

22.0 FORMATION, HIGH TEMPERATURE STABILITY, AND MECHANICAL PROPERTIES OF MICROEUTECTICS IN BULK SOLIDIFIED AL-FE-V-SI AND RELATED ALLOYS

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22.1 Project Overview and Industrial Relevance

The purpose of this project is to develop a high-performance structural aluminum alloy with acceptable high temperature strength through the formation of a lamellar microeutectic microstructure composed of aluminum and the cubic intermetallic phase α -Al₁₃(Fe,V)₃Si. The reason this alloy is of particular interest is that this microstructure can be formed at cooling rates of 10² to 10³ K/s, which is orders of magnitude lower than rapid solidification (RS) cooling rates. This suggests this alloy system could represent a lower cost alternative to current high-temperature aluminum alloys produced by rapid solidification (e.g., RS8009), or by related methods such as powder metallurgy. The development of a lower cost aluminum alloy with acceptable high temperature mechanical properties would allow for improvements in part performance in industries where current RS alloys are prohibitively expensive.

In order to develop an alloy system that has a favorable microstructure, it is critical to minimize or prevent the formation of unwanted phases. In the case of the AlFeVSi system, a potentially deleterious phase may form that is of primary concern—the hexagonal Al_{12.8}(Fe,V)₃Si_{0.3} phase (h-phase) with similar composition and a crystal structure related to the Al₁₃(Fe,V)₃Si α -phase, but with a coarse dendritic morphology. Additionally, due to the high content of Fe in the baseline 8009 alloy, large Al₁₃Fe₄ (θ -phase) particles may form in sections on the order of 1cm in diameter in chill castings. It is therefore essential that mitigation strategies promote α -phase, while removing h-phase and θ -phase. To this end, concepts from physics/chemistry will be used to identify the workable composition space and will be supplemented by density functional theory (DFT) calculations and data from the literature.

The detailed characterization of the h-phase and incorporation of electronic structure information can not only be used to promote the microeutectic between Al₁₃(Fe,V)₃Si and aluminum, but may also provide information about how to improve existing RS alloys and develop new alloys optimized for additive manufacturing. Commercial RS8009 alloys are known to contain the h-phase, which is typically coarser than the desired dispersion of α -Al₁₃(Fe,V)₃Si [22.1]. The use of conceptual tools from chemistry and physics, coupled with DFT, should allow for the rapid optimization of microeutectic volume fraction in a large composition space. The methodology used in this work will be applicable to essentially all Al-TM (transition metal) and Al-TM-Si alloys.

22.2 Previous Work

Several important findings were made prior to this reporting period. First, the as-cast microeutectic structure was found to have hardness values comparable to extruded RS8009 and was stable at temperatures well above potential operating temperatures (250 to 300 °C). The thermal stability and high hardness of the microeutectic were two of the initial findings that suggested its potential. Since high hardness alone is not sufficiently indicative of desirable mechanical properties, a three-point bending test was performed on a sample that contained a significant volume fraction of the microeutectic structure. The fracture surface was indicative of ductile fracture. The high hardness, thermal stability, and ductility of the microeutectic indicate that if it can be produced throughout a cast part, it would likely exhibit desirable mechanical properties.

Another important result was the development of a detailed crystal structure model for the h-phase using synchrotron x-ray and neutron powder diffraction at U.S. DOE user facilities, coupled with charge flipping [22.2]. Based on this model, minor alloying additions of Co and Mn, and major alloying additions of Si were examined and found to be beneficial for removing the h-phase, where the Si additions were especially effective. DFT calculations on the Pm $\bar{3}$ AlMnSi-type structure for the α -phase [22.3] were used to determine workable compositions for the α -phase in Al alloys. It was found that V, Cr, Mo, Mn, and Fe were effective in stabilizing the α -phase and compositional rules for incorporating them were developed. Small additions of B were found to sometimes promote α -phase particle nucleation in the melt.

Process control during casting was refined by developing a new casting protocol to improve consistency. Cooling rates were measured, since they are quantitative indicators of the conditions in the casting during solidification. Cooling rates can also be used as part of future in-depth solidification studies.

