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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

Fall 2018 Semi-Annual Meeting
Colorado School of Mines, Golden, CO
October 2-4, 2018

Student: Joe Jankowski (Mines)
Faculty: Michael Kaufman, Amy Clarke, Robert Field, Steve Midson (Mines)
Industrial Mentors: Krish Krishnamurthy (Honeywell), Paul Wilson (Boeing)

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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- Student: Joe Jankowski (Mines)
- Advisors: 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

- Analysis of synchrotron x-ray diffraction on α-phase
- Electron microprobe analysis of α-phase
- Chose final alloy system
- Liquidus characterization

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

Project Motivation

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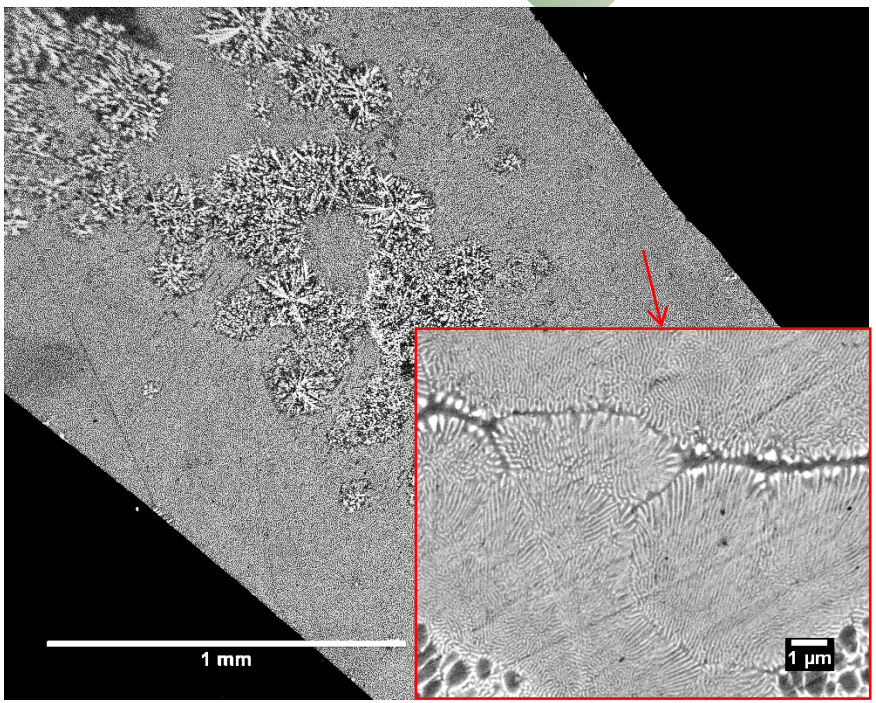
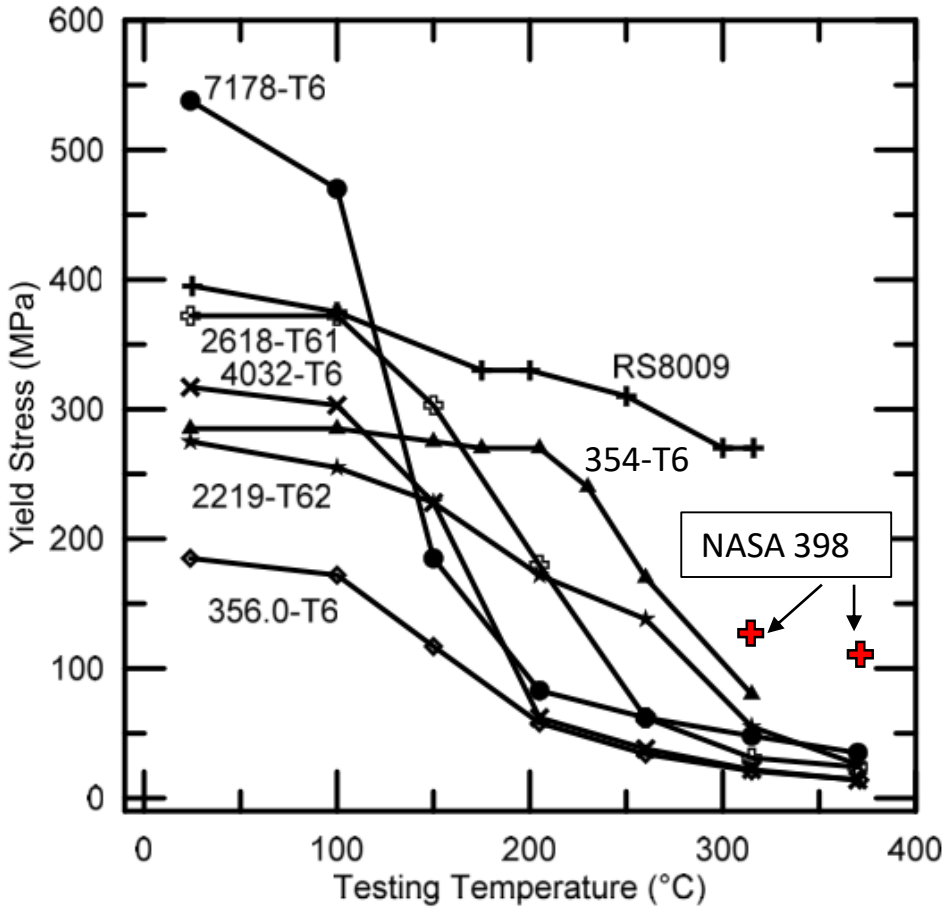
- Microeutectic between Al and α-$Al_{13}(Fe,V)_3Si$ in chill castings
- Hardness of microeutectic similar to RS8009
- Lower cooling rate than rapidly solidified alloys
  - 10^2-10^3 K/s vs. 10^4-10^6 K/s
- Potential high-temperature Al structural alloy



