Improving Aluminum Casting Alloy and Process Competitiveness

Report 08 #2 - A.4

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PROJECT STATEMENT

Objectives

The objective of this project is to obtain a new family of aluminum-silicon alloys that can be processed by high-pressure die-casting at significantly lower than usual temperatures and therefore is cost-effective; and that is heat-treatable, and therefore is capable of significantly higher ductility, with no sacrifice in other mechanical properties.

Strategy

The project is divided into three phases as follows:

Phase 1 concentrates on developing a new family of aluminum-silicon alloys that is castable at significantly lower than usual temperatures, and therefore are cost-effective; and that is heat-treatable, and therefore is capable of significantly higher than typical mechanical properties. Within the context of Phase 1 is the development of an optimum heat treatment schedule for the new alloy system.

Phase 2 focuses on adapting the alloy system developed in Phase 1 to the die-casting process. The underlying premise is that die-casting at sufficiently low temperatures will cause negligible soldering of the alloy to the die. Accordingly, much lower iron content than that which is typical to die casting alloys will be required in the new alloy system, thus allowing significantly higher than typical mechanical properties to be attained.

Phase 3 explores the possibility of heat-treating die cast samples of the new alloys to further enhance their performance characteristics. Within the context of Phase 3 is measurement and documentation of the mechanical properties of heat-treated, die-cast samples.

PROJECT TASKS

The following tasks will be performed.

Phase 1

Task 1: Literature review and project planning

Task 2: Thermodynamic simulations and theoretical alloy design

Task 3: Sample production via permanent molds and microstructure analysis

Task 4: Optimization of heat treatment of permanent mold samples

Task 5: Mechanical property measurement and optimization

Sub Task 5.1: Production and heat treatment of tensile test bars (Permanent mold samples)

Sub Task 5.2: Measurement and optimization of room temperature mechanical properties (Permanent mold samples)

Phase 2

Task 6: Sample production via die-casting and microstructure analysis

Task 7: Mechanical property measurement and optimization

Sub-Task 7.1: Production and heat treatment of tensile test bars
(Die cast samples)

Sub-Task 7.2: Measurement and optimization of room temperature mechanical properties
(Die cast samples)

Phase 3

Task 8: Optimization of heat treatment of die cast samples

ACHIEVEMENTS TO DATE

Literature Review is in progress (Task 1).

Thermodynamic Simulations and Theoretical Alloy Design (Task 2).

Sample production via permanent molds and microstructure analysis (Task 3).

Mechanical property measurements and optimization (Task 5) – in progress.

See Appendixes A and B.

CHANGES IN PROJECT STATEMENT

None

WORK PLANNED BEFORE THE NEXT ACRC MEETING

- Optimization of heat treatment (high pressure die castings)
- Mechanical property measurement and optimization (high pressure die castings)

PROJECT DELIVERABLES

Deliverables from this project will include:

- A new family of aluminum-silicon alloys that is castable in permanent molds at significantly lower than usual temperatures, and therefore is cost-effective; and that is heat-treatable, and therefore is capable of significantly higher than typical mechanical properties.
- A new family of aluminum-silicon alloys that is die-castable at significantly lower than usual temperatures, and therefore is cost-effective. These alloys will contain less than usual iron and are heat-treatable; therefore they are capable of significantly higher than typical mechanical properties.

PROJECT SCHEDULE

The expected completion date of the project is December 2009.

APPENDIX A

Chemical Modification of the Morphology of the Mg_2Si Phase in Hypereutectic Al-Si-Mg Alloys

Chemical Modification of the Morphology of the Mg_2Si Phase in Hypereutectic Aluminum-Silicon-Magnesium Alloys

Hypereutectic aluminum-silicon alloys that contain more than 3wt% Mg exhibit a microstructure that consists of eutectic Si and Mg_2Si in α-Al matrix that is devoid of primary silicon particles. The Mg_2Si phase is desirable in the Al-Si microstructure because of its high melting temperature, low density, high hardness, low coefficient of thermal expansion, and high elastic modulus. However, at such relatively high concentrations of Mg, the Mg_2Si phase tends to be in a morphology that detracts from the alloys' mechanical properties. Several chemical modifiers were added to the alloy in order to refine the morphology of the Mg_2Si phase. A combination of strontium and misch metal was found to yield the best results in that the microstructure obtained after a standard T6 heat treatment exhibits almost spherical Mg_2Si particles. Tensile test bars cast from the modified alloy in steel molds have very good room temperature tensile properties and good hardness.