22.3 Recent Progress

First, a finite element analysis (FEA) using the program SYSWELD was performed to simulate an autogenous TIG welding solidification study. This demonstrated the viability of performing a solidification study with known processing conditions, as well as good starting parameters for experiments. Second, the crystallography of the α -phase was compared in Al-Mn-Si, Al-Fe-Mn-Si, Al-Fe-Cr-Si, and Al-Fe-V-Si alloys using electron microprobe analysis (EPMA) and synchrotron x-ray powder diffraction performed at beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory. Finally, the alloy system selected for future solidification studies was Al-Fe-Mn-Cr-Si, based on results from the crystallographic study of the α -phase, as well as previous work examining equilibrium liquidus temperatures.

22.3.1 TIG Welding Solidification Study

TIG welding was identified as a potential analogue to the chill casting process used for producing alloys in this project, due to similar length scales and cooling rates between the processes. A welding solidification study will help to deconvolute the fundamental parameters that go into the measured cooling rates in the chill castings. If a well characterized alloy is used, the cooling rate can be determined experimentally [22.4]. However, the cooling rate is a convolution of two different, more fundamental parameters: the thermal gradient at the solid/liquid interface and the solidification velocity. In a welding experiment, the cooling rate can experimentally be determined and the solidification velocity is experimentally known. It is a simple matter of then applying the equation $dT/dt = dT/dx * dx/dt$ to find the thermal gradient at the solid/liquid interface. The microstructure in the TIG weld can be correlated to the thermal gradient at the solid/liquid interface and solidification velocity to obtain information about microstructural formation conditions. It is hoped that this study will contribute to a better understanding of whether desirable microstructures can be achieved in the Al-Fe-Mn-Cr-Si alloy system, and how they may be achieved.

Before performing any experimental work, a feasibility study was done using FEA in SYSWELD to model the TIG welding process. This was done to establish reasonable operating parameters for an autogenous TIG welding solidification study. Specifically, the plate dimensions, power, and weld speed were determined for a typical TIG welding setup using the material parameters of the Al-Fe-Mn-Cr-Si alloys being studied. It was found that cooling rates consistent with those found in the Cu chill molds used for casting in this project were consistent with what was achievable in TIG welding. Plate dimensions of 2 x 2 x 40 mm were identified to be optimal, given constraints on the volume of each casting and the need to approximate steady-state conditions during the weld. A range of weld speeds and powers were identified for the 2 x 2 x 40 mm plate that would likely work for an experimental setup, and also give a range of solidification velocities for a given cooling rate.

22.3.2 Crystallography of the α -Phase

In order to clarify the crystallography of the α -phase across different alloy systems of interest, EPMA and synchrotron x-ray powder diffraction experiments were performed on Al-Mn-Si, Al-Fe-Mn-Si, Al-Fe-V-Si, and Al-Fe-Cr-Si α -phase compositions. No study to date has proven conclusively that the α -phase in Al-Fe-V-Si or Al-Fe-Cr-Si alloys is isomorphic to the α -phase in Al-Fe-Mn-Si alloys, due to the complexity of the unit cell of the α -phase. For example, a lattice parameter change of only 1% in the Pm-3 α -phase can be indicative of a different crystal structure (different Wyckoff positions) [22.3, 22.5]. Better naming conventions may be needed in the future to reduce confusion regarding which α -phase crystal structure is being discussed.

Preparing samples for Al-Mn-Si and Al-Fe-Mn-Si compositions was fairly simple—buttons were arc melted at the α -phase composition reported in the literature and heat treated at 500 °C for 400 hours. The buttons were then powdered using an agate mortar and pestle. For Al-Fe-Cr-Si and Al-Fe-V-Si compositions, buttons couldn't be produced at the α -phase composition, due to the low diffusivity of Cr and V in the Al matrix [22.6]. Instead, α -phase forming compositions with 3.5 at% total TM were chosen, based upon prior experiments and DFT results. After arc melting the alloys, buttons were remelted using induction heating in air and cast into a wedge-shaped Cu chill mold 1 cm thick with an angle of 25 °. The Al matrix in the wedges was dissolved using a solution of methanol, tartaric acid, and iodine. The secondary phases were separated from the solution by vacuum filtration. After isolating these phases, they were ground using an agate mortar and pestle to improve counting statistics in the powder diffraction pattern. Results from the EPMA and synchrotron experiments are summarized in Tables 22.1 and 22.2.

