CANFSA

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

Project 22: Development of Novel High Temperature Aluminum Alloys

Fall 2019 Semi-Annual Meeting
Colorado School of Mines, Golden, CO
October 9 - 11, 2019

Student: Joe Jankowski (Mines, ATI)

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

Industrial Mentors: Krish Krishnamurthy (Honeywell), Paul Wilson (Boeing)

NSF | COLORADO SCHOOL OF MINES | IOWA STATE UNIVERSITY

Project 22: Development of Novel High Temperature Aluminum Alloys

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

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

Project Duration

PhD: June 2015 to December 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

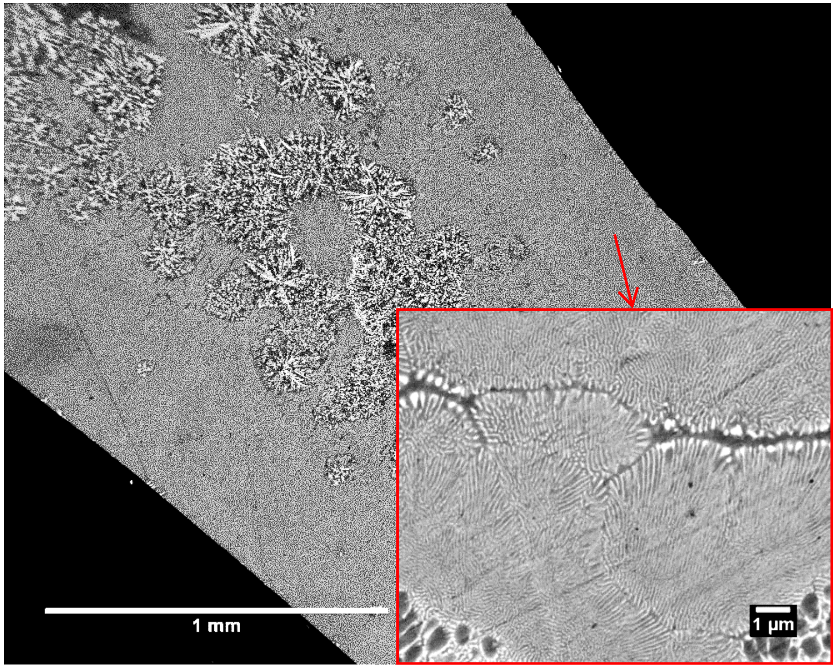
- Defended thesis

Metrics

Description	% Complete	Status
1. Develop experimental protocols for reproducible castings	100%	●
2. Mechanical testing and characterization of microeutectic-containing microstructures	100%	●
3. Develop crystallography / phase stability knowledge of α-phase	100%	●
4. Assess ability to produce microeutectic in chill castings	100%	●
5. Determine how fundamental solidification parameters affect microeutectic formation	100%	●

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
  - 10^3 vs. 10^6 K/s
- High microstructural stability at elevated temperatures

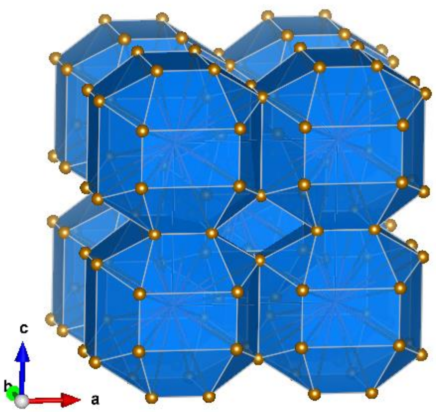


Alloy	Al (at%)	Fe (at%)	V (at%)	Si (at%)
RS8009	Bal.	4.3	0.7	1.7

RS8009 Microstructure

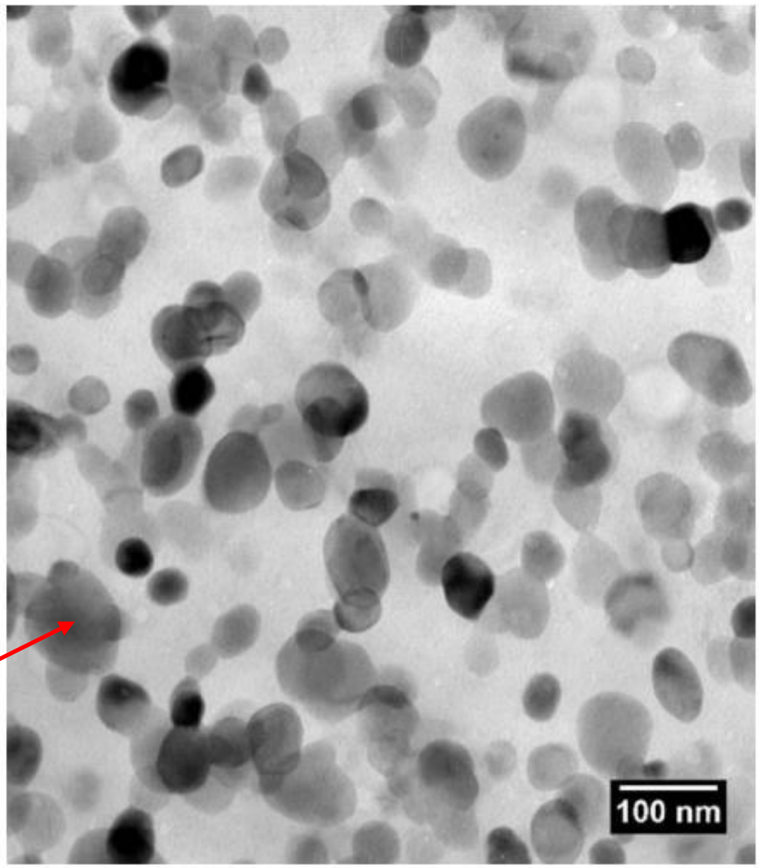
- Stable microstructure at 400 °C (0.7 T_m)
- Good tensile strength up to 315 °C
- Requires rapid solidification (~10^6 K/s)
- Strengthened by fine dispersion of $Al_{13-x}(Fe,V)_3Si_x$ α-phase intermetallic

1.26 nm



α-phase crystal structure [2]

α-phase dispersoids and Al matrix [1]



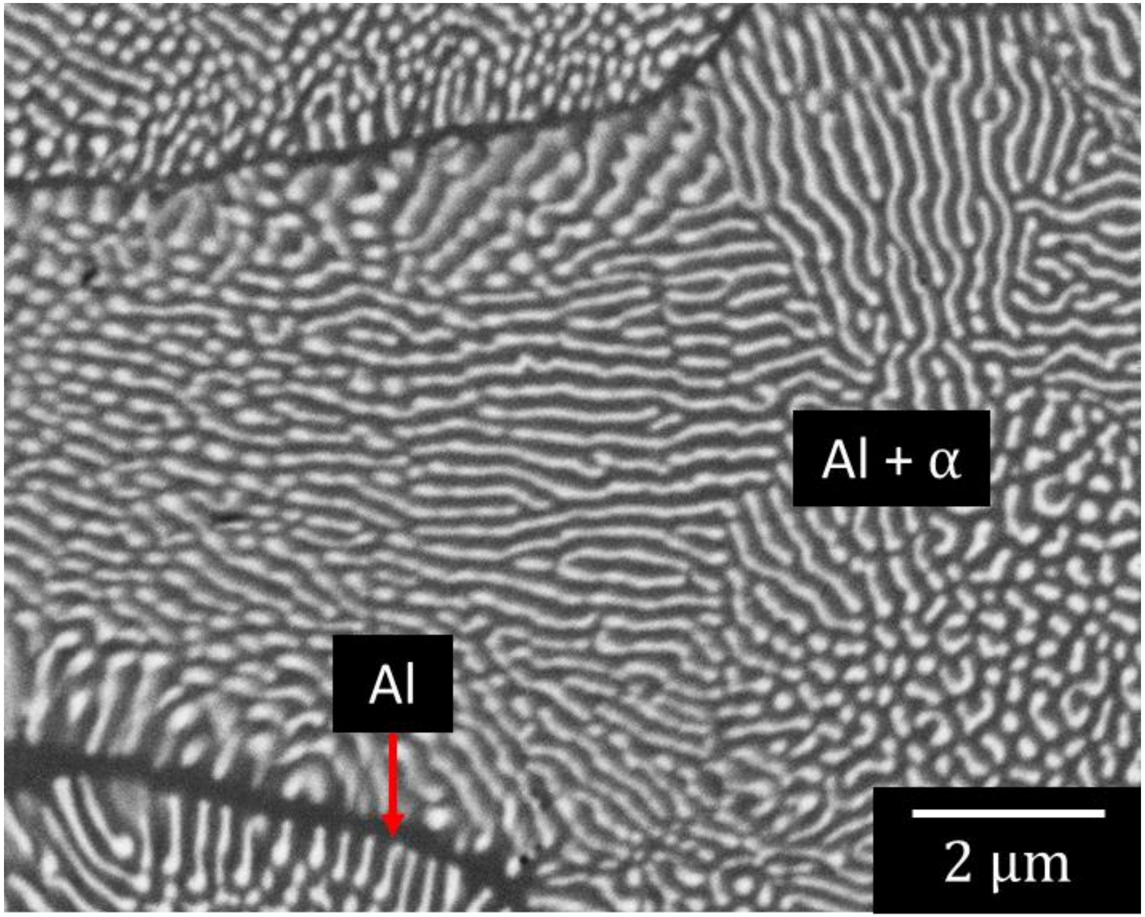
Al (at%)	Fe (at%)	V (at%)	Si (at%)
Bal.	4.3	0.7	1.7