Introduction

A quick review of the open literature shows that most of the research performed on hypereutectic Al-Si-Mg alloys in the past two decades has been confined to compositions with less than 0.6 wt% Mg[1-5], and today almost all aluminum engine blocks are produced by die-casting 390 alloy[6], which contains about 0.5wt% Mg. The microstructure of this alloy consists of uniformly distributed primary Si crystals in an Al-Si eutectic matrix. This microstructure is responsible for the alloy's outstanding wear resistance, low thermal expansion, high thermal conductivity, and good elevated temperature strength and hardness.[1,7] However, proper control of the size and distribution of the primary Si particles in the microstructure is of paramount importance for attaining these desirable properties, and despite the many efforts that have been dedicated to achieving this goal[8-12], it is still sometimes difficult to control the primary Si particle size and distribution. Recent investigations have indicated that hypereutectic Al-Si-Mg alloys with Mg levels in excess of 2% exhibit a microstructure in which the Si particles are inherently refined and well distributed.[13] At these high Mg levels, large Mg_2Si particles tend to form and their number and size increase with increased Mg. The Mg_2Si phase is desirable in aluminum alloys because of its high melting temperature (1085^{o}C), low density (1.99 g/cc), high hardness (4.5 GPa), low coefficient of thermal expansion (7.5×10^{-6} K^{-1}), and reasonably high elastic modulus.[14] However, its presence in the form of large blocky or Chinese script particles significantly detracts from the alloys' mechanical properties. Hence, the focus of this work was twofold: (1) to eliminate primary Si from the microstructure of hypereutectic Al-Si-Mg alloys by optimizing the Mg content of the alloy and obtain a uniform distribution of Si in the matrix, and (2) to change the morphology of the Mg_2Si phase from the undesirable blocky or Chinese script form to a less detrimental form by means of chemical modifiers.

Materials and Procedures

Establishing the Base Alloy

A hypereutectic Al-Si alloy with the nominal composition Al-14Si-0.2Fe was chosen as the starting material and Mg additions in the range 1 to 5 wt% were made to this material in order to produce the alloys listed in Table 1. The alloys were constituted from commercially pure aluminum ingots, and Al-50%Si, Al-52%Mg, and Al-80%Fe master alloys; and their chemical composition was measured using spark emission spectrometry[a]. Samples for microstructure analysis were extracted from castings made in sand molds and prepared using standard metallographic techniques. The samples were always obtained from identical locations in the castings in order to ensure that the microstructures represent similar cooling rates. The cooling rate was measured to be 45°C/min.

Table 1 Composition of Al-14Si-0.2Fe-xMg alloys used for the study

Alloy	Si	Fe	Mg	Al
A0	14.05	0.23	-	Bal.
A1	13.95	0.22	1.08	Bal.
A2	13.98	0.23	2.05	Bal.
A3	14.01	0.21	3.06	Bal.
A4	14.06	0.25	4.01	Bal.
A5	14.04	0.25	5.02	Bal.

Fig. 1 shows the microstructures obtained from the alloys listed in Table 1. Fig. 1(a) shows the typical microstructure of the alloy without Mg. It contains mainly eutectic silicon and a few primary silicon particles dispersed in an α-Al matrix. Addition of 1 wt% Mg to this alloy - Fig. 1(b) - leads to the formation of a few Mg_2Si particles with Chinese script morphology, together with primary Si particles and eutectic Si particles (which seem to coarsen slightly as compared to the alloy without Mg). This coarsening may be attributed to the larger solidification range of the alloy with 1 wt% Mg (35°C) compared to that of the alloy without Mg (22°C). When the Mg content is increased to 2 wt% - Fig. 1(c) - the amount and size of the Mg_2Si particles in the alloy increase, and no change happens to the morphology of the Mg_2Si phase, but the primary Si particles completely disappear from the microstructure. When the Mg content is increased to 3 wt% - Fig. 1(d) - a significant change happens in the microstructure: The eutectic Si becomes refined. When the Mg content is increased to 4 wt% - Fig. 1(e) - no significant change happens to the size of the Mg_2Si particles with respect to the alloy containing 3 wt% Mg, but the Si particles begin to coarsen. Finally, when the Mg content is increased to 5 wt% - Fig. 1(f) - blocky Mg_2Si crystals (~40 μm) with sharp corners appear in the microstructure along with the coarse Chinese script Mg_2Si particles. Based on the preceding results, it is clear that the base alloy should have the composition: Al-14Si-0.2Fe-3Mg. Fig. 2 shows the effect of cooling rate on the grain size of this alloy, and Fig. 3 shows the effect of cooling rate on its microstructure: Although the fast cooling rate causes a significant decrease in the size of the Mg_2Si particles (the