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

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)

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

Presentation Overview

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- Prior Work
- Recent Progress
- Project Timeline

Prior Work

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Goal: Develop alloy with high volume fraction of microeutectic constituent, improve understanding of system

Completed work

- Structure determination of deleterious h-phase using powder diffraction
- Develop method of using density functional theory (DFT) to screen compositions
- Experimental validation of DFT
- Determination of cooling rates in Cu chill mold

h-Phase Crystal Structure

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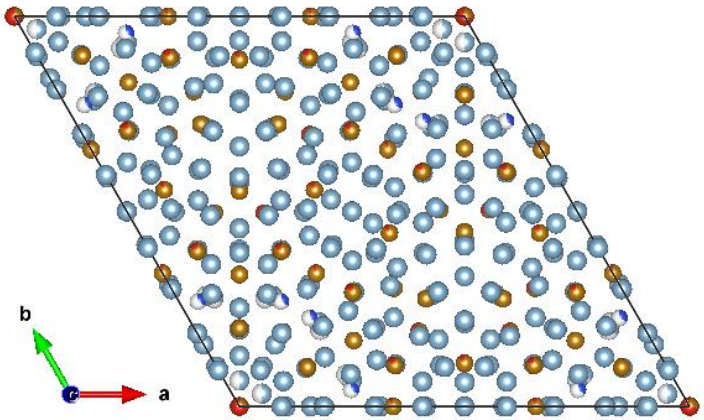
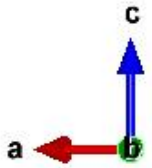
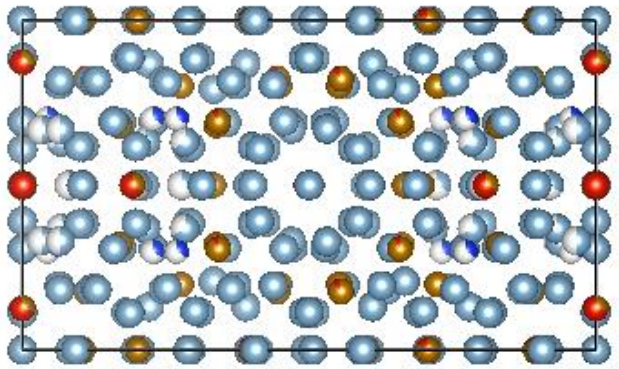
- Most complex intermetallic crystal structure solved by powder diffraction, ~472 atoms per unit cell, 4 different elements present

- Used synchrotron x-ray and neutron powder diffraction







DFT Composition Screening

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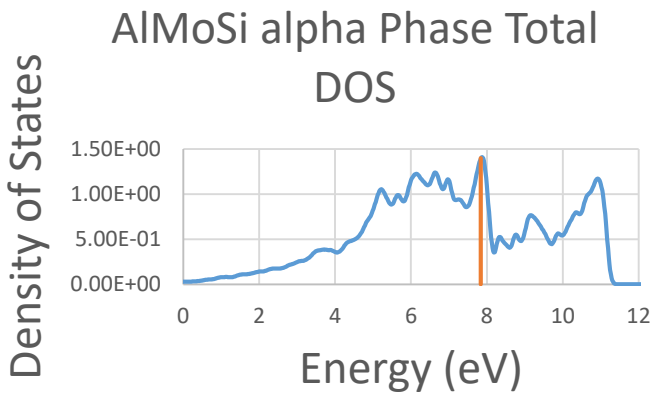
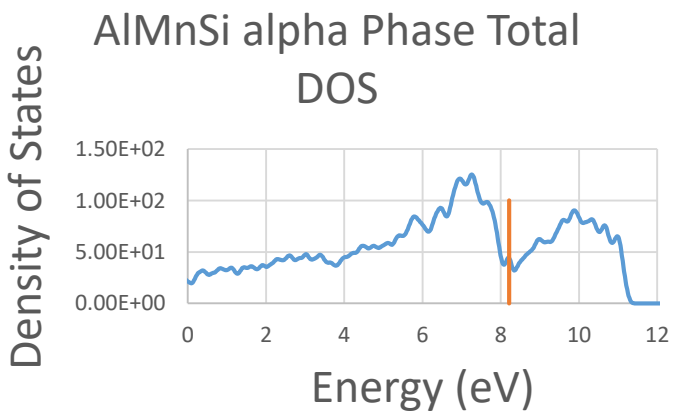
- Density of states (DOS)
  - Relatively inexpensive calculation
  - Large unit cells for α and h-phase
  - Easier to get useful DOS vs. enthalpy/charge density
- Based on actual physics of system
- Intuitive visual representation of bonding interactions in 2D

