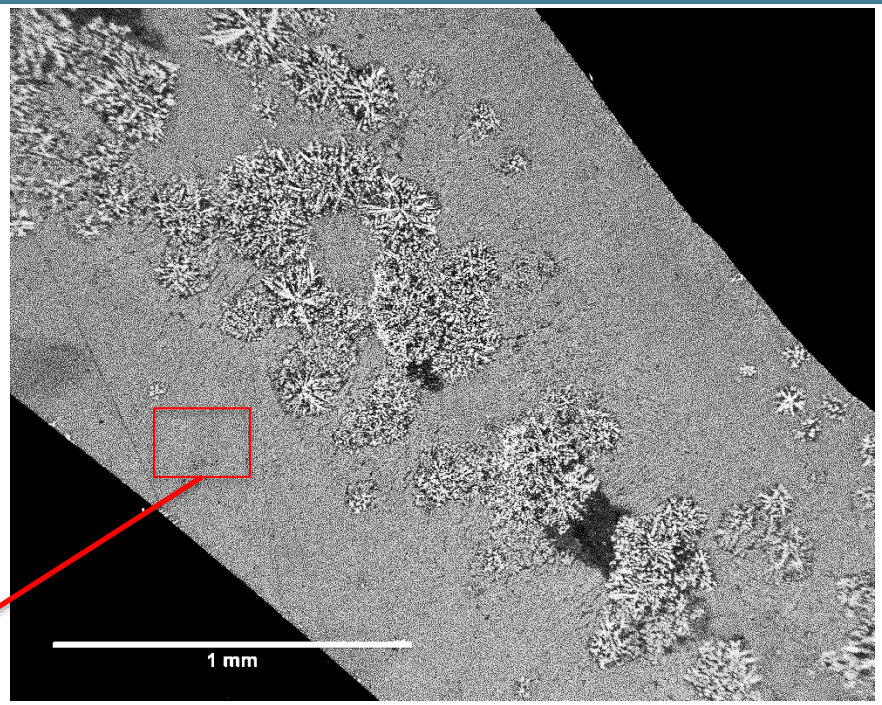


Alloy	Al (at%)	Fe (at%)	V (at%)	Si (at%)
RS8009	Bal.	4.3	0.7	1.7

Background

- Most of the literature examines cooling rates <10 K/s or >10^4 K/s for this alloy
- Present study looks at cooling rates between 10^2 K/s and 10^3 K/s

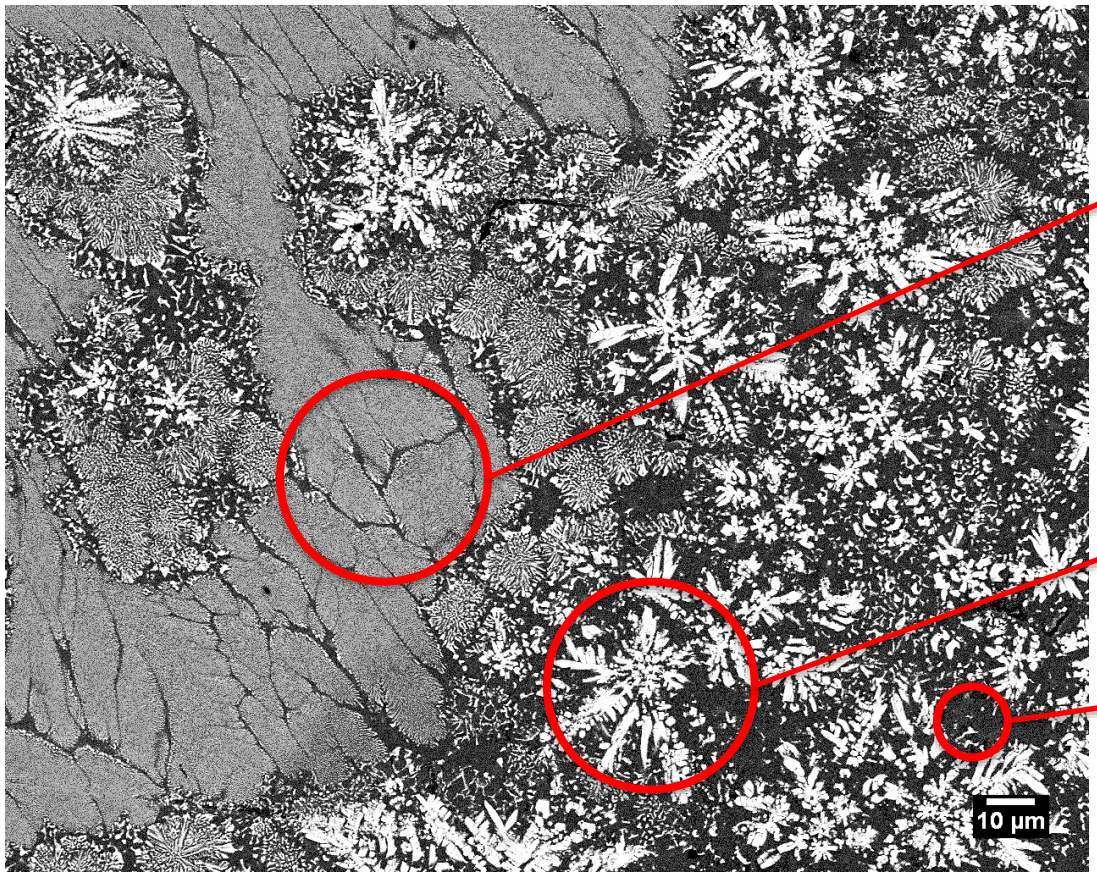




- Lamellar microeutectic microstructure in as-cast condition
- Potential application as lightweight high temperature structural alloy