Instead of going through each result individually, only the important results will be described. The compositions from Table 22.1 all appear to be consistent with the compositions of the α -phase in the Al-Fe-Mn-Si quaternary system

[22.7], except for the as-cast V-containing samples. The as-cast, high-V sample appeared to only have one type of primary α -phase particle, and it was not consistent with the literature of α -Al(Fe,Mn)Si, as expected. Instead, the Si content of the α -phase was near the nominal Si content (3.5 at%) of the alloy. This is far below the ~8 at% threshold for the α -Al(Fe,Mn)Si crystal structure. Additionally, the total transition metal content was too high for the α -Al(Fe,Mn)Si crystal structure—there would be 25 transition metal atoms per unit cell as opposed to 24 out of ~140 atoms total. In addition to novel crystallography, the morphology of the primary α -phase particles in the as-cast high-V sample was less desirable than in samples containing primary α -phase particles with compositions consistent with α -Al(Fe,Mn)Si. The low-Si α -phase primary particles are less compact than the α -Al(Fe,Mn)Si type particles under identical processing conditions. The as-cast, low-V sample possessed some of the low Si phase at the core of its primary α -phase particles and some α -phase consistent with α -Al(Fe,Mn)Si on the outside of its particles, forming a shell of higher Si α -phase around the low-Si α -phase core. On heat treating at 500 °C for 50 h, the low-Si phase disappeared and the α -phase reached a new, higher Si content, consistent with Mn-rich α -Al(Fe,Mn)Si [22.7]. Finally, h-phase in Al-Fe-V-Si and an unexplained (low-Si?) α -phase in Al-Fe-Cr-Si were observed with powder diffraction, but not EPMA.

The crystallography of the α -phase appeared to be the same between all compositions in the heat-treated conditions, based on the results from EPMA and synchrotron x-ray diffraction. In the cases where α' phase is shown, there were three distinct α -phase peaks present in the pattern. The α and α' phases are assumed to be the primary particles based on peak broadening, phase fraction, and lattice parameter. The low-Si α -phase has a smaller lattice parameter than the higher-Si α -phase. This is assumed to be from more metallic-type bonding, as evidenced by an extra transition metal atom. Other than the low-Si α -phase, which is a separate crystal structure, the results show that the transition metals appear to have the biggest effect on lattice parameter, not Si. After heat-treatment, the primary α -phase grows richer in Si and decreases the lattice parameter. This behavior is not fully understood, but may have to do with the strength of bonding in the intercluster “glue” regions of the α -phase. The main conclusion to date is that in the heat-treated condition, which should be close to equilibrium, the α -phase appears to have the same structure in all of the alloy systems examined.

22.3.3 Selection of Alloy System

Based on equilibrium liquidus considerations, the final quinary alloy system chosen for this project was Al-Fe-Mn-X-Si, with X being either Cr or V. However, due to the presence of the deleterious low-Si α -phase and the h-phase in Al-Fe-V-Si, it was determined that Al-Fe-Mn-Cr-Si should be pursued. Cr has a higher diffusivity than V in the Al matrix, but can still produce a coarsening-resistant microstructure. Trying to optimize the microstructure between Al and the desirable α -phase, while trying to prevent excessive levels of the h-phase and deleterious α -phase, presents additional difficulties at the current level of understanding of the Al-Fe-Mn-V-Si alloy system. The Al-Fe-Mn-Cr-Si alloy system serves as a model system, provided the microstructure is sufficiently desirable.

22.4 Plans for Next Reporting Period

The future work for the project has been described, but the planned work for the next reporting period is as follows:

- Design mold for producing plates for TIG welding solidification study;
- Examine the effect of liquidus temperature and superheat on microstructure of Al-Fe-Mn-Cr-Si alloys;
- Complete microstructure/cooling rate/composition correlation study for Al-Fe-Mn-Cr-Si alloys;
- Examine the effect of B on selected Al-Fe-Mn-Cr-Si alloy;
- Begin autogenous TIG welding study.

22.5 References

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22.6 Figures and Tables

Table 22.1—Compositions of α -Phase (at%) Determined from EPMA

	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

Table 22.2—R Values and Lattice Parameters from Rietveld Refinement

	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