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





DFT Validation

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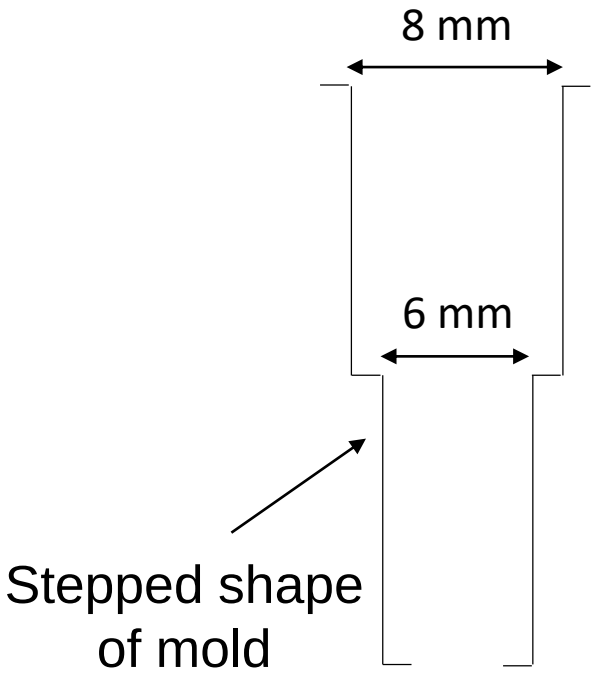
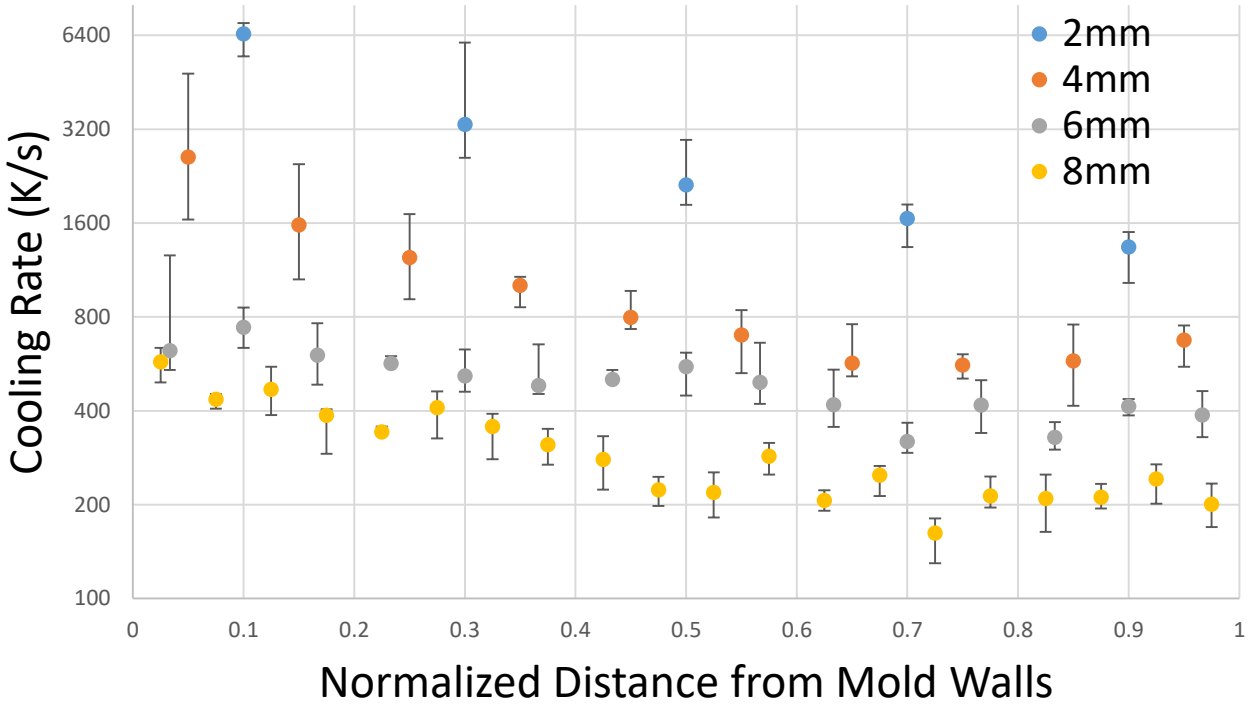
- Method assesses possibility, does not determine if something will actually form
- Best for extrapolation from known system, for example Al-Fe-V-Si
- Results for α-phase are promising
- Potential to accelerate alloy design in **all metallic systems**

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

Cu Chill Mold Cooling Rates

- Measure of repeatability
- Indicative of solidification conditions
- Evidence cooling rates are between 10^2 and 10^3 K/s





Recent Progress

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- Synchrotron results for α-phase
- Microprobe results for α-phase
- Choice of final alloy system
- Liquidus characterization of alloy system

Synchrotron X-ray Diffraction

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Goal: Determine if crystallography of α-phase is consistent between quaternary systems (Al-Fe-V-Si, Al-Fe-Mn-Si, Al-Fe-Cr-Si)

- Looked at as-cast and heat-treated conditions
- Al-Mn-Si, Al-Fe-Mn-Si, Al-Fe-Cr-Si, and Al-Fe-V-Si samples
- MEM/Rietveld method used to analyze results

Nominal Compositions

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	Al	Si	Fe	Mn	Cr	V	B
AlMnSi	69.6	13		17.4			
Al(Fe,Mn)Si	73.3	9.3	11.7	5.7			
Low-V casting	92.9	3.5	3.0			0.5	0.1
High-V casting	92.9	3.5	2.8			0.7	0.1
Low-Cr casting	92.9	3.5	2.4		1.1		0.1
High-Cr casting	92.9	3.5	2.0		1.5		0.1

- B added as inoculant
  - Unknown effectiveness in V-containing samples
- AlMnSi and Al(Fe,Mn)Si synthesized at nominal composition of α-phase
- Dissolved Al matrix for Cr,V-containing samples