[1] R. Marshall (2016). Master's thesis
[2] J. Tibballs, R. Davis, and B. Parker (1989). Journal of Materials Science

Al + α-Phase Microeutectic

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

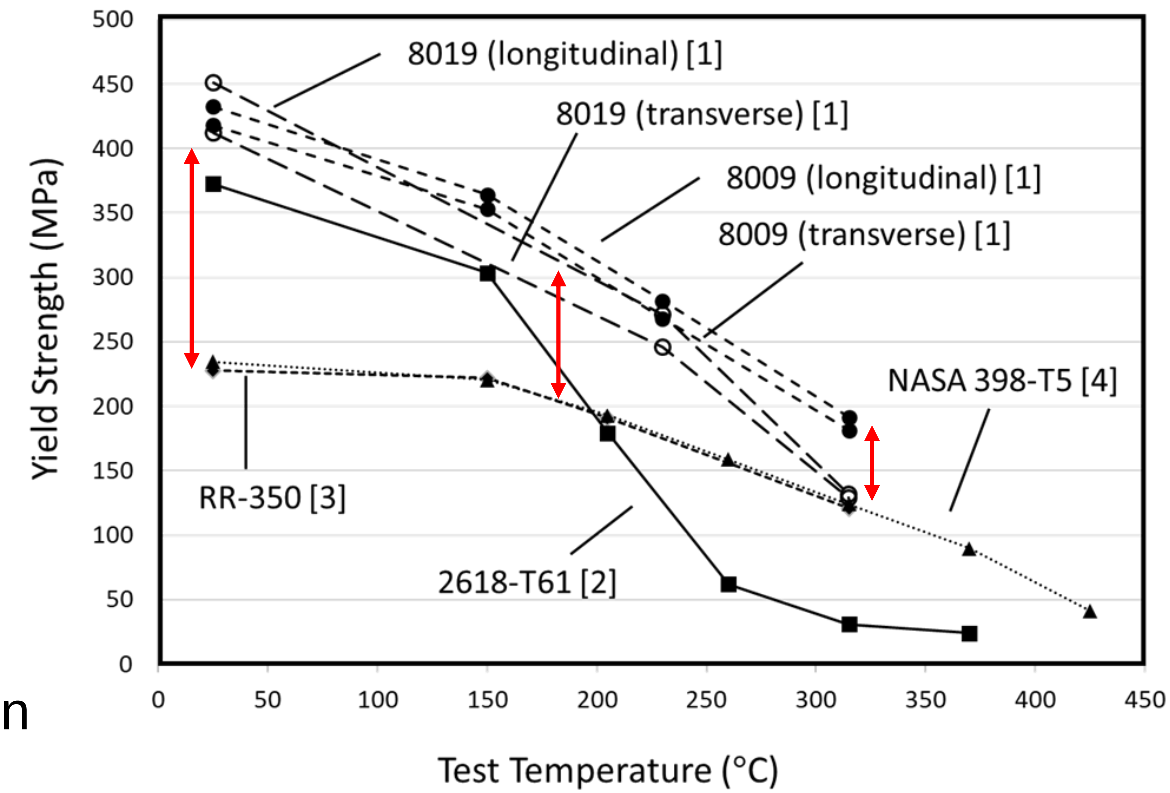
- α-phase also forms eutectic with Al at cooling rates of ~10^3 K/s
- Eutectic can have hardness similar to rapidly solidified 8009
- Potential for thermally stable strengthening mechanism at lower cooling rates



Al + α-phase microeutectic

Industrial Relevance

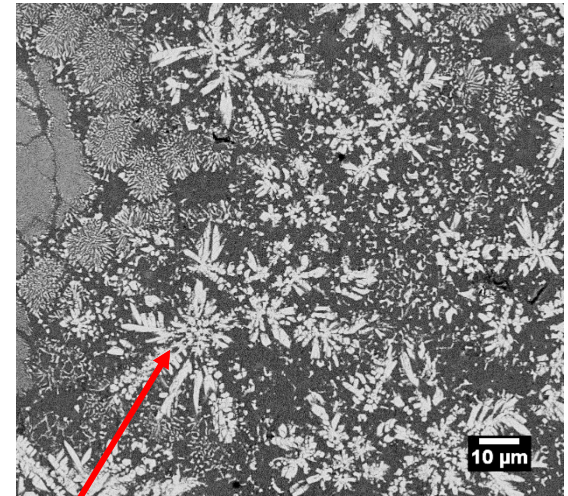
- Aluminum alloys are temperature-limited
- Fe-rich alloys have high performance and cost
- Large gap between conventional alloys and rapidly solidified alloys
- Potential for cost savings in material selection

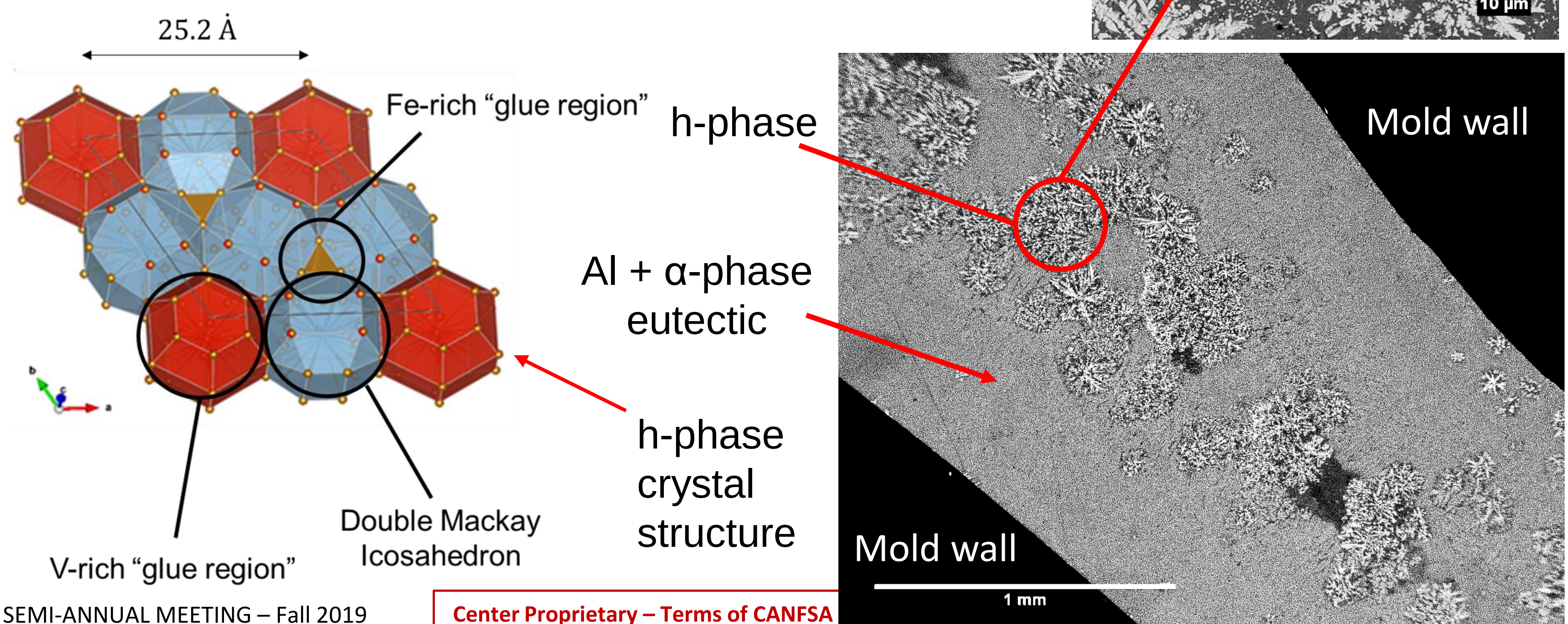


[1] M.A. Phillips and S.R. Thompson (1994). Air Force Materiel Command
[2] ASM International (1990). ASM Handbook Vol. 2
[3] A.W. Gunderson (1969). Air Force Materials Laboratory
[4] J. Lee (2001). NASA 398 Material Properties Data Sheet.

h-Phase in 8009 castings

- Competitive h-phase particles
  - Brittle phase
  - Coarse, dendritic morphology
- Need to identify method of removing h-phase and promote Al + α-phase eutectic