Background

Morphology of phases in chill cast 8009

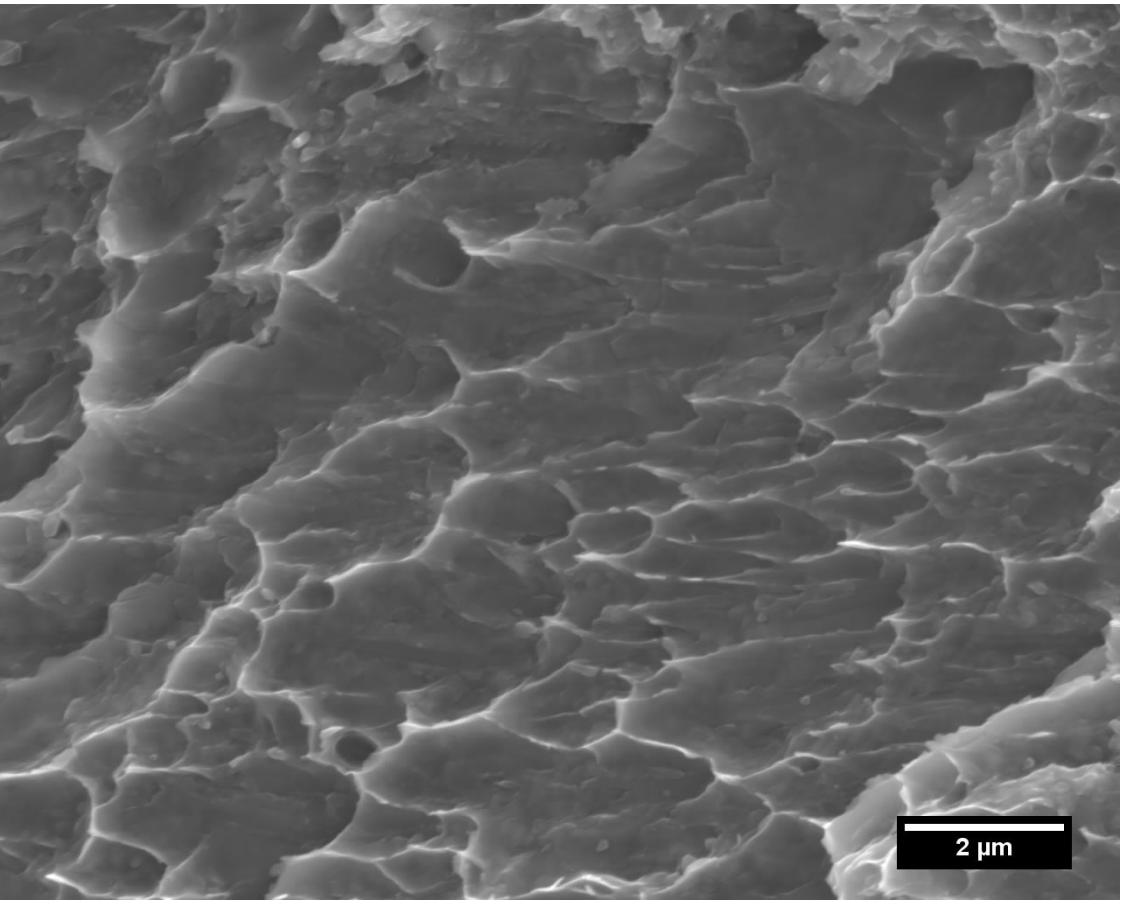


Microeutectic (FCC Al + BCC $Al_{13}(Fe,V)_3Si$) α-phase

Hexagonal $Al_{13}(Fe,V)_3Si_{0.3}$ h-phase

Al dendrites + interdendritic phases

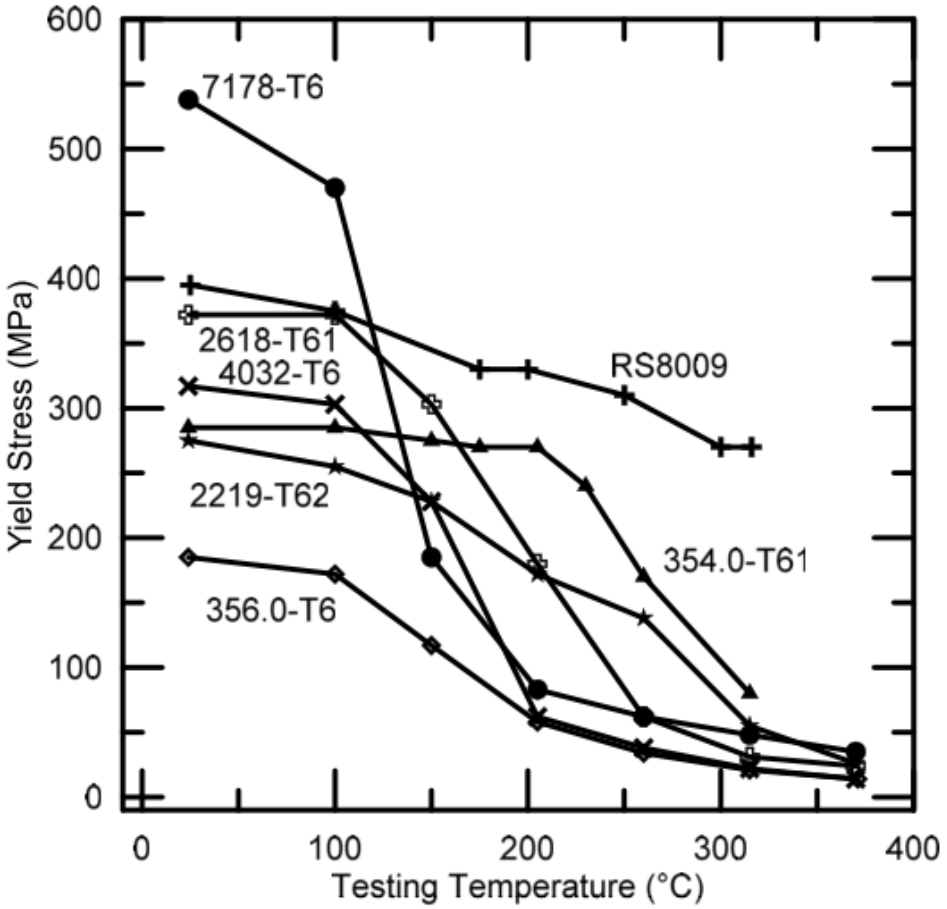
Background



- Microeutectic fracture surface
- Dimpled surface
- Indicative of ductile fracture

Industrial Relevance

- Development of a lower cost high-temperature Al structural alloy
- Identify alternative processing routes for high-temperature Al alloys
- Rapid screening of composition space for nonequilibrium systems



Mechanical properties of selected Al alloys (RS8009 is high-temperature alloy)

Marshall, R. (2016). Master's Thesis.

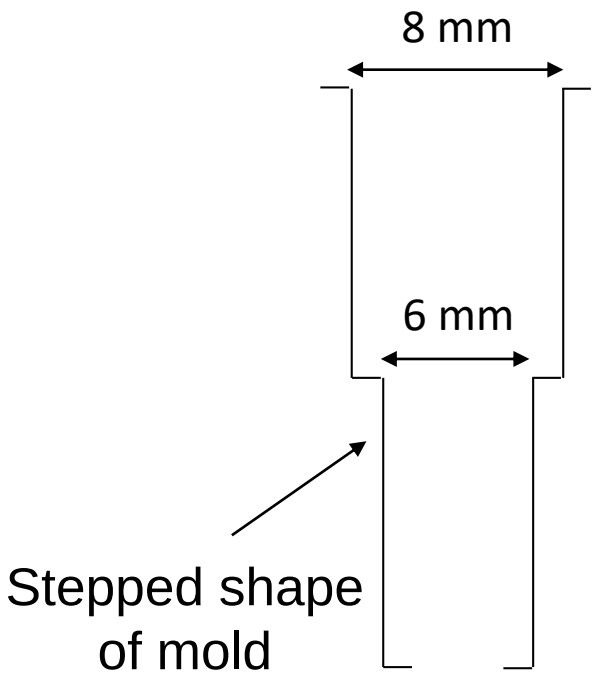
Presentation Overview

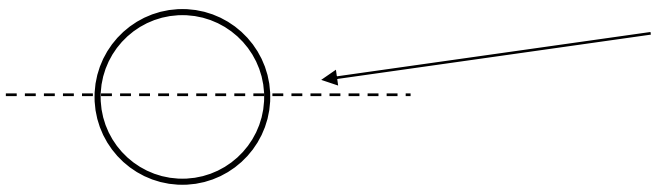
- Recent Progress
  - Cooling Rate / Repeatability
  - Differential Scanning Calorimetry (DSC)
  - MEM/Rietveld Charge Density

- Future Work
  - Proposal Topics

Early Repeatability Testing

- Tested repeatability of castings
  - 4 at a fixed composition
  - Etched with Keller's reagent to highlight different constituents

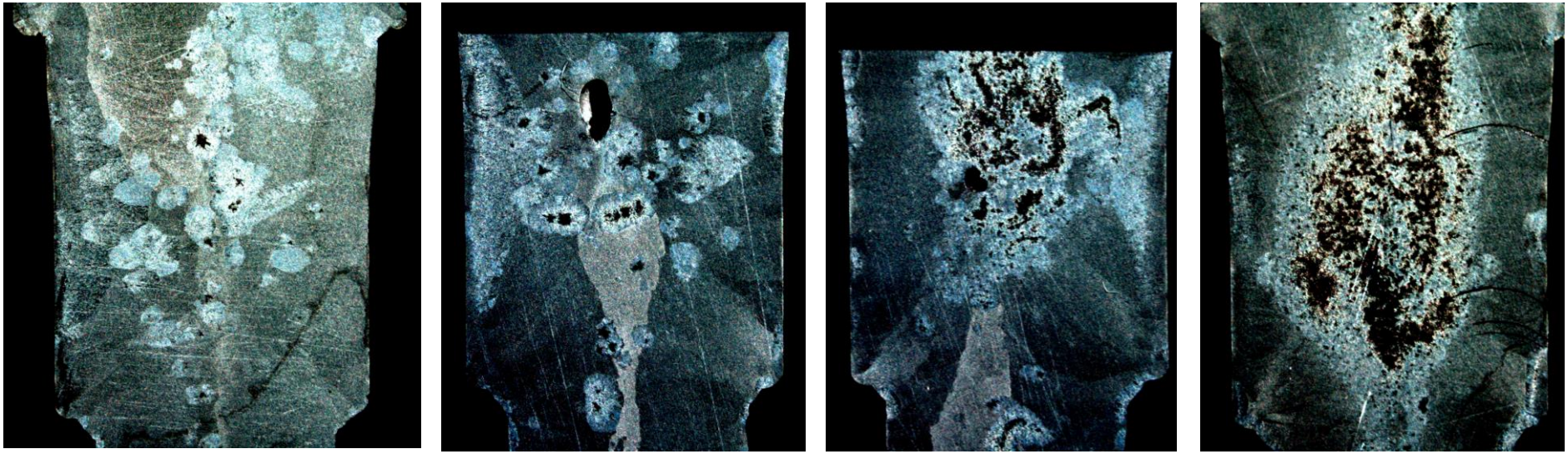




Al (at %)	Fe (at %)	Mn (at %)	Cr (at %)	Si (at %)
Bal.	1.5	1.5	0.4	2.0

Early Repeatability Testing

Four castings of the same Al-Fe-Mn-Cr-Si alloy using old procedure (8 mm diameter)