Rietveld Refinement Results

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	R Values				Lattice Parameters		
	R_{wp}	$R_{F,\alpha}$	$R_{F,\alpha'}$ *	$R_{F,\alpha''}$ **	a_{α} (nm)†	$a_{\alpha'}$ (nm)*	$a_{\alpha''}$ (nm)**
AlMnSi	9.91%	4.01%			1.266		
Al(Fe,Mn)Si	18.61%	5.79%			1.258		
Low-V as-cast	7.98%	~2.5%	3.35%	2.64%	1.265	1.252	1.257
Low-V heat-treated	8.78%	1.95%	2.25%	2.31%	1.257	1.261	1.254
High-V as-cast	8.07%	1.99%		1.81%	1.253		1.256
Low-Cr as-cast	9.82%	3.56%	6.66%	6.77%	1.266	1.253	1.258
Low-Cr heat-treated	12.73%	2.39%		4.61%	1.262		1.255
High-Cr as-cast††	8.66%	2.36%		3.07%	1.269	<1.259	1.259

* α' refers to a second α-phase compositionally and structurally distinct in the primary particles from the majority phase

** α'' refers to interdendritic/eutectic α-phase

† α-phase in multiphase samples defined as majority α-phase constituent

†† α' lattice parameter not accurately determined

Rietveld Refinement Results

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	Al	Si	$Al_9Fe_2Si_2$	Al_9Mn_3Si	$Al_{10}V$	h	α	α' *	α'' **	unknown present
AlMnSi		0.2		7.1			92.7			
Al(Fe,Mn)Si	1.8	0.1					98.1			yes
Low-V as-cast	4.5	6.0				9.1	29.3	30.2	20.8	
Low-V heat-treated	6.2	3.6	14.4			4.9	46.5	11.1	13.2	
High-V as-cast	19.3	2.3	3.3		0.9	11.2	34.6		28.4	
Low-Cr as-cast		8.8					57.6	8.7	24.8	yes†
Low-Cr heat-treated	5.9	3.0	3.7				76.9		10.0	yes†
High-Cr as-cast	9.1	3.5					63.2		24.3††	yes†

* α' refers to a second α-phase compositionally and structurally distinct in the primary particles from the majority phase

** α'' refers to interdendritic/eutectic α-phase

† Present only in small quantities

†† α'' includes contribution from α' due to difficulties fitting the pattern

Microprobe

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Goal: Obtain spatially resolved compositional information to complement diffraction experiment

- Looked at as-cast and heat-treated conditions
- Al-Mn-Si, Al-Fe-Mn-Si, Al-Fe-Cr-Si, and Al-Fe-V-Si samples
- Compositional maps and point analyses

α-Phase Compositions (EPMA)

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	Al	Si	Fe	Mn	Cr	V
α-AlMnSi	69.4	12.8		17.8		
α-Al(Fe,Mn)Si*	73	8.7	12.5	5.8		
Low-V α-Al(Fe,V)Si as-cast†	79	3.5	13.9			3.6
Low-V α-Al(Fe,V)Si as-cast†	76.6	6.7	13.8			2.9
High-V α-Al(Fe,V)Si as-cast	78.6	3.2	13.9			4.3
Low-Cr α-Al(Fe,Cr)Si as-cast	74.9	7.8	11.2		6.1	
High-Cr α-Al(Fe,Cr)Si as-cast	75.2	7.6	9.6		7.6	
Low-V α-Al(Fe,V)Si heat-treated‡	71.4	11.1	14.5			3
High-V α-Al(Fe,V)Si heat-treated	71	11.6	13.4			4
Low-Cr α-Al(Fe,Cr)Si heat-treated	70.5	12	11.2		6.3	
High-Cr α-Al(Fe,Cr)Si heat-treated	70.3	12.4	9.5		7.8	

* Taken from a single point, may not be representative

† Taken from a single point, low overall counts, and chance the measurement was not entirely from one phase

‡ Taken from 3 points, high variability between measurements

Al-(Fe,Mn)-Si α-Phase

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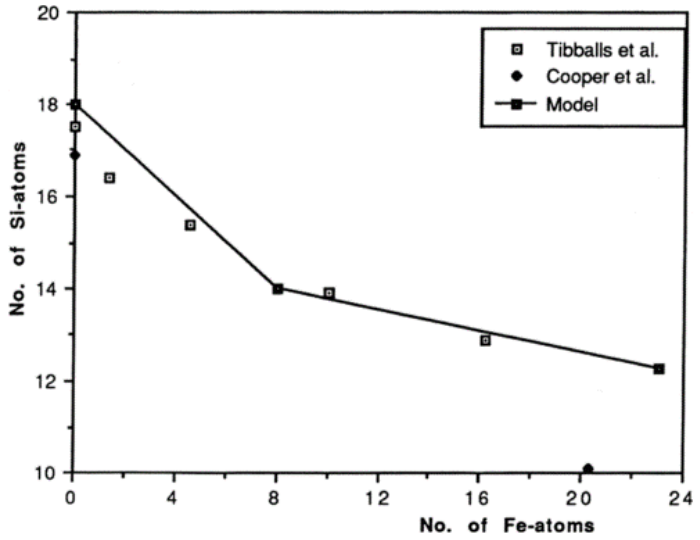
- Reference system
- Composition consistent with literature
- Si content between ~8 and ~13 at%
- Transition metal content ~17.4 at%



α-phase Si dependency on Fe content*

	Al	Si	Fe	Mn	Cr	V
α-AlMnSi	69.4	12.8		17.8		
α-Al(Fe,Mn)Si*	73	8.7	12.5	5.8		

*Simensen and Bjornklett. Light Metals 2017. (2017).