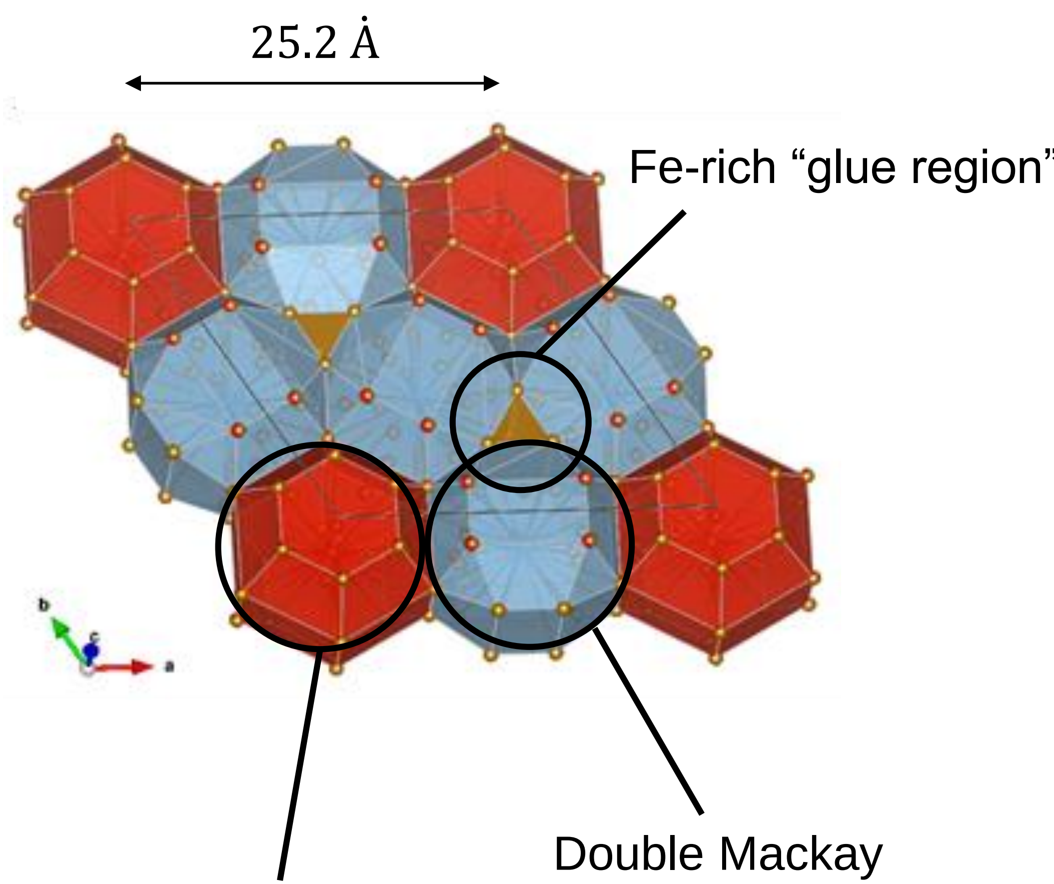
Research Goal

Identify + characterize alloy compositions that:

1. Promote α-phase formation (over h-phase)
2. Retain thermal stability of RS8009
3. Promote Al + α-phase eutectic
4. *Potential applications for additive manufacturing*

h-Phase Crystal Structure

- Double Mackay (DM) icosahedra have near-bulk Fe:V ratio
- "Glue" regions are enriched in one of the two transition metals
- "Segregation" of Fe,V within unit cell to preferential sites



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

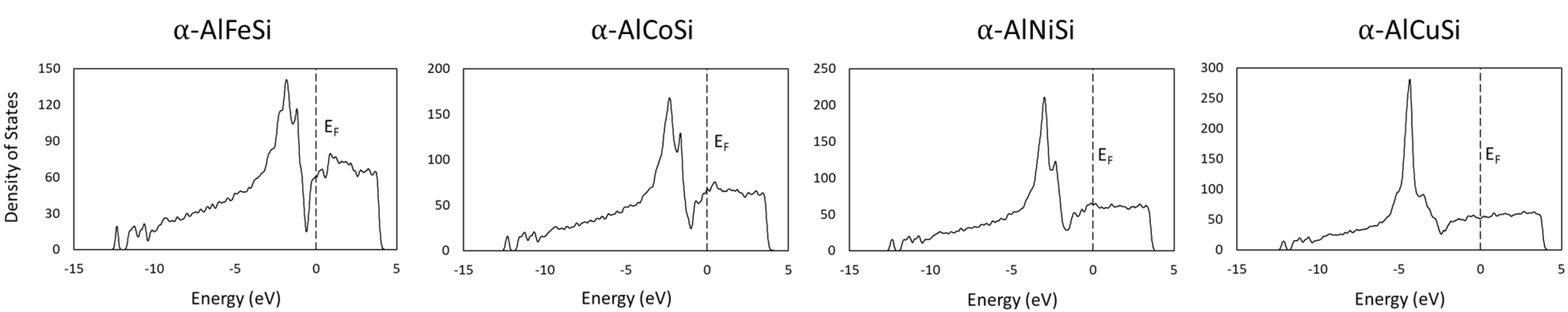
α-Phase Stability at Arbitrary Compositions

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Valence electron counting from transition metal content of α-phase
- Likelihood of formation estimated from electronic density of states (DOS)

α-$Al_{12}X_3Si_2$ ternary phase	Deficient/excess valence electrons per atom
Ti	-3
V	-2
Nb	-2
Cr	-1
Mo	-1
Mn	0
Fe	1
Co	2
Ni	3
Cu	4

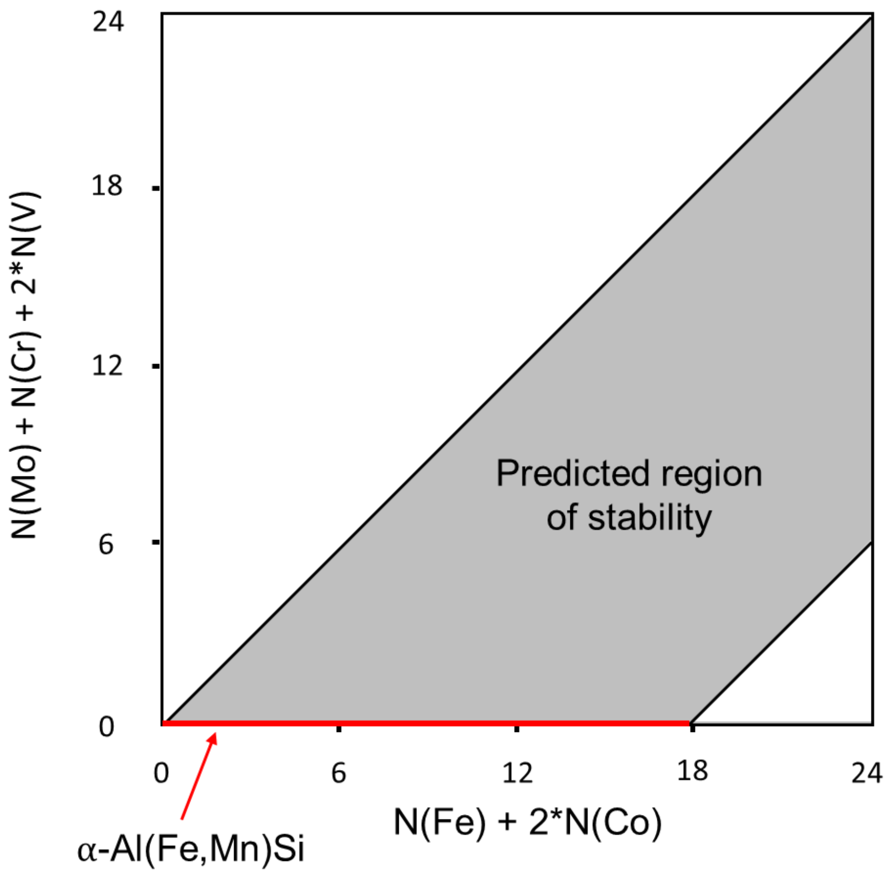
Calculated DOS for theoretical α-$Al_{13}M_3Si_2$ phases



Predicted α-Phase Compositions

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Fe:Mn ratio can range from 0:1 to 3:1 (conservatively) [1]
  - $Al_{83-x}Mn_{17}Si_x$ to ~$Al_{83-x}Fe_{13}Mn_4Si_x$
- Define this composition range as “stable” electron counts
- Can extend to arbitrary compositions by balancing electrons