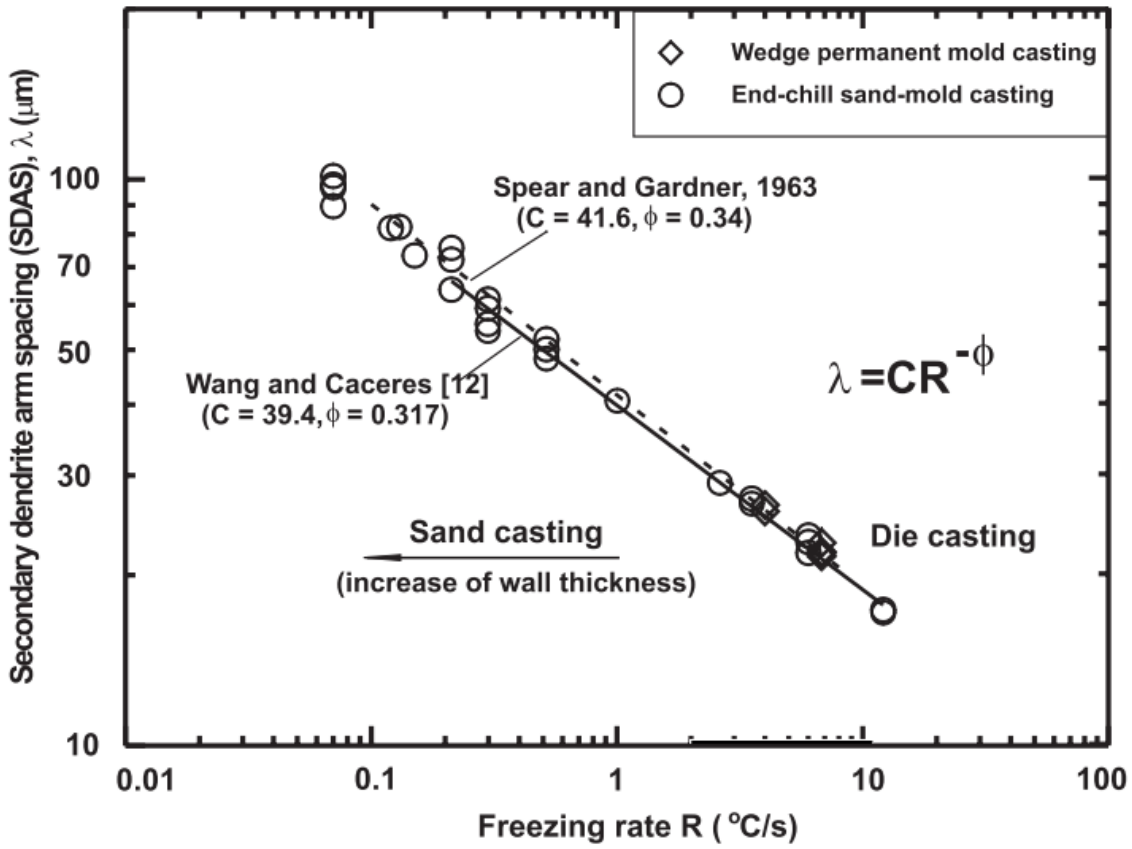
- Used indirect melt temperature measurement
  - Changes in superheat between castings
  - Melt temperature not linked to physical parameter
- Lack of consistent as-cast structure

Current Repeatability Study

- Use 356 as test alloy
- Experimental determination of cooling rate
  - Using secondary dendrite arm spacing (SDAS)
- Focus on developing a reproducible protocol
  - Superheat
  - Direct measurement of melt temperature
- Cast at 100 °C above liquidus of 356 (720 °C)

SDAS and Cooling Rates

- Correlation extends to rapid solidification cooling rates
- Some inherent scatter
- Sensitive to Si content

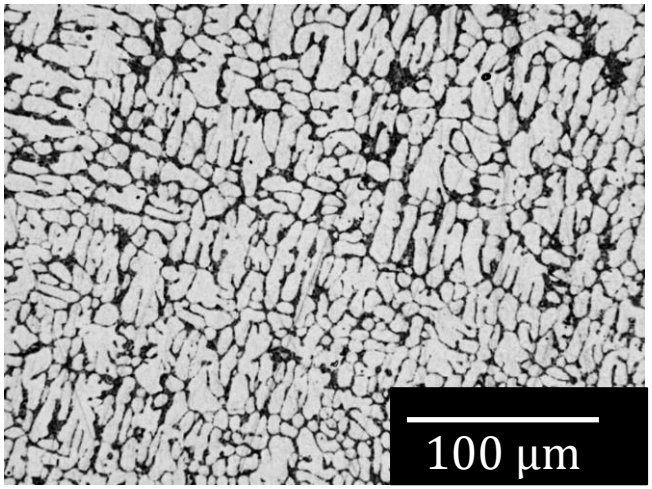


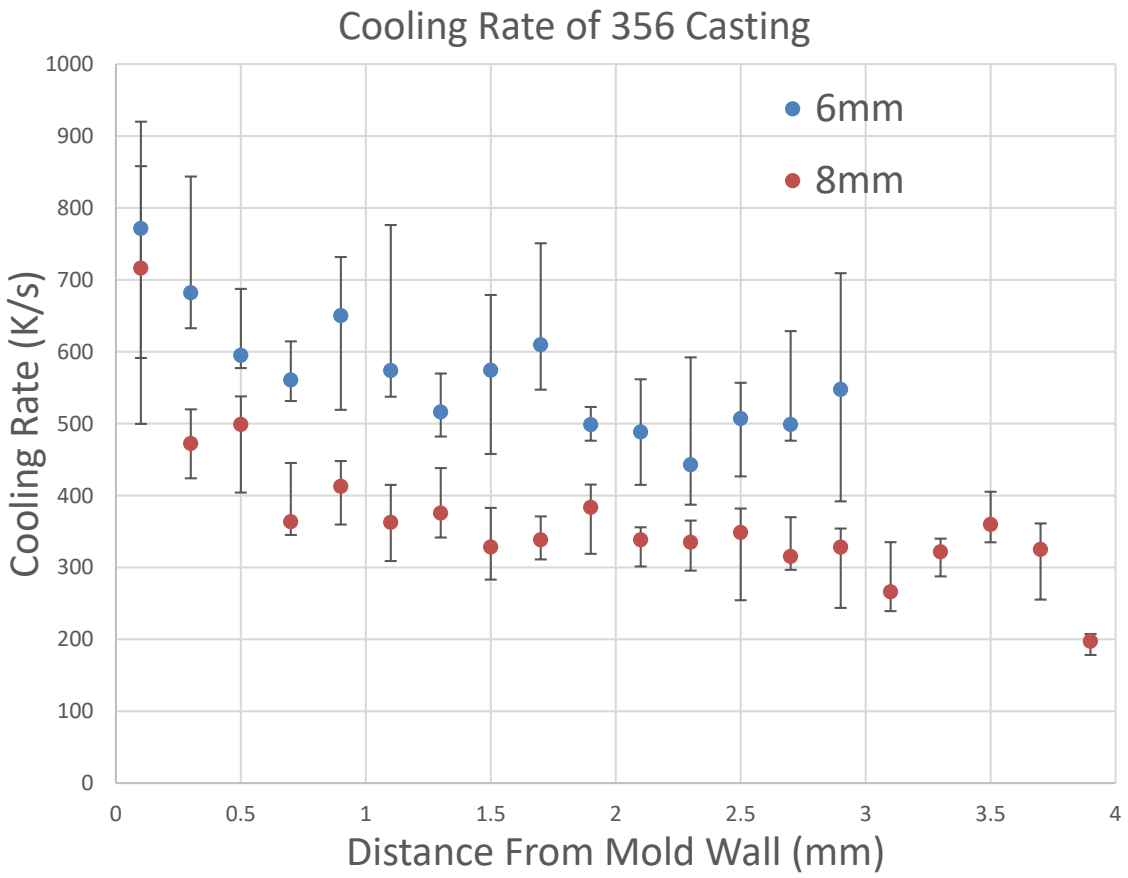
Correlation between SDAS and Cooling Rate for A356/357

Q.J. Wang *et al* (2001). *Journal of Light Metals*.