[a] Model Spectro-Lab Max LMXM3, Spectro Analytical Instruments, Fitchburg, MA, USA. Accuracy of the spark transmission spectrometer is Si ± 0.3, Fe ± 0.0003 when Fe < 0.01, and ± 0.0022 when Fe > 0.1. Other relevant elements show negligible measurement errors.

dark particles in the image), it does not cause a significant change in their morphology and the Chinese script persists.

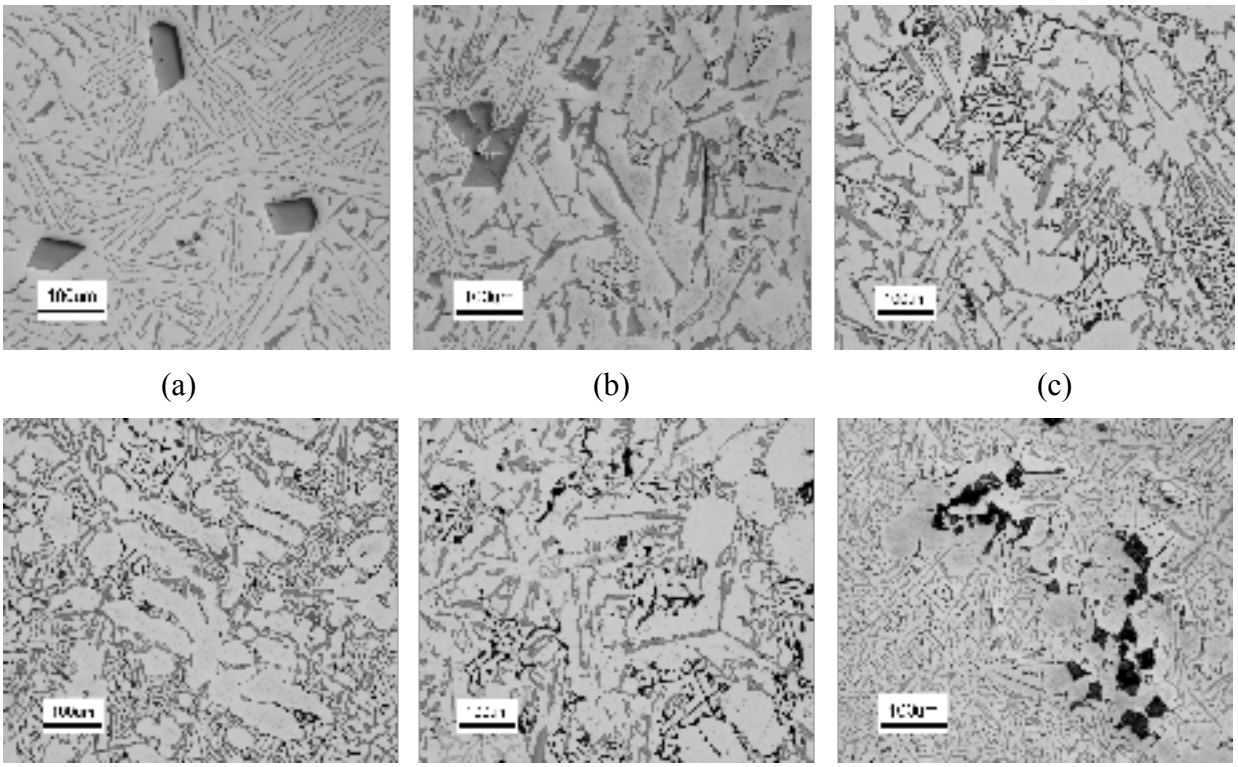


Fig. 1. Microstructure of Al-14Si-0.2Fe-xMg alloys solidified at 45 °C. (a) No Mg, (b) 1wt% Mg,(c) 2wt% Mg, (d) 3wt% Mg, (e) 4wt% Mg, and (f) 5wt% Mg.