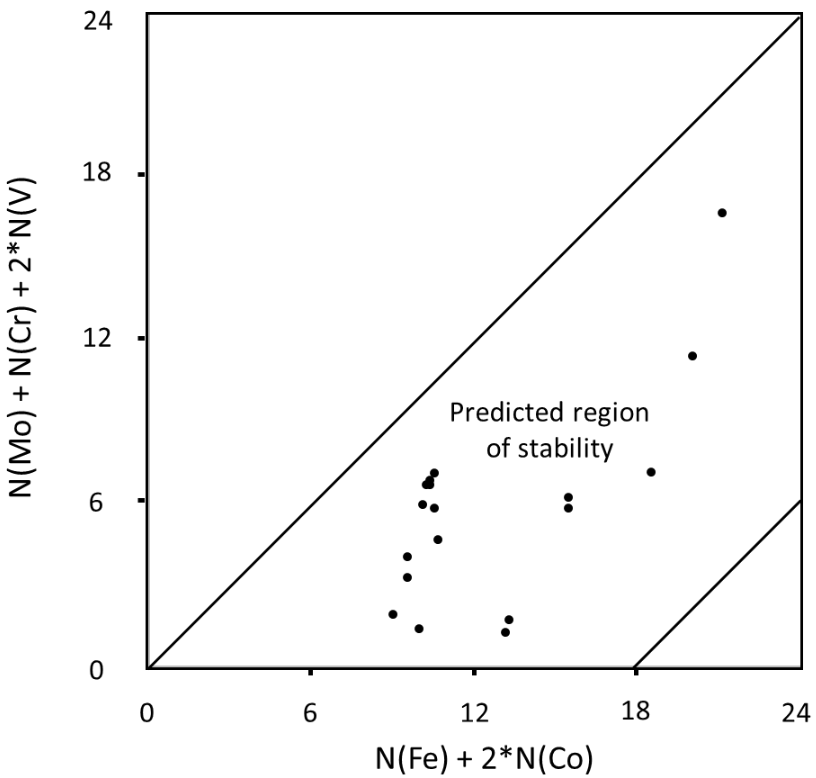


[1] C.J. Simensen and A. Bjørneklett (2017). Light Metals 2017

Experimental Validation

α-phase compositions from WDS

α (at%)
Al-14.5Fe-3.0V-11.1Si
Al-13.4Fe-4.0V-11.6Si
Al-11.2Fe-6.3Cr-12.0Si
Al-9.5Fe-7.8Cr-12.4Si
Al-7.8Si-11.2Fe-6.1Cr
Al-7.6Si-9.6Fe-7.6Cr
Al-7.3Si-2.4Cr-0.8V-0.4Co-6.9Fe-7.2Mn
Al-6.1Si-3.0Cr-1.4V-0.3Co-6.6Fe-6.6Mn
Al-6.5Si-2.6Cr-1.1V-6.5Fe-7.1Mn
Al-7.3Si-2.4Cr-0.9V-6.9Fe-7.4Mn
Al-5.5Si-3.6Cr-6.9Fe-6.9Mn
Al-15.3Fe-1.7Mo-0.8V-4.3Si
Al-7.6Fe-7.7Mn-1.7Mo-0.9V-4.5Si
Al-7.6Fe-8.0Mn-2.2Cr-5.2Si
Al-7.5Fe-7.9Mn-2.4Cr-6.4Si
Al-7.4Fe-7.8Mn-2.3Cr-4.8Si
Al-7.5Fe-7.6Mn-2.3Cr-5.7Si
Al-7.3Fe-7.5Mn-2.7Cr-4.3Si

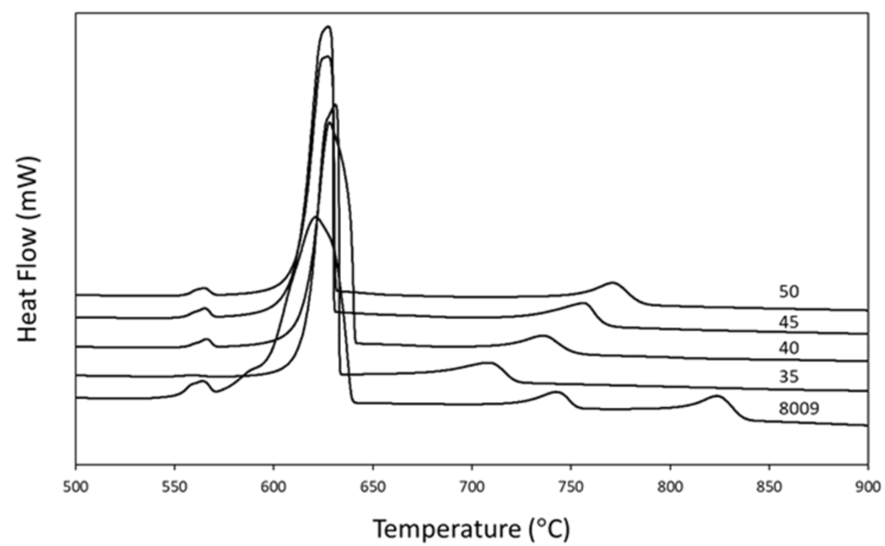


Electron counting predicts variety of α-phase compositions.

Selection of Novel Alloy Compositions

- Cr substitutions for V shown in previous work to suppress h-phase [1]
  - In agreement with crystal structure
  - Cr has higher diffusivity than V in Al [2]
- 8009 has high equilibrium liquidus
  - High superheats required
  - Mn lowers equilibrium liquidus
  - Reduced solubility of low diffusivity elements

DSC cooling curves for 8009 and model Al-Fe-Mn-Cr-Si alloys



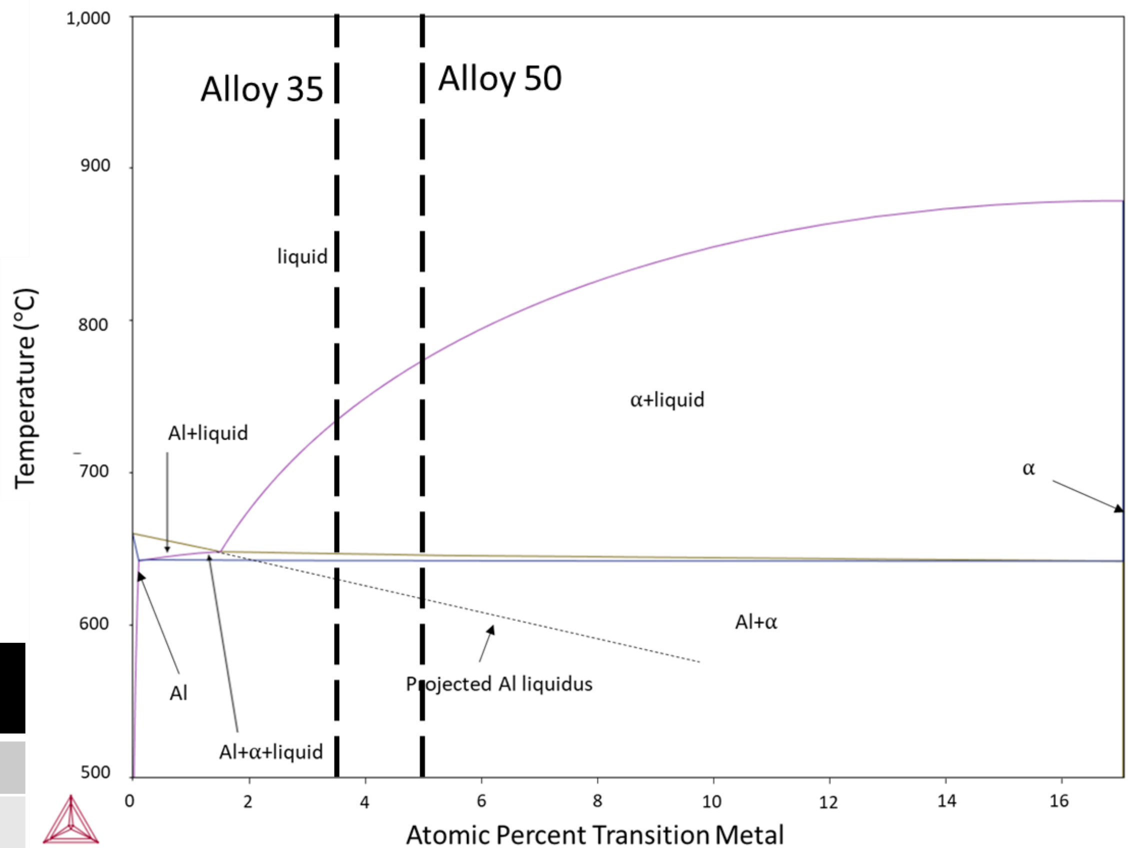
Alloy	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	V (at%)	Si (at%)
35	Bal.	1.5	1.5	0.4	-	1.6
40	Bal.	1.8	1.8	0.5	-	1.8
45	Bal.	2.0	2.0	0.6	-	2.1
50	Bal.	2.2	2.2	0.7	-	2.3
8009	Bal.	4.4	-	-	0.6	1.8

[1] J. Jankowski *et al.* (2019). Light Metals 2019
[2] K. Knipling, D. Dunand, and D. Seidman (2006). Z. Metallkd.