Cooling Rates in Castings

- A356.2 castings
- Data points are median
- Error bars are quartiles





DSC Motivation

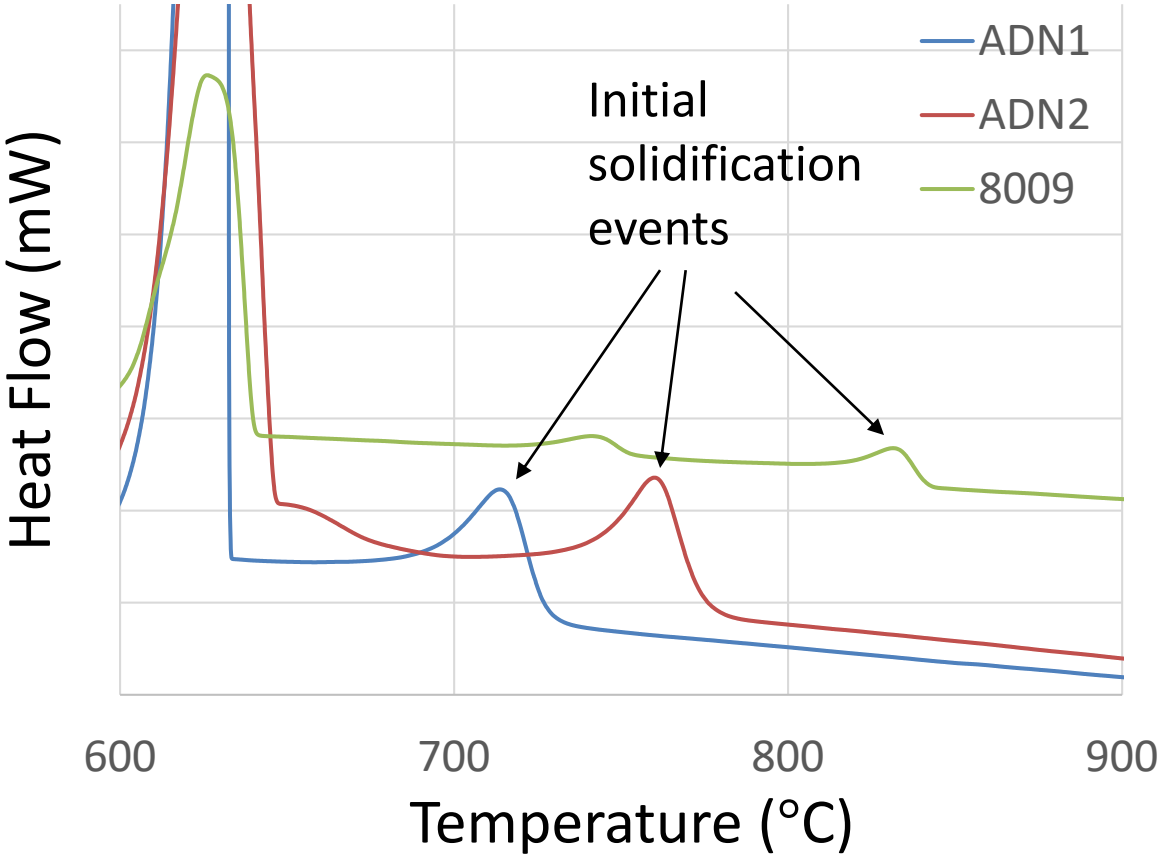
- Current goal of alloying is to reduce equilibrium liquidus temperature
  - Reduce superheat
  - Increase undercooling

ADN1 = 3.4 at% TM
ADN2 = 4.5 at% TM
8009 = 5.0 at% TM

- Assess liquidus of new compositions vs. 8009

	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	V (at%)	Si (at%)
ADN1	Bal.	1.5	1.5	0.4	n/a	2.0
ADN2	Bal.	2.0	2.0	0.5	n/a	2.7
8009	Bal.	4.3	n/a	n/a	0.7	1.7

Liquidus of ADN1 vs. ADN2 vs. 8009



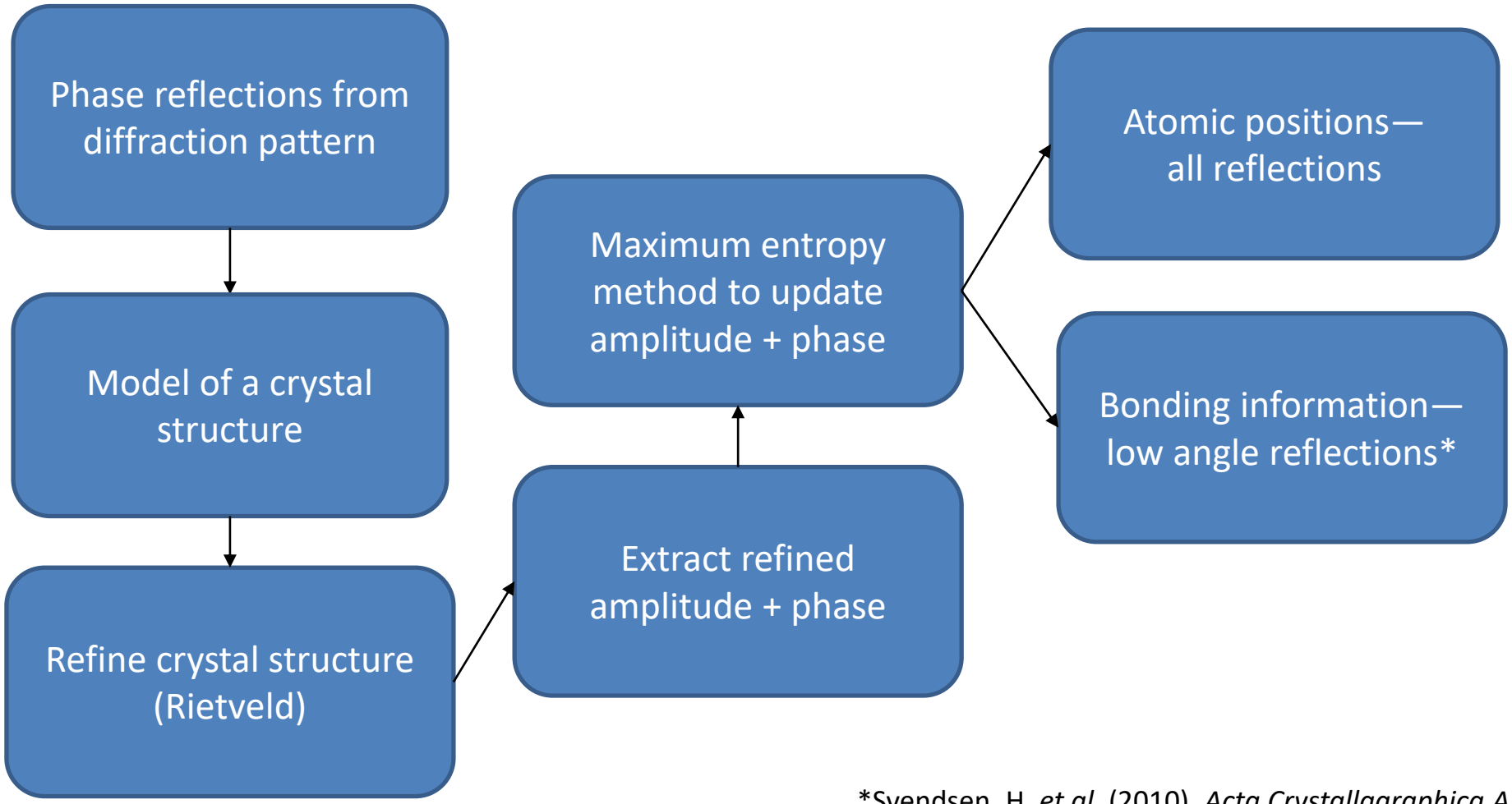
ADN1 = 3.4 at% TM
ADN2 = 4.5 at% TM
8009 = 5.0 at% TM

Alloy	Liquidus (Experimental)	Liquidus (Thermo-Calc)
ADN1	~725 °C	725 °C
ADN2	~775 °C	758 °C
8009	~850 °C	852 °C

MEM / Rietveld Method

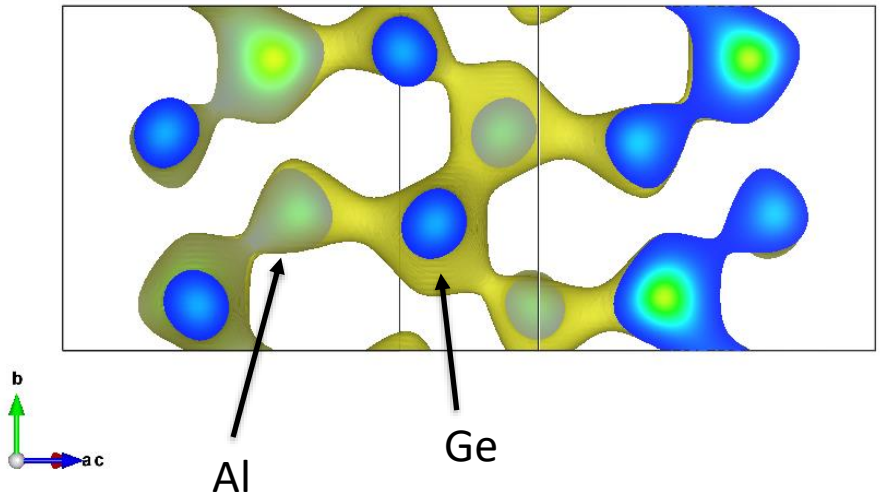
- Can be used to determine charge density
  - From diffraction experiments
- Bonding information
- Atomic positions
- Use to improve DFT predictions
  - α-phase/alloy composition
  - Charge density validation