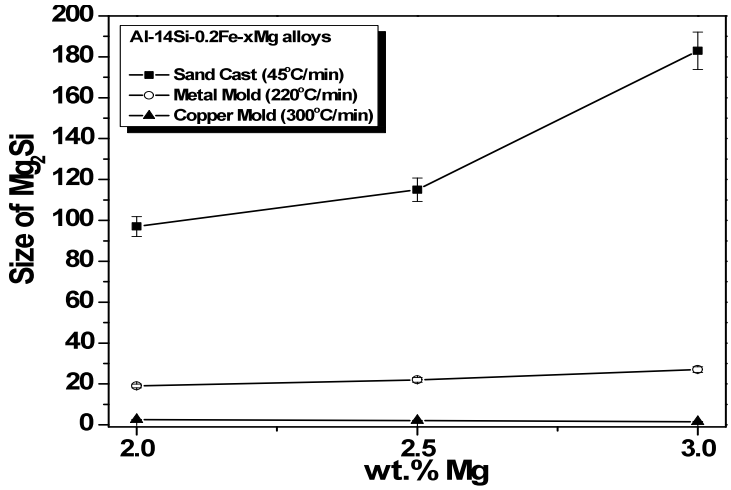
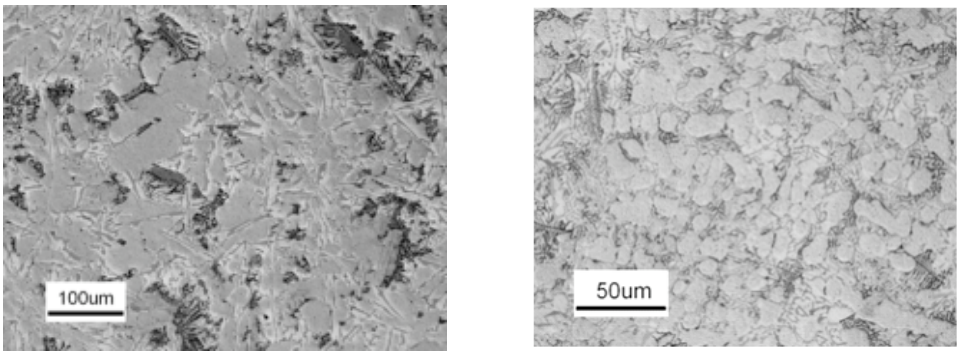


Fig. 2. Change in size of Mg_2Si particles in Al-14Si-0.2Fe-xMg alloys solidified at different cooling rates as a function of Mg content.



(a) (b)

Fig. 3. Optical micrographs of Al-14Si-3Mg-0.2Fe alloy solidified at (a) 220°C/min (b) 300°C/min.

Procedure for Microstructure Analysis

Microstructures were analyzed using optical[b] and scanning electron microscopy[c], and particle size analysis was performed using an image analyzer[d]. Images were taken from different regions in a sample and analyzed to arrive at an average value. All the samples used for optical microscopy and image analysis were etched with Kellers reagent. For SEM analysis, the samples were deep etched with 2% HF acid solution.

Procedure for Chemical Modification of the Mg_2Si Phase

The base alloy, namely Al-14Si-0.2Fe-3Mg, was treated with different chemical modifiers that were believed may change the morphology of the Mg_2Si phase from Chinese script to a more useful morphology. Table 2 lists the amounts of master alloys and elements used.