"Phase Diagram" of Al + α-Phase Eutectic

- Fe:Mn ratio of 1:1, Al-Fe-Mn-Si quaternary alloy
- Only Al, α-phase, liquid shown
- Al + α-phase coupled growth possible due to undercooling
- Three possible solidification modes: primary Al, coupled growth, and primary α-phase

Alloy	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	Si (at%)
35	Bal.	1.5	1.5	0.4	1.6
40	Bal.	1.8	1.8	0.5	1.8
45	Bal.	2.0	2.0	0.6	2.1
50	Bal.	2.2	2.2	0.7	2.3



As-Cast Microstructures

- Continuous transition between microstructures
- Cooling rates compatible with conventional processing routes [1,2]
- Cooling rates required increase with alloying

Cooling Rates Required for Formation (K/s)			
	Microstructure		
Alloy	Primary Al	Coupled Growth	Primary α-phase
35	>200	200-1,000	n/a
40	>500	400-1,000	<400
45	>1,000	>500	<500
50	>2,000	>500	<500

Alloy	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	Si (at%)
35	Bal.	1.5	1.5	0.4	1.6
40	Bal.	1.8	1.8	0.5	1.8
45	Bal.	2.0	2.0	0.6	2.1
50	Bal.	2.2	2.2	0.7	2.3

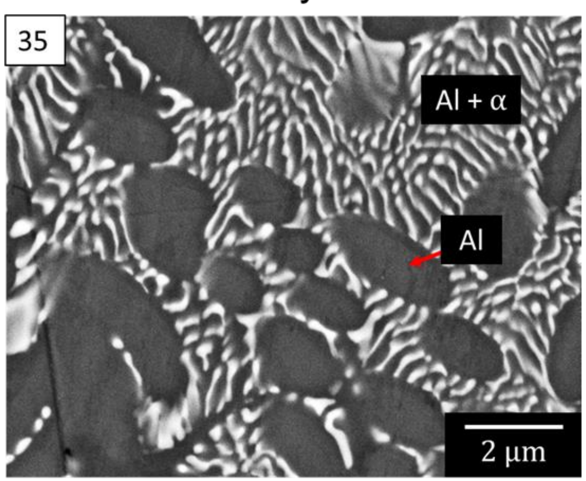
[1] M. Okayasu *et al.* (2012). Materials Science and Engineering A
[2] M. Okayasu *et al.* (2014). Materials Science and Engineering A

Microhardness of As-Cast Microstructures

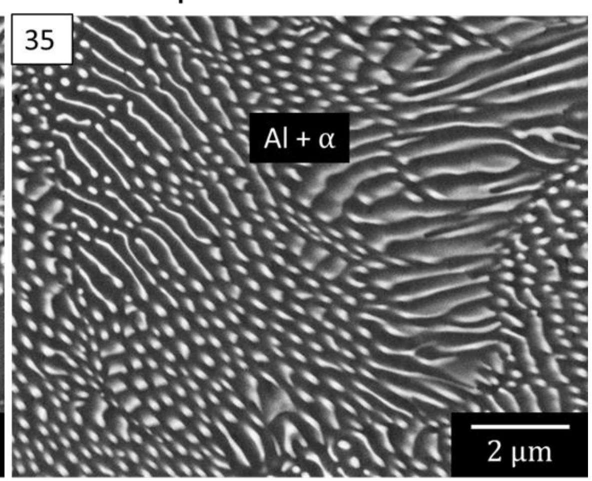
- **Primary Al microstructures have higher microhardness than eutectic colonies**
- Microhardness increases with transition metal concentration

Alloy	Microstructure	HV (Avg.)	St. Dev.
35	Primary Al	91	5.2
	Coupled Growth	78	3.0
40	Primary Al	111	4.0
	Coupled Growth	102	3.1
45	Primary Al	129	2.7
	Coupled Growth	95	2.8
50	Primary Al	135	4.6
	Coupled Growth	108	4.4
8009	Extrusion As-Provided	135	14

Primary Al

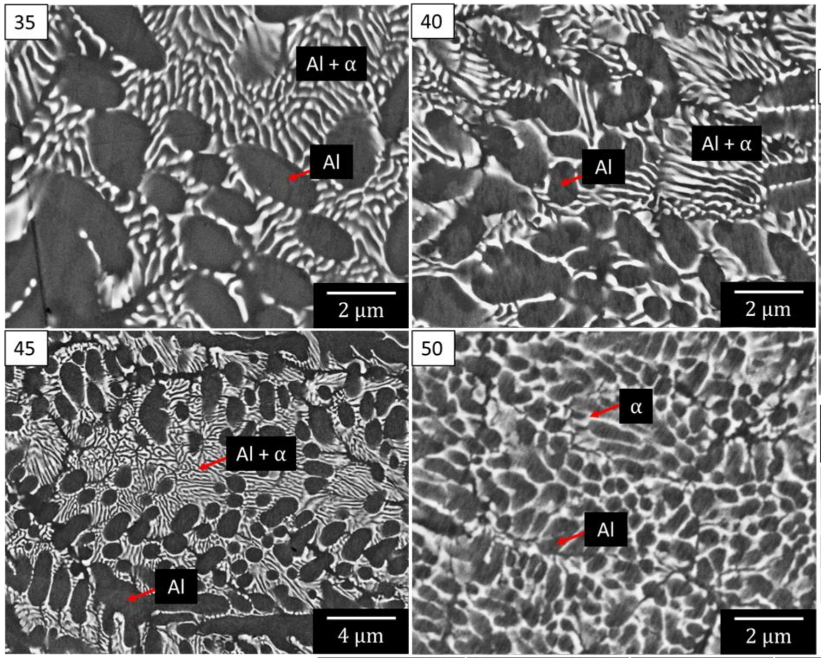


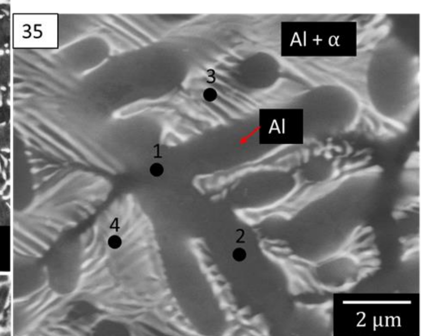
Coupled Growth



Alloy	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	Si (at%)
35	Bal.	1.5	1.5	0.4	1.6

As-Cast Microstructure—Primary Al





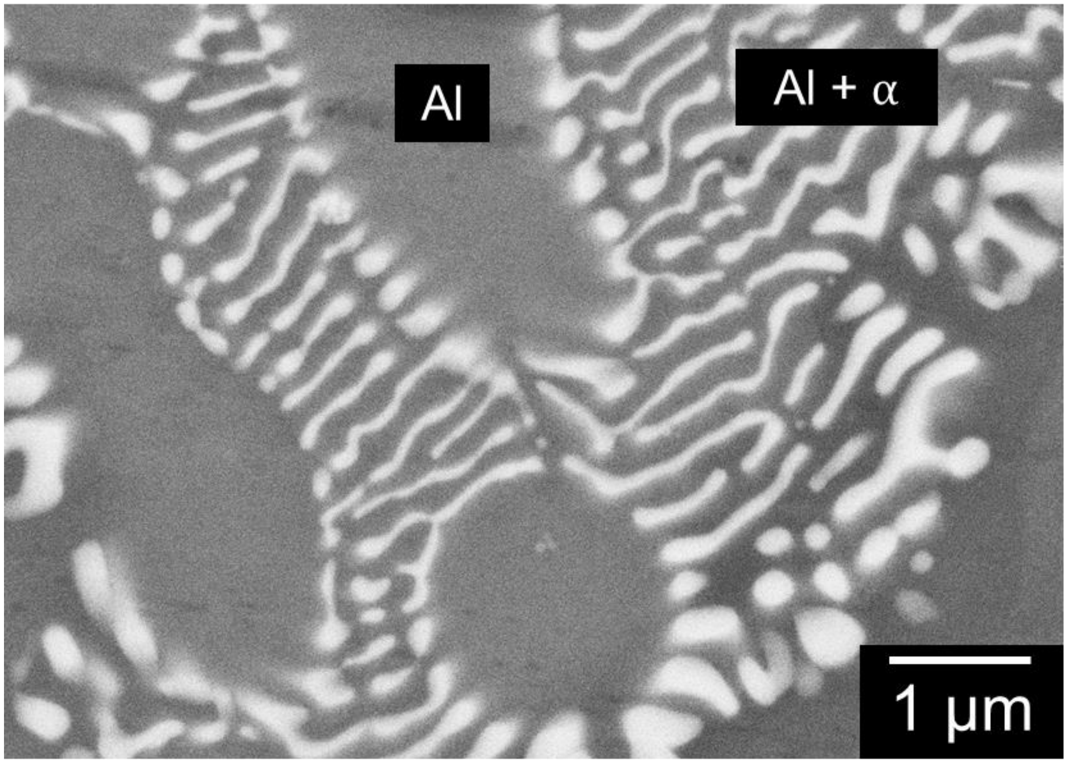
Spot	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	Si (at%)
1	96.6	0.9	1.1	0.3	1.1
2	96.8	0.8	1.1	0.4	0.9
3	95.0	1.4	1.5	0.5	1.7
4	93.9	1.8	1.7	0.4	2.2

Alloy	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	Si (at%)
35	Bal.	1.5	1.5	0.4	1.6
40	Bal.	1.8	1.8	0.5	1.8
45	Bal.	2.0	2.0	0.6	2.1
50	Bal.	2.2	2.2	0.7	2.3