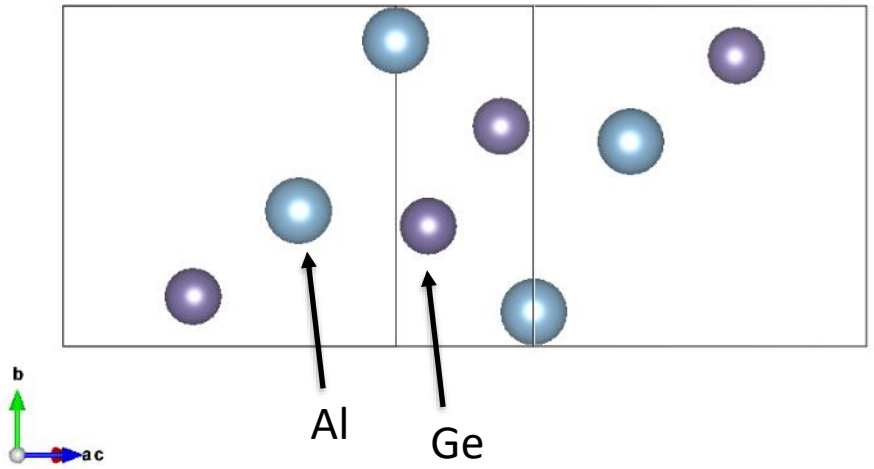
MEM / Rietveld Method



*Svendsen, H. *et al*. (2010). *Acta Crystallagraphica A.*

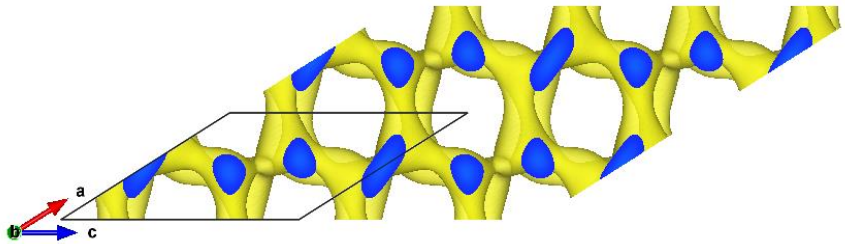
Example Charge Density (Al-Ge)

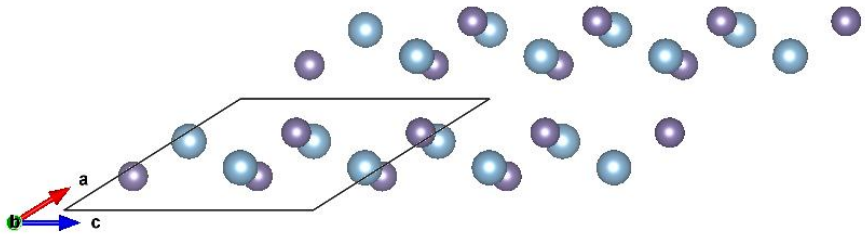




Light blue = Al
Purple = Ge

Qualitative agreement with DFT results!





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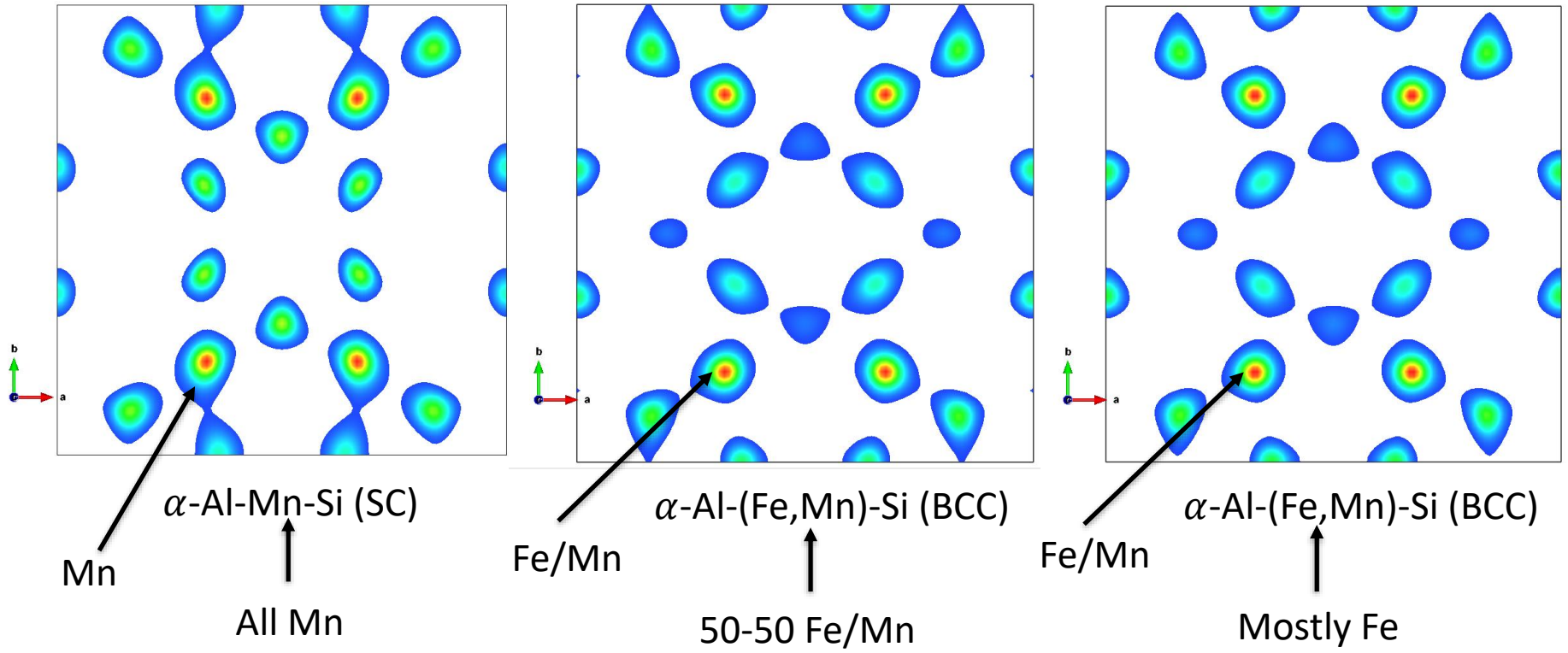
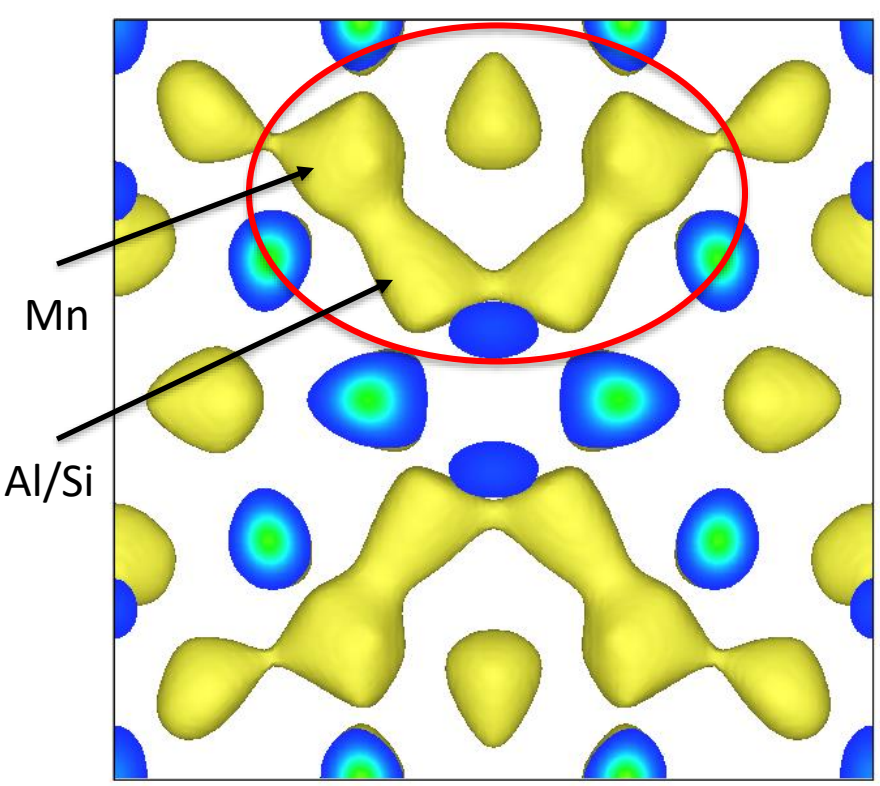
Example Charge Density (α-Phase)