As-Cast α-Phase

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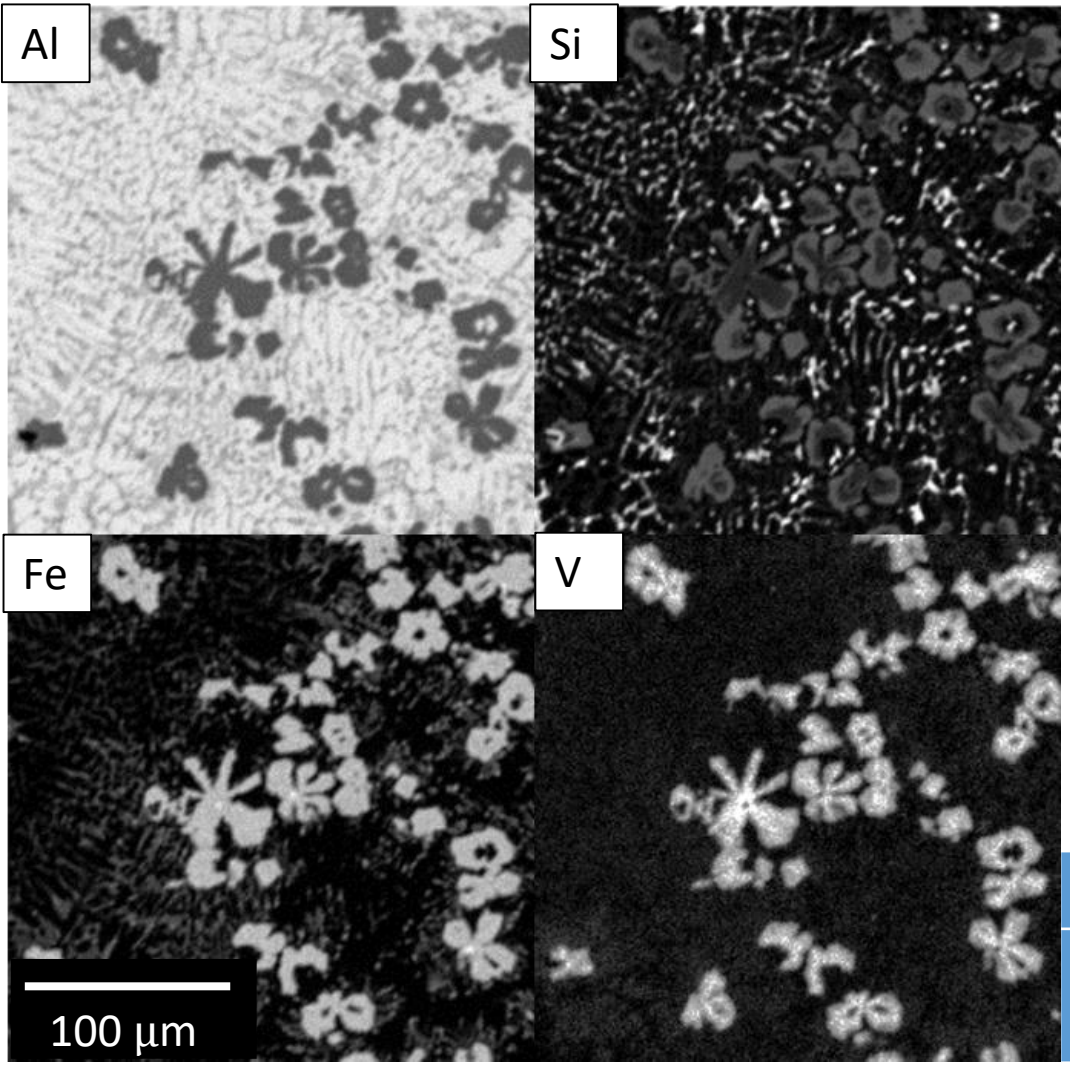
- Two different phases, one previously unreported

- Can differentiate by Si and transition metal content
  - One has ~8 at% Si and ~17.4 at% TM like α-Al(Fe,Mn)Si
  - Other has ~3.5 at% Si and ~18 at% TM

	Al	Si	Fe	Mn	Cr	V
Low-V α-Al(Fe,V)Si as-cast†	79	3.5	13.9			3.6
Low-V α-Al(Fe,V)Si as-cast†	76.6	6.7	13.8			2.9
High-V α-Al(Fe,V)Si as-cast	78.6	3.2	13.9			4.3
Low-Cr α-Al(Fe,Cr)Si as-cast	74.9	7.8	11.2		6.1	
High-Cr α-Al(Fe,Cr)Si as-cast	75.2	7.6	9.6		7.6	

WDS Map of Al-Fe-V-Si Casting



- Primary particles are α-phase
- "Shell" of higher-Si α-phase
- Core of low-Si α-phase
- h-phase present but not clearly distinguishable

	Al	Si	Fe	V	B
Low-V casting	92.9	3.5	3.0	0.5	0.1

Heat-Treated α-Phase

- Transformation to high-Si α-phase consistent with α-Al(Fe,Mn)Si
  - 11-13 at% Si
  - ~17.4 at% TM

- Transformation of two distinct α-phases to a new α-phase

	Al	Si	Fe	Mn	Cr	V
Low-V α-Al(Fe,V)Si heat-treated‡	71.4	11.1	14.5			3
High-V α-Al(Fe,V)Si heat-treated	71	11.6	13.4			4
Low-Cr α-Al(Fe,Cr)Si heat-treated	70.5	12	11.2		6.3	
High-Cr α-Al(Fe,Cr)Si heat-treated	70.3	12.4	9.5		7.8	

Summary of EPMA Results

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As-Cast Condition

Low-Si α-phase

and/or

Higher-Si α-phase

500 °C →

Heat-Treated Condition

High-Si α-phase

	α-Al(Fe,Mn)Si?
Low-Si	No
Higher-Si	Yes
High-Si	Yes

Choice of Final Alloy System

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- Selected Al-Fe-Mn-X-Si as final alloy system previously

- Fe:Mn ratio of 1:1 to reduce equilibrium liquidus temperature
  - Lower superheats with respect to the α-phase liquidus
  - Greater achievable undercoolings

- X is the low-diffusivity element to improve coarsening resistance
  - Either Cr or V*
  - Other possibilities with less desirable phase diagrams

- Transition metal to Si ratio determined by stoichiometry of α-phase
  - TM:Si is ~2:1 in the as-cast condition

*K.E. Knipling, D.C. Dunand, D.N. Seidman. Z. Metallkd. (2000).