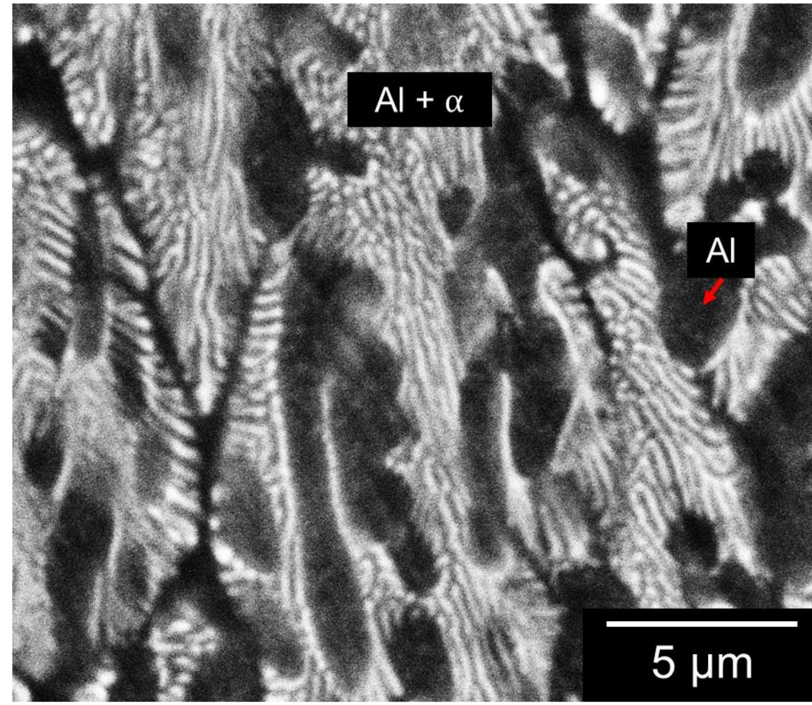
- Primary Al solidification observed in all alloys
- Requires higher cooling rates as transition metal content increases
- Primary Al dendrites are Mn-rich

Alloy 35 Microstructural Stability

As-cast primary Al microstructure



Primary Al microstructure after 100 hours at 370 °C



- Little coarsening visible on length scale of ~1 μm

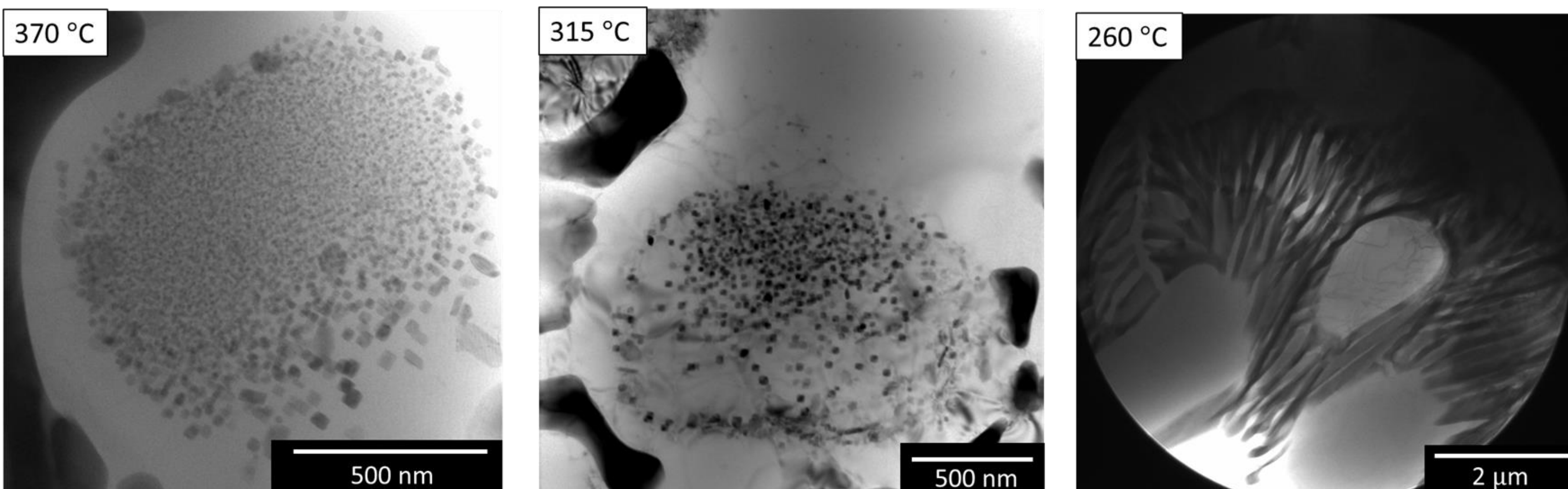
Alloy	Al (at%)	Fe (at%)	Mn (at%)	Cr (at%)	Si (at%)
35	Bal.	1.5	1.5	0.4	1.6

Alloy 35 Microstructural Stability

- Evolution of precipitates at temperatures of at least 315 °C
- Potential cause of hardness drop

Alloy	Microstructure	HV (Avg.)	St. Dev.
35	Primary Al	91.2	5.2
	Primary Al (100 hr at 260 °C)	90.2	3.2
	Primary Al (100 hr at 370 °C)	79.7	2.8

BFTEM on Al dendrites after 100 hours at temperature

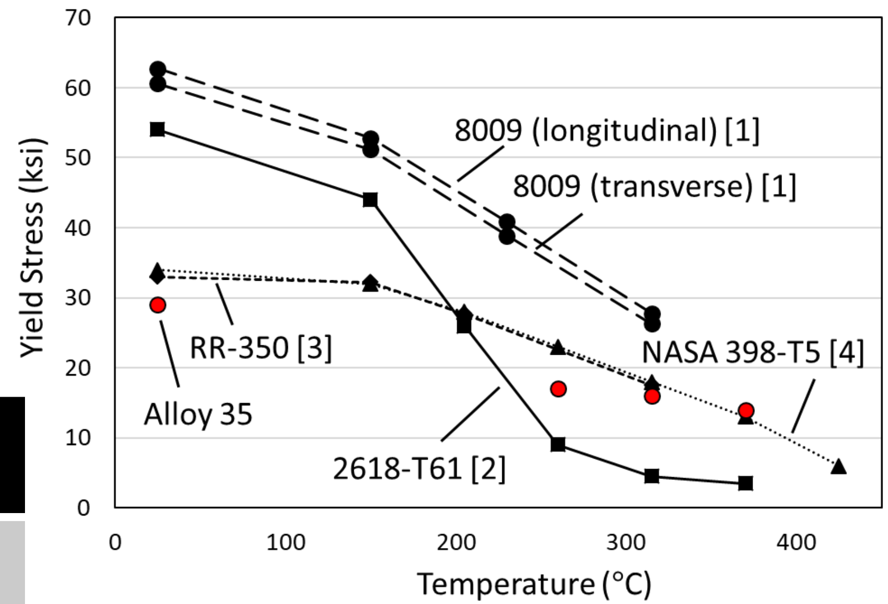


Alloy 35 Elevated Temperature Testing

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Negligible changes in strength after 100 hours at temperature
- Superior strength retention vs. Al-Cu alloys at elevated temperatures

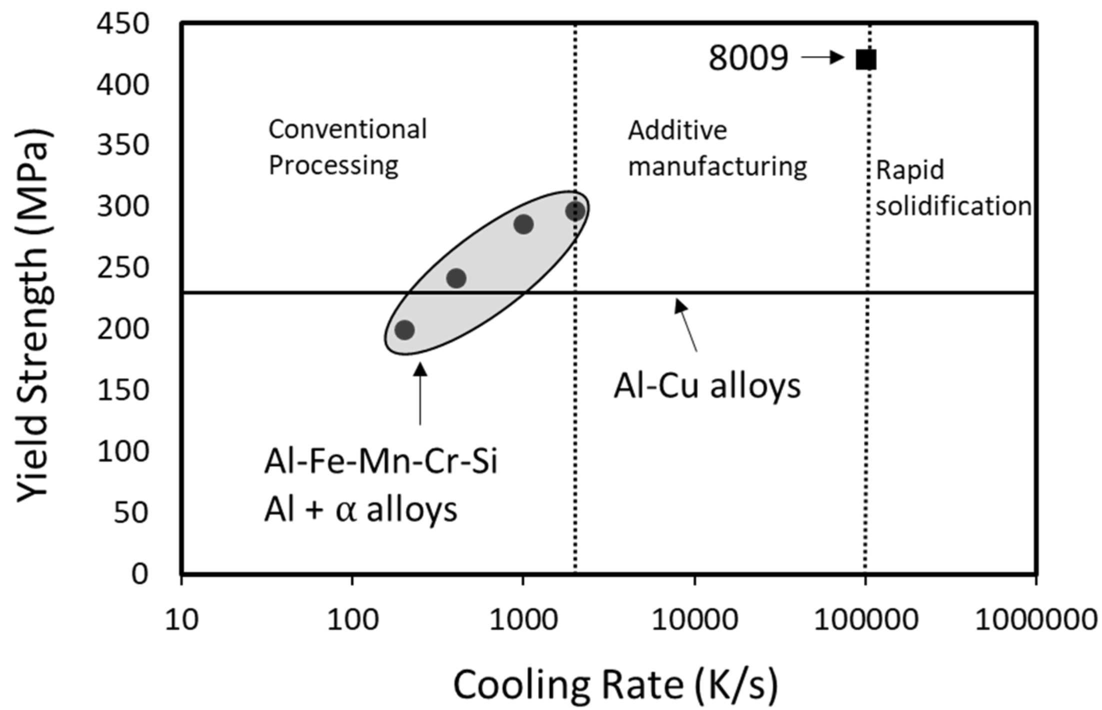
Heat Treatment	Test Temperature	YS (ksi)
n/a	Ambient	28, 30, 30
0.5 hr 260 °C	260 °C	17
100 hr 260 °C	260 °C	17, 19
0.5 hr 315 °C	315 °C	17
100 hr 315 °C	315 °C	14, 16
0.5 hr 370 °C	**370 °C**	**13**
100 hr 370 °C	**370 °C**	**14**