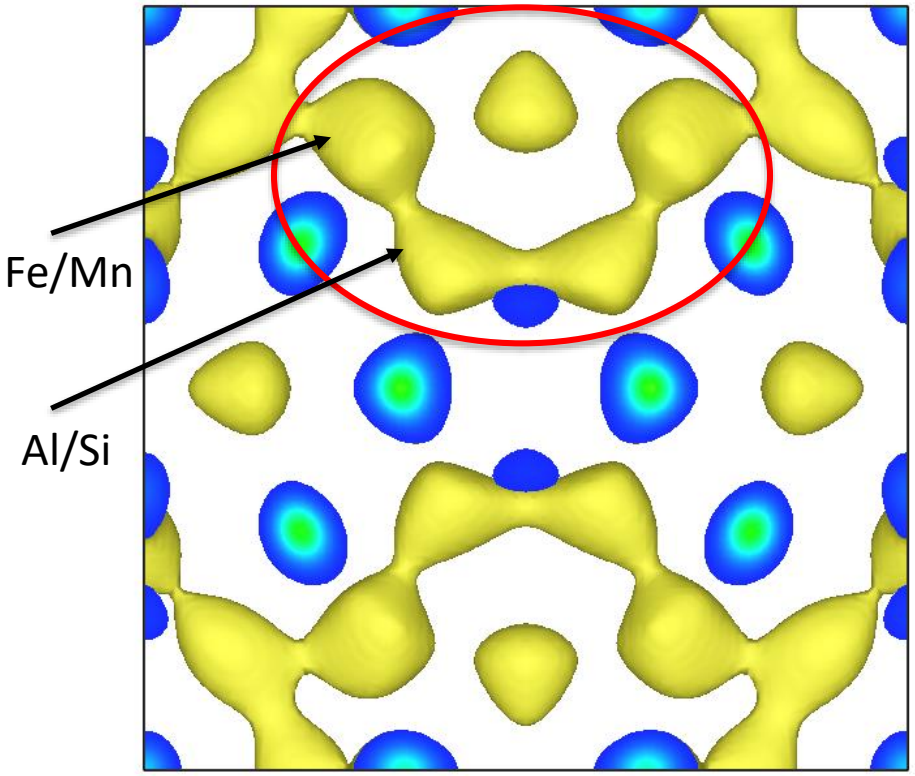


Charge densities in 100 plane for α-Al-(Fe,Mn)-Si (experimental)

Charge Density (α-Phase)



α-AlMnSi

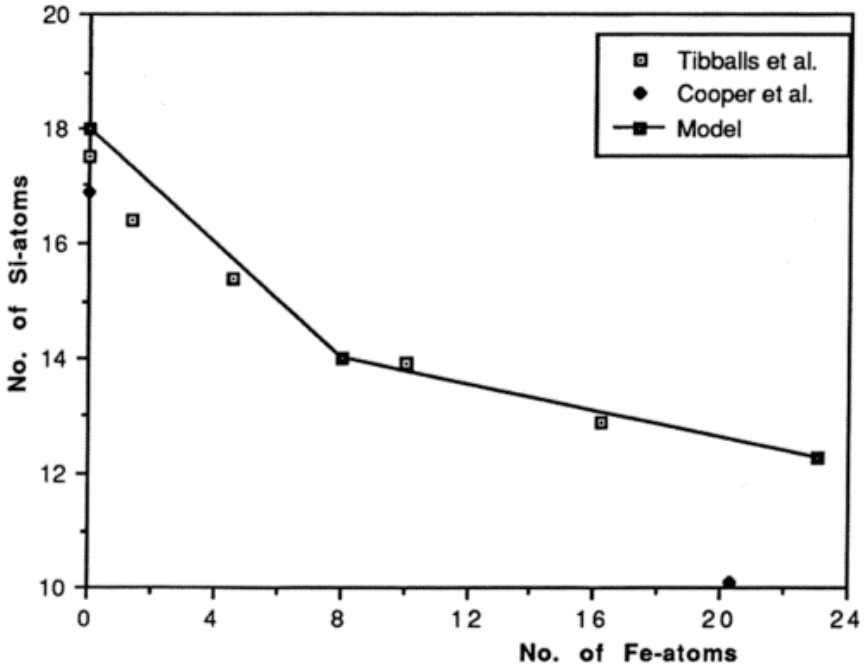


α-Al(Fe,Mn)Si

Visible change in charge density of TM-(Al,Si) bonds, can be used in conjunction with DFT to fully determine crystal structure

MEM/Rietveld Progress

- Samples for ~9 compositions of α-phase prepared
  - 3 Al-Fe-Mn-Si
  - 3 Al-Fe-Cr-Si
  - 3 Al-Fe-V-Si
- Use for detailed crystallographic analysis
  - Determine actual structure



- Will allow for full compositional prediction from DFT
  - Transition metals and Si
  - Si content of α-phase varies from <6% to ~13%

Simensen and Bjornklett (2016).

Proposed Work

- TIG welding study
- Microstructure / cooling rate study
- DFT calculations
- B addition study
- Mechanical properties

TIG Welding

- Perform autogenous TIG welds on plates
- Controlled solidification velocity
  - Tie microeutectic formation to fundamental solidification behavior
- Use SYSWELD modeling to design experiment
  - Plate dimensions
  - Arc power
  - Weld speed

Microstructure / Cooling Rate

- Build off of 356 cooling rate study
- Link cooling rate, composition, and microstructure in chill mold
- Do for several alloys
  - Al-Fe-Mn-Cr-Si or (Al-Fe-Mn-V-Si)
  - 3.5 to 5.0 at % transition metals
- Assess ability to form microeutectic in chill mold

Alloy	Al	Fe	Mn	Cr	V	Si
~3.5 at% TM	Bal.	1.5 (1.6)	1.5 (1.6)	0.4 (n/a)	n/a (0.2)	2.0
~4.0 at% TM	Bal.	1.8 (1.9)	1.8 (1.9)	0.5 (n/a)	n/a (0.2)	2.3
~4.5 at% TM	Bal.	2.0 (2.1)	2.0 (2.1)	0.6 (n/a)	n/a (0.3)	2.6
~5.0 at% TM	Bal.	2.2 (2.4)	2.2 (2.4)	0.7 (n/a)	n/a (0.3)	2.9

New DFT Calculations

- Use MEM/Rietveld method to determine crystal structure of α-phase
  - Al-Fe-Cr-Si
  - Al-Fe-V-Si
  - Al-Fe-Mn-Si
- Characterize bonding and Si atomic positions
- Use to perform high accuracy DFT modeling
  - Predict full phase composition

DFT Composition Prediction

Already completed

Workflow

DFT → $TM_{\alpha}=aFe+bMn+cCr+dV$, a, b, c, d given by DFT, Si unknown

Produce compositions using rules from DFT

experiment → Si content as f(Fe, Mn, Cr, V) in select quaternaries from WDS

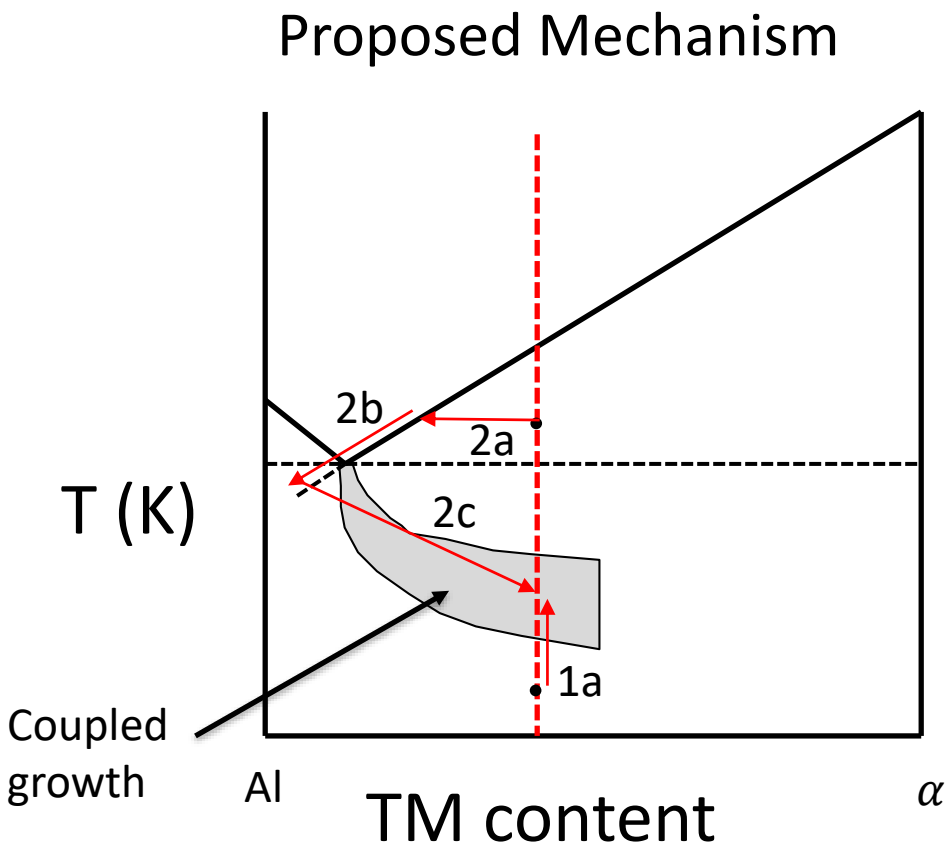
Use MEM/Rietveld to determine Si atomic positions