Cr or V?

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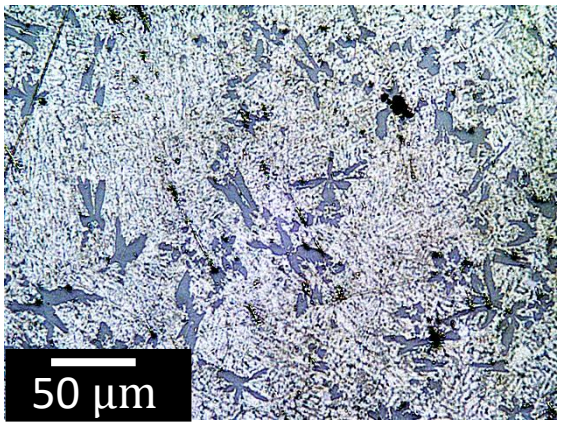
- V is default choice
  - Al-Fe-V-Si system relatively well characterized
  - V has diffusivity 3 orders of magnitude lower than Cr in Al*
- α-phase appears to have higher solubility for Cr than for V
  - Easier to lower equilibrium liquidus to α-phase liquidus
- Both have upsides, but V seems better at first glance

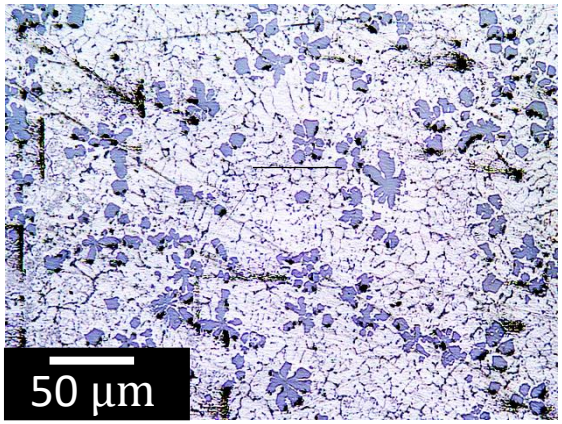
*K.E. Knipling, D.C. Dunand, D.N. Seidman. Z. Metallkd. (2000).

Issues With V

- Al-Fe-V-Si system has some issues
  - Need to simultaneously optimize for low-Si α-phase, h-phase, and high-Si α-phase
  - h-phase has detrimental morphology and solidification behavior
  - Low-Si α-phase has detrimental morphology
  - Too many poorly characterized sources of detrimental behavior to effectively optimize
    - Better understanding may make this possible in the future



Low-Si α-phase morphology



High-Si α-phase morphology

- Al-Fe-Cr-Si has none of these issues
  - Good for building a model microstructure
  - Performance should be close to that of V-containing alloys

Final Decision

- Al-Fe-Mn-Cr-Si alloys were chosen
  - Mostly for liquidus temperature
  - Mn has high solid solution solubility
- Use to assess ability to produce microeutectic in chill castings
- Use 4 transition metal contents
  - Want to maximize reinforcing phase without producing too many primary α-phase particles

Composition (at%)

Alloy	Al	Fe	Mn	Cr	Si
J35	Bal.	1.5	1.5	0.4	1.6
J40	Bal.	1.8	1.8	0.5	1.8
J45	Bal.	2.0	2.0	0.6	2.1
J50	Bal.	2.2	2.2	0.7	2.3

Liquidus Characterization

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Goal: Characterize liquidus temperatures with DSC in order to assess improvement over RS8009 baseline and determine processing conditions.

Alloy	Liquidus (°C, approx.)	Total TM (at%)
J35	730	3.4
J40	760	4.1
J45	780	4.6
J50	800	5.1
RS8009	850	5.0

- Lower TM content leads to much lower liquidus
- Lower liquidus even at same TM content
- Greater achievable undercoolings

Future Work

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

Good Things to Come!

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- Have achieved large volume fractions of microeutectic in 4-6 mm diameter sections (~500 K/s)