[1] M.A. Phillips and S.R. Thompson (1994). Air Force Materiel Command
[2] ASM International (1990). ASM Handbook Vol. 2
[3] A.W. Gunderson (1969). Air Force Materials Laboratory
[4] J. Lee (2001). NASA 398 Material Properties Data Sheet.

Processing vs. Properties

- Yield strengths estimated from hardness:yield strength of alloy 35 (bulk)
- Primary Al microstructures
- Potential for significantly higher strength than high temperature Al-Cu alloys
- Cooling rates consistent with die casting, strip casting [1,2]

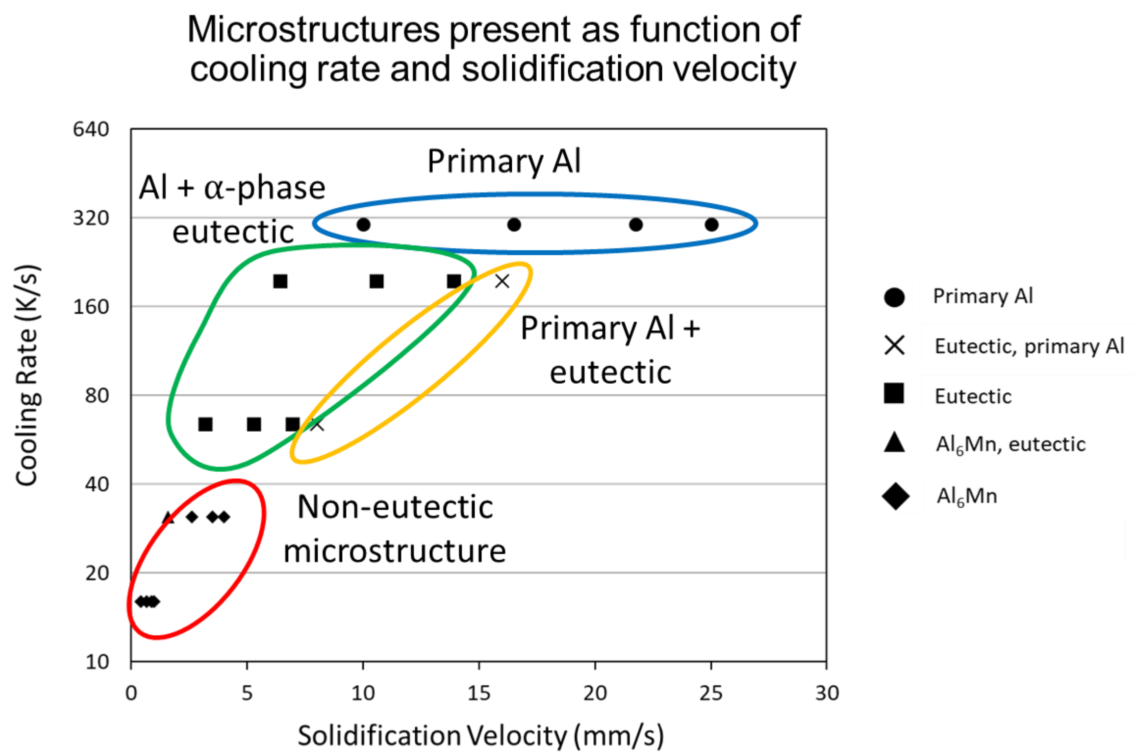


[1] M. Okayasu *et al.* (2012). Materials Science and Engineering A
[2] M. Okayasu *et al.* (2014). Materials Science and Engineering A

Microstructure-Cooling Rate-Solidification Velocity Relationships in Alloy 35

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Calculated from autogenous welding experiment
- Cooling rates of ~60 K/s required for Al + α-phase microstructures
- Primary Al achievable at cooling rates above ~300 K/s
- Higher solidification velocity seems to promote primary Al



Additive Manufacturing Alloy Design

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- h-Phase grows in competition with α-phase dispersoids

Two approaches to h-phase removal

1. Substitution of Fe and V by elements with different valence electron counts (Mo,Mn)
2. Increasing Si content (at stoichiometric levels)

Goal

- Lowest coarsening rates
- Fine dispersoids of α-phase

Diffusivity of select elements in Al matrix from [1]

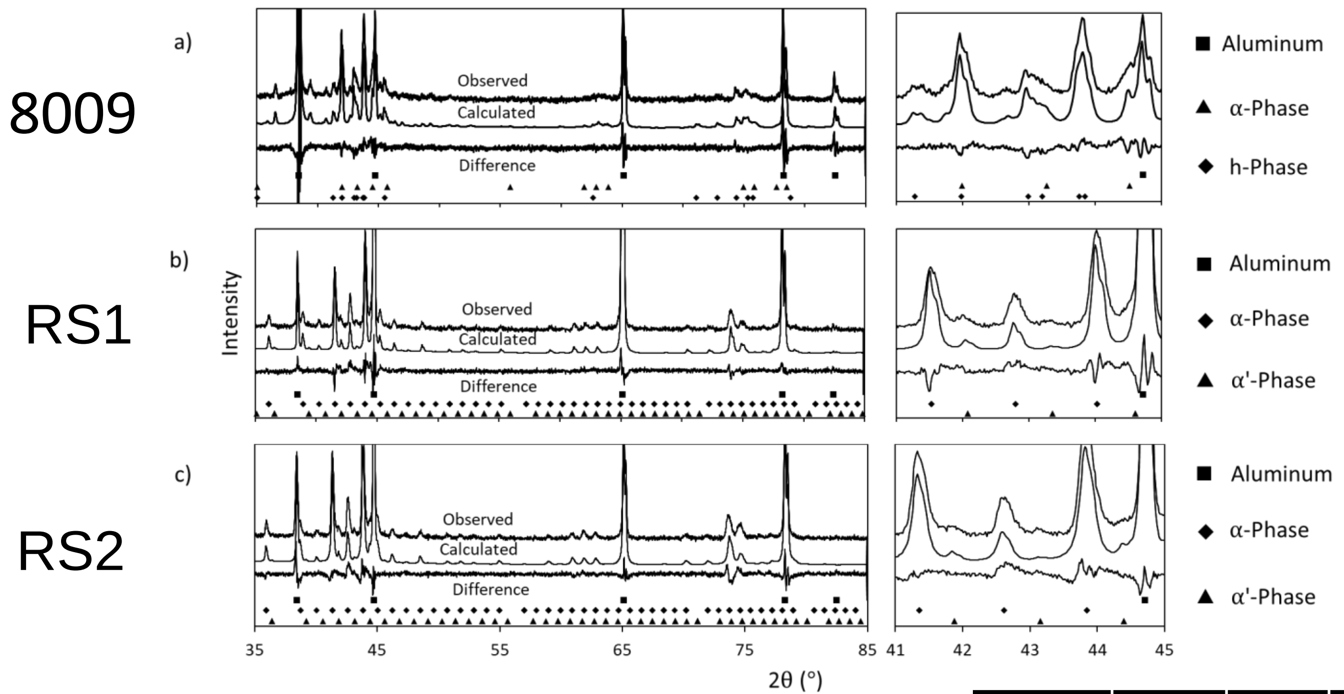
Element	Diffusivity at 400 °C ($m^2 s^{-1}$)
Fe	5.41×10^{-18}
V	4.85×10^{-24}
Mo	5.52×10^{-23}
Mn	6.24×10^{-19}

Compositions of alloys studied (at%)

Alloy	Al	Fe	Mn	Mo	V	Si
8009	Bal.	4.4	n/a	n/a	0.6	1.7
RS1	Bal.	4.4	n/a	0.4	0.2	2.3
RS2	Bal.	2.2	2.2	0.4	0.2	2.3