DFT → Calibrate simulations using quaternary results

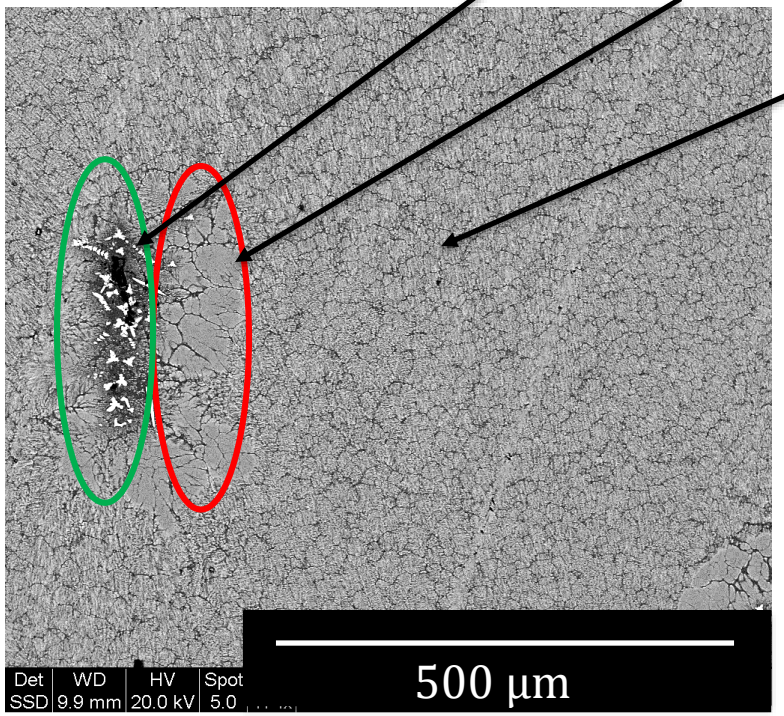
Use DFT to predict possible compositions including Si content

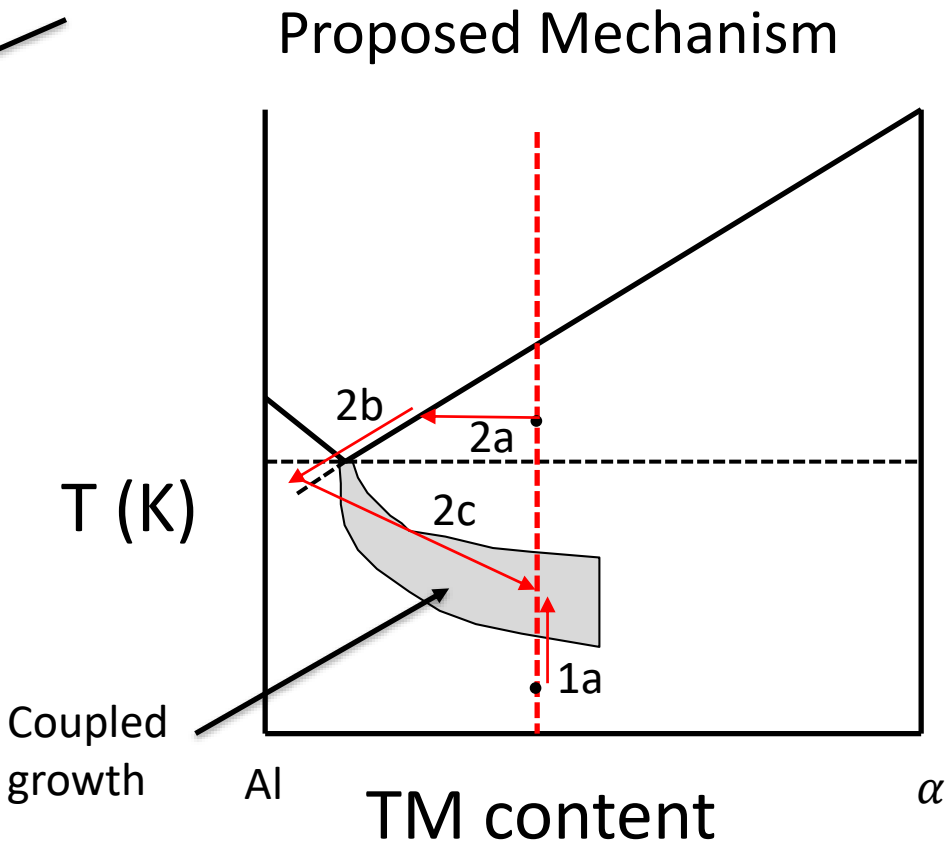
B additions

- Observed to promote primary α-phase nucleation
  - In Cr, V, Mo containing alloys
- May promote microeutectic formation
  - Vs. dendritic Al + microeutectic
- 2 apparent solidification pathways
  - For Al + α-phase alloys

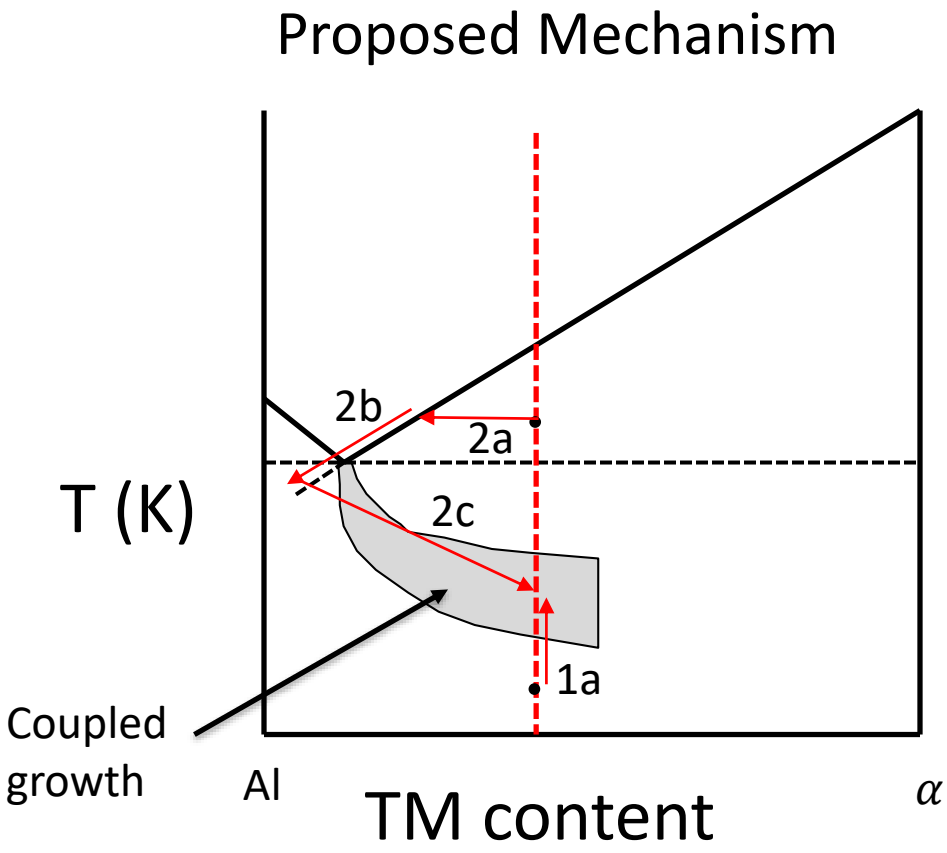


As-Cast Microstructure





B Addition Goal



1a) liquid undercools enough to nucleate Al, grows as primary Al dendrite until undercooling decreases