- Still needs more characterization

Alloy	Section Thickness	HV
J35	6 mm	75-80
J40	4 mm	80-100

Progress

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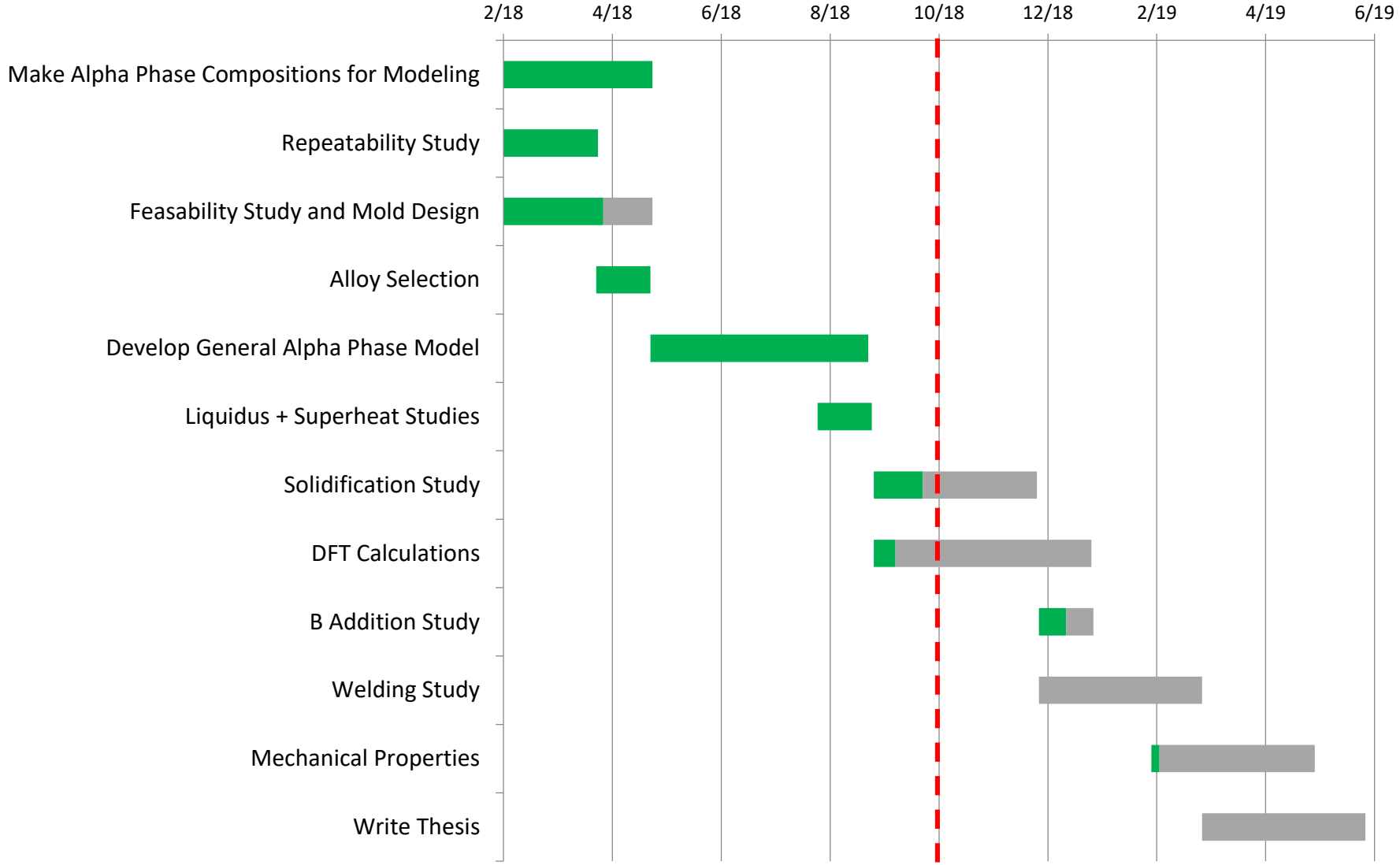

Questions/Discussion

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Thank you!

Joe Jankowski

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Student: *Joe Jankowski*

Faculty: *Michael Kaufman, Amy Clarke, Robert Field, Steve Midson (Mines)*

Industrial Partners: *Krish Krishnamurthy (Honeywell), Paul Wilson (Boeing)*

Project Duration: *June 2015 - August 2019*

Achievement

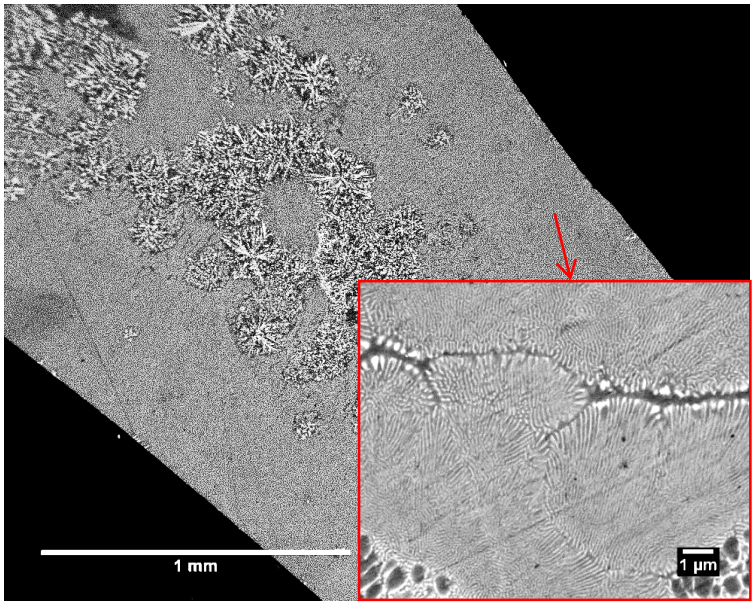
- Production of aluminum alloys with high strength at high homologous temperatures utilizing conventional processing routes, identified using *ab initio* DFT calculations

Significance and Impact

- Reduced cost of high performance Al structural alloys, improved methods for metastable alloy design.

Research Details

- Performed DFT calculations to determine promising alloy compositions and identified required solidification conditions to form microeutectic constituent.