[1] K.E. Knipling, D.C. Dunand, and D.N. Seidman (2006). Z. Metallkd

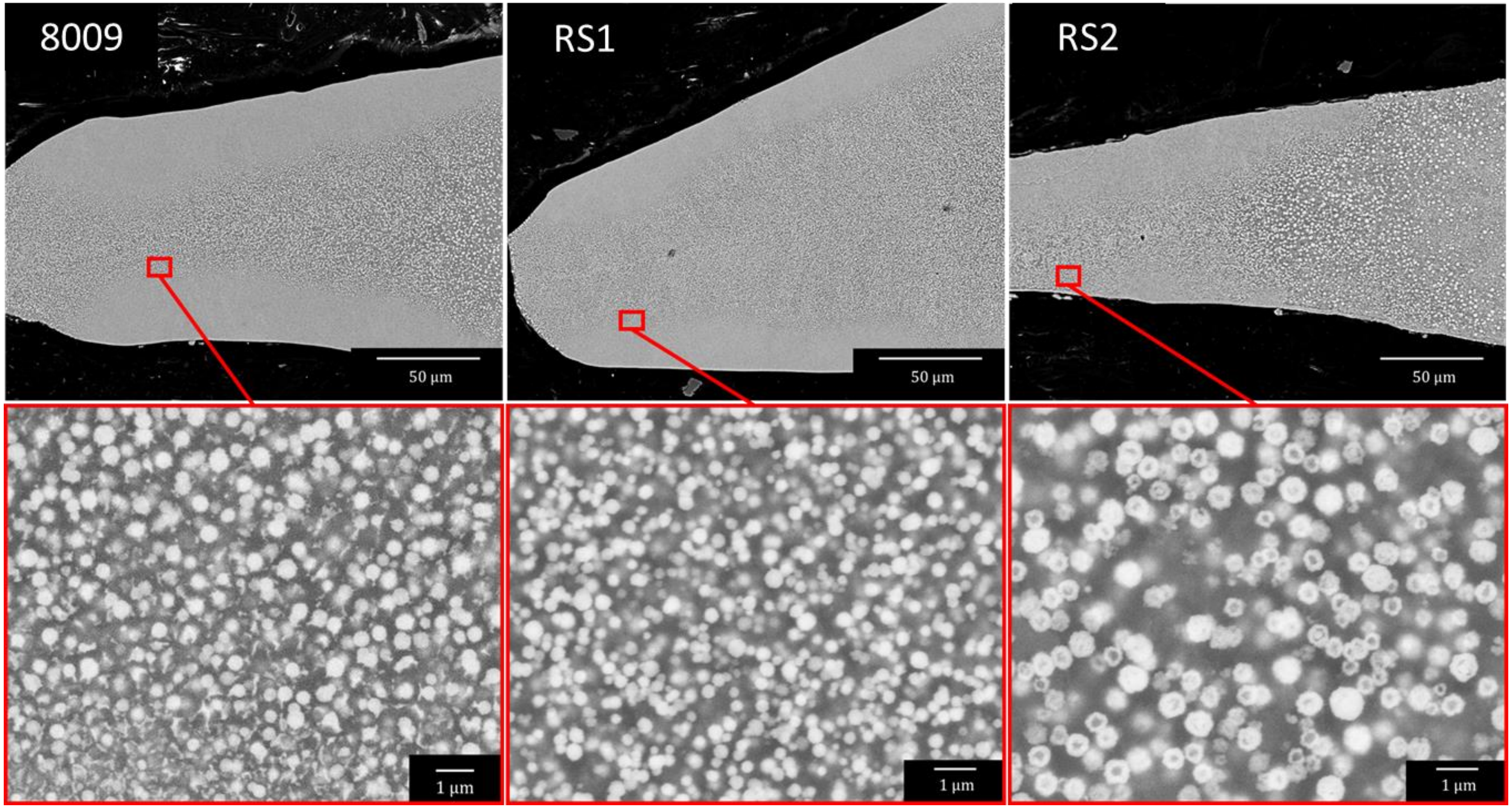
XRD Analysis—Phase Identification



- No detectable h-phase in chill castings of RS1 or RS2.
- Only Al and α-phase detected

Alloy	Al	Fe	Mn	Mo	V	Si
8009	Bal.	4.4	n/a	n/a	0.6	1.7
RS1	Bal.	4.4	n/a	0.4	0.2	2.3
RS2	Bal.	2.2	2.2	0.4	0.2	2.3

α-Phase/Dispersoid Morphology



- RS1, RS2 do not appear to contain h-phase (from XRD)
- Fine dispersoids in RS1, better primary particle selection

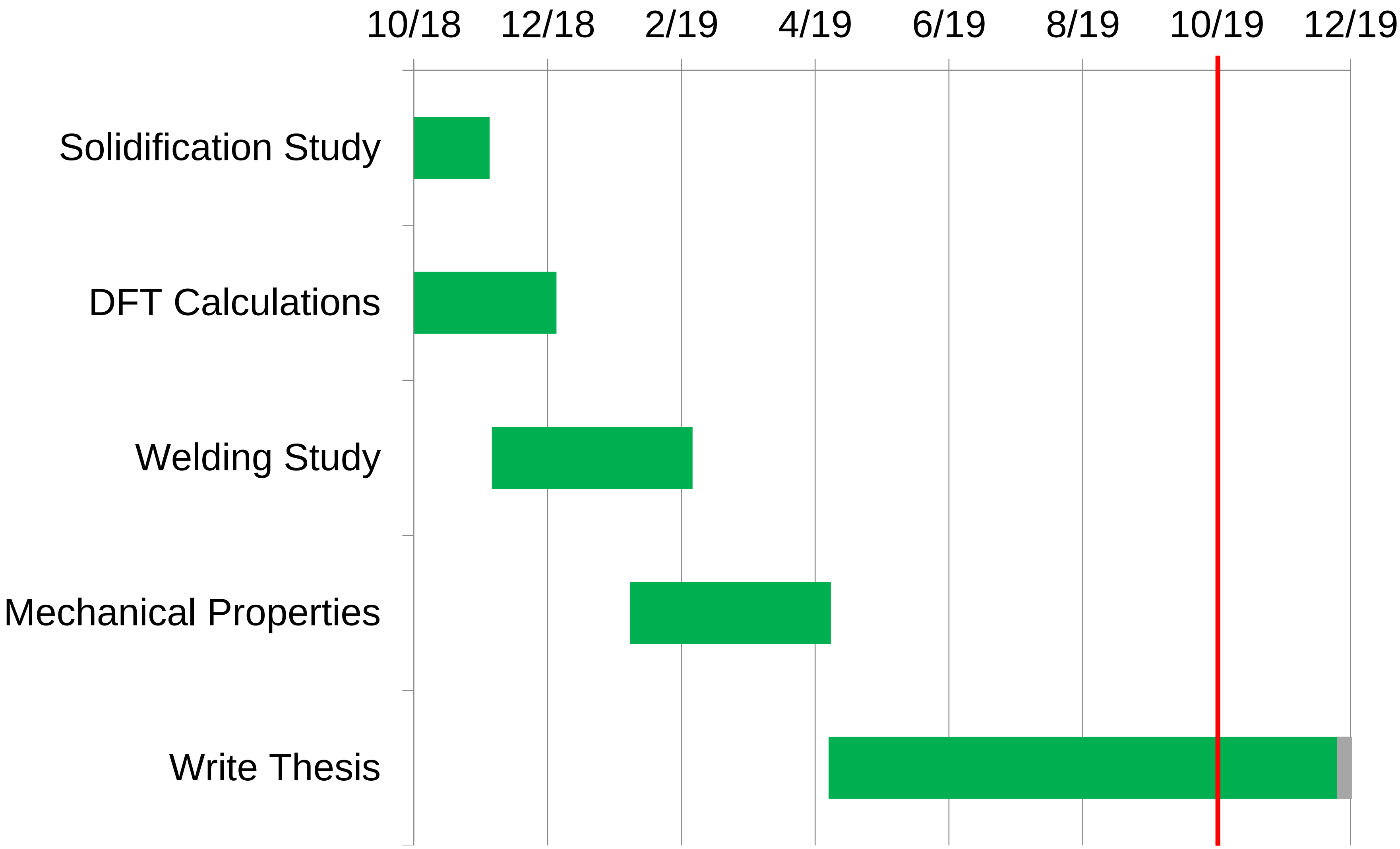
Alloy	Al	Fe	Mn	Mo	V	Si
8009	Bal.	4.4	n/a	n/a	0.6	1.7
RS1	Bal.	4.4	n/a	0.4	0.2	2.3
RS2	Bal.	2.2	2.2	0.4	0.2	2.3

Summary/Conclusions

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Developed Al + α-phase eutectic and dispersoid alloys
- Properties at room temperature and elevated temperature appear similar to commercial high-temperature Al-Cu alloys
- Can be produced at cooling rates achievable through conventional processing (die casting, strip casting)
- Difficult to produce—microstructure strongly dependent on parameters like undercooling, solidification velocity
- Potential for significant increases in elevated temperature strength over Al-Cu alloys processed similarly

Progress


10/18
12/18
2/19
4/19
6/19
8/19
10/19
12/19
Solidification Study
DFT Calculations
Welding Study
Mechanical Properties
Write Thesis

Thank you!

Joe Jankowski
jjankows@mines.edu