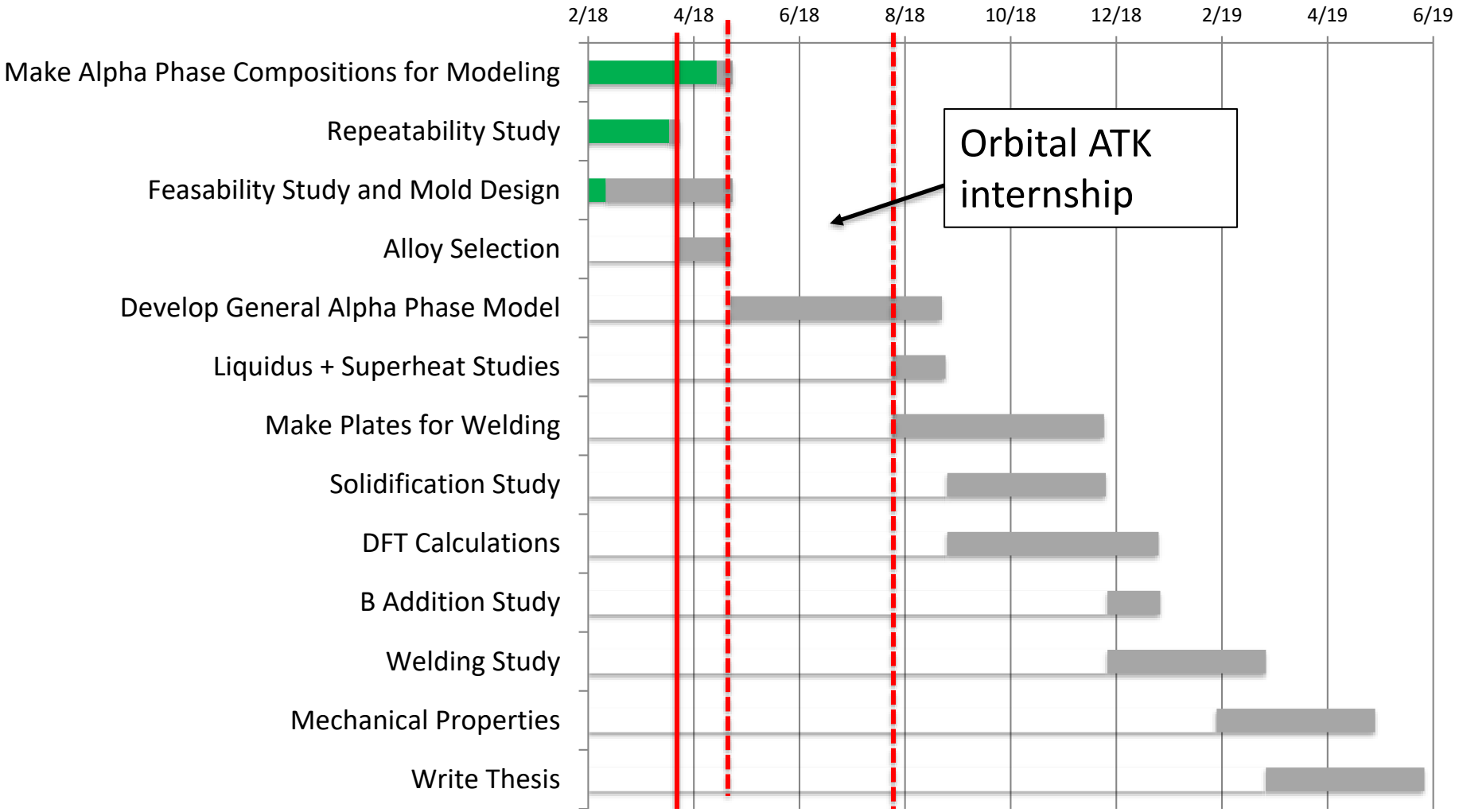
2a) primary α-phase particle forms
2b) primary α-phase in local equilibrium with liquid
2c) local liquid undercooled, nucleates Al and grows out into coupled growth region

B addition may promote second pathway, reduce undercooling required

Mechanical Properties

- Quantify properties of microeutectic
- Method depends on success in producing microeutectic
  - Hardness/microhardness
  - Compression
  - Tension
- Goal is to test at room temperature and elevated temperature (300 °C)

Gantt Chart



Questions/Discussion

Thank you!

Joe Jankowski

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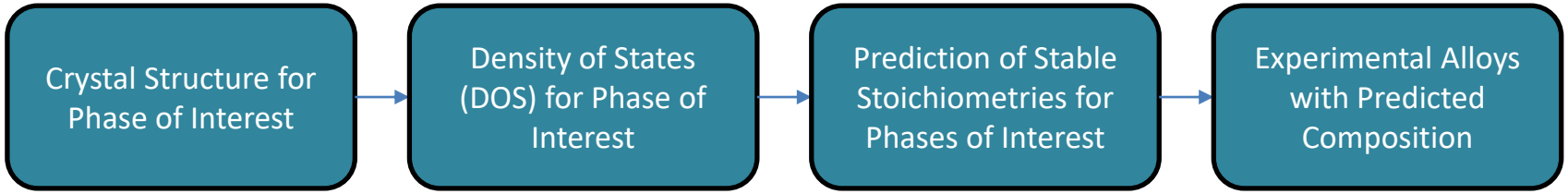
Alloying Strategy



- From literature or diffraction
- For this study, α-phase

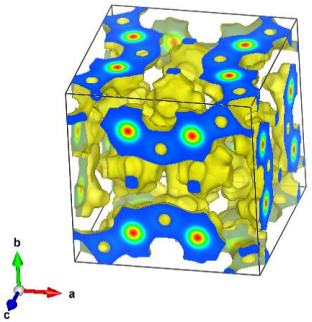
- Reference experimental composition
- Unknown theoretical compositions

- Compare theoretical DOS to reference DOS
- Apply "maximum bonding criterion"

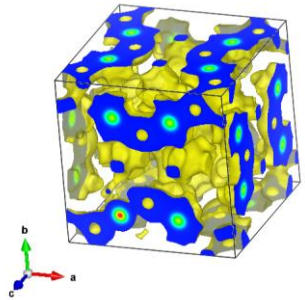
- Predict ratio of transition metals
- Refine stability criteria

Why Density of States?

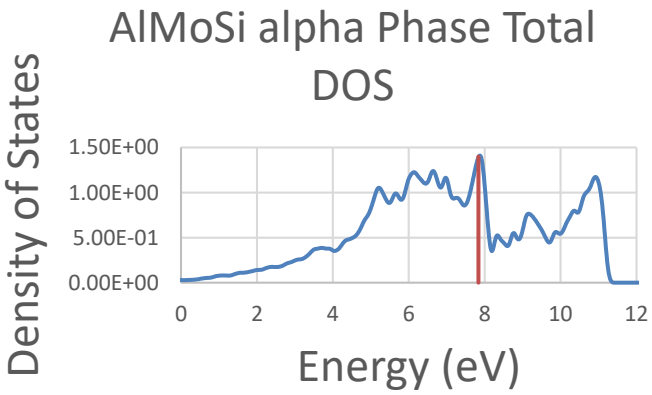
- Relatively inexpensive calculation
  - Large unit cells for α and h-phase
  - Easier to get useful DOS vs. enthalpy/charge density
- Based on actual physics of system (vs. e/a approach)
- Intuitive visual representation of bonding interactions in 2D

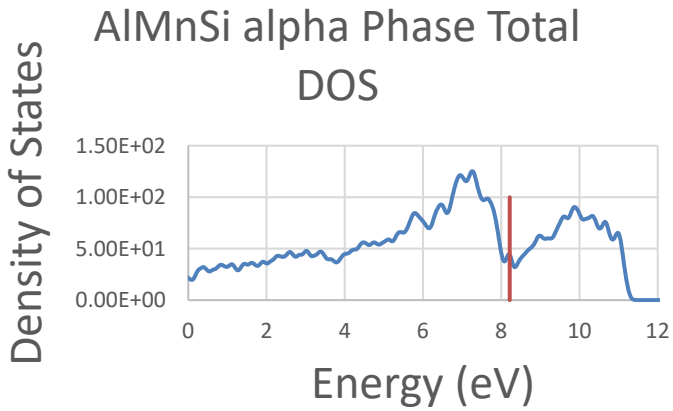


α-AlMoSi charge density (bonding)



α-AlMnSi charge density (bonding)





Calculation Results

- Ti, V, Cr too few electrons
- Fe, Co, Ni, Cu too many electrons
- Co, Ni, Cu have shallow pseudogap
  - Weak bonding interaction
  - Not expected to form α-phase

α-AlXSi ternary phase	Area under curve from "stable" to calculated Fermi level	Deep pseudogap
Ti	-245	Yes
V	-117	Yes
Cr	-49	Yes
Mn	0 (reference)	Yes
Fe	22	Yes
Co	120	Borderline
Ni	145	No
Cu	130	No

Predictions vs. Reality

- Al-Fe-V-Si and Al-Fe-Mn-Cr-Si verified by chill castings
- Others verified under equilibrium conditions (XRD + EDS)
  - First time Al-Fe-Cr-Si observed in equilibrium*
- Co not expected to form α-phase due to low d-band energy
- DFT useful for downselecting possible composition space
  - Not exact, but identifies useful design space

Alloy System	Expected to form?	α-phase?
Al-Fe-V-Si	Yes	Yes
Al-Fe-Cr-Si	Yes	Yes
Al-Co-Ti-Si	No	No
Al-Co-Cr-Si	No	No
Al-Fe-Mn-Cr-Si	Yes	Yes

**Processing of Structural Metals by Rapid Solidification*. (1986).