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Industrial Partners: *Krish Krishnamurthy (Honeywell), Paul Wilson (Boeing)*

Project Duration: *June 2015 - August 2019*

Program Goal

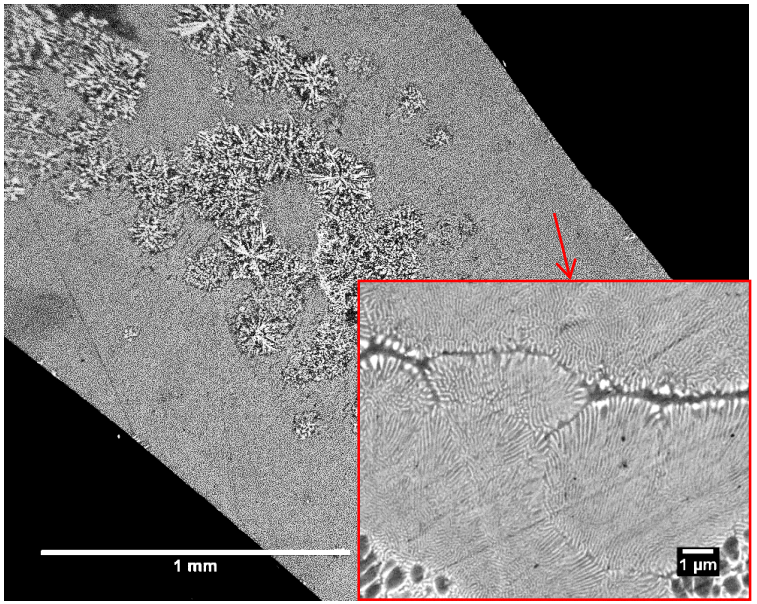
- Develop Al alloys with high volume fraction of microeutectic between Al and α-phase intermetallic.

Approach

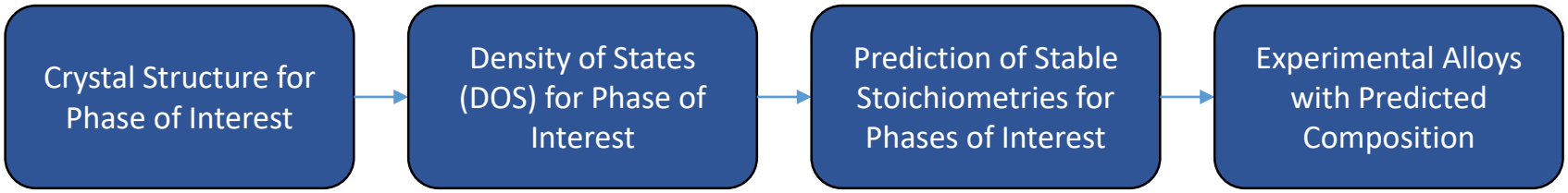
- Utilize DFT calculations and characterization techniques to develop a new class of Al alloys based on the eutectic between Al and α-phase.

Benefits

- Improved scientific understanding of microeutectic, new high performance Al alloys, new method of metastable alloy design.



Alloying Strategy



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

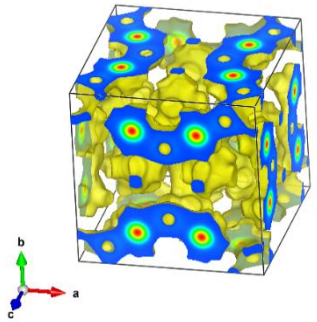
- Reference experimental composition
- Unknown theoretical compositions

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

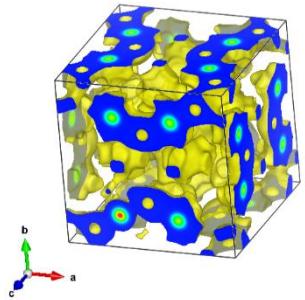
- Predict ratio of transition metals
- Refine stability criteria

Why Density of States?

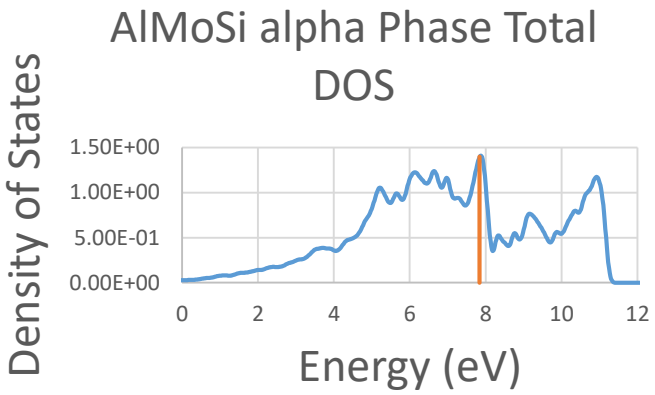
- Relatively inexpensive calculation
  - Large unit cells for α and h-phase
  - Easier to get useful DOS vs. enthalpy/charge density
- Based on actual physics of system (vs. e/a approach)
- Intuitive visual representation of bonding interactions in 2D

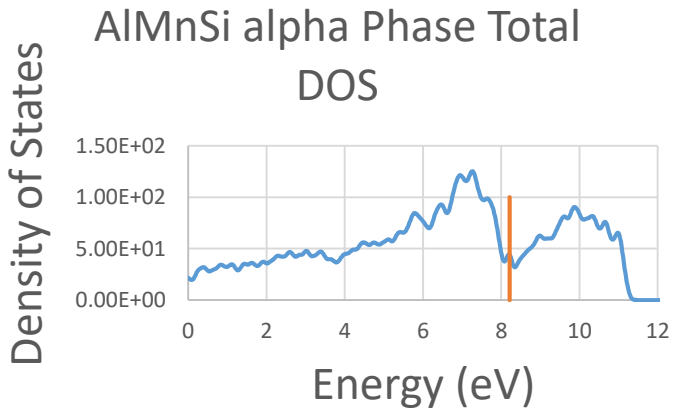


α-AlMoSi charge density (bonding)



α-AlMnSi charge density (bonding)





Calculation Results

CANFSA
Center for ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- 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).