Table 2 Master alloys used to modify the morphology of Mg_2Si particles

Master Alloy	Addition amounts (wt%)
Al-87%Y	0.25, 0.50, 0.75, and 1.00
Al-99%Ce	0.25, 0.50, 0.75, and 1.00
Al-10wt%Sr	0.025, 0.050, 0.5, and 1.00
Cu-15wt%P	0.02, 0.05, 0.2, and 0.5
Al-10wt%Ca	0.2, 0.5, and 1.0
Al-5.7%Ti	0.20, 0.50, and 1.00
Pure Sn	0.20, 0.50, and 1.00
Pure Zr	0.02, 0.50, and 1.00
Misch Metal	1, 2, and 3

[b] Nikon ACT-1 Version 2.63, Nikon Corporation

[c] Model JEOL JSM-840

[d] Model Nikon C5405-01, Japan

Because mish metal offered a less expensive alternative to elemental Ce, a systematic study of the effect of misch metal on the base alloy was performed. The amount of misch metal, and its reaction time and temperature with the base alloy were identified as key parameters for optimizing the alloy's microstructure. The tested magnitudes of these parameters are listed in Table 3.

Table 3 Parameters used to optimize the addition of misch metal

Variable	Magnitude
Amount of Misch Metal (wt%)	1, 2, and 3
Reaction Time (hr)	1, 2, 3, and 4
Reaction Temperature (^{o}C)	750, 850, 950

Procedure for Making Tensile Test Bars and Measurement of Room Temperature Tensile Properties

In order to make tensile test bars, the charge materials were melted in an induction furnace in clean silicon carbide crucibles whose interior was coated with boron nitride. The alloys were heated to 750-800°C for at least 30 minutes in order to ensure complete dissolution of the alloying elements. The melt's chemical composition was checked using spark emission spectrometry and adjusted until the target composition was achieved. The melts were then degassed using a rotary degasser for 40 minutes. ASTM standard tensile test bars[15] were produced in a steel mold that was preheated and maintained at 425±5^{o}C during pouring. The tensile test bars were solution heat treated immediately after casting.

Measurement of the tensile properties was conducted at room temperature with a Universal Testing machine[e]. Strain was measured using an axial extensometer[f] with a gage length of 2 inches. The extensometer was used until the specimen fractured and the machine's crosshead speed was 0.1 in/min. The tensile test results reported are averages of at least six measurements. Hardness measurements were performed according to ASTM standard E18[16]. The measurements were performed on a Rockwell Hardness Tester[g] with a 1/16 inch ball and 100 kg_f load. Rockwell Hardness scale B was used in all measurements and all the hardness values reported herein are averages of ten readings.

Results and Discussion

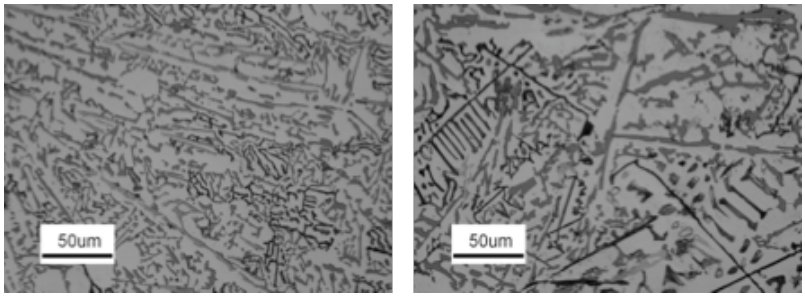
Microstructure analysis proved that the morphology and size of the Mg_2Si phase are not significantly affected by the addition of Y, P, Ca, Ti, Zr, and Sn to the base alloy. However, the addition of Ce, Sr, and misch metal had a significant effect on the morphology of the Mg_2Si phase as well as the eutectic silicon. Ce has a pronounced effect on the size distribution of the

[e] Instron Servo-Hydraulic Tension-compression System model 1332 equipped with an 8500 controller and a 5620 pound load cell.

[f] MTS extensometer model 634.25

[g] Model 3DR, Tester No. 266, WILSON, United Service Company, CT, USA

coarse Mg_2Si particles. At slow cooling rates, the typical Chinese script morphology of the Mg_2Si phase is modified and/or fragmented into smaller Mg_2Si particles. Such fragmentation is seen in the case of the alloys modified with 0.25 and 0.50 wt% Ce - Fig. 4. However the beneficial effect of Ce seems to fade at higher addition levels. This is evident from the microstructure in Fig. 4(b) in which the coarse Chinese script reappears. Also Ce does not seem to modify the eutectic Si, though it has been reported to modify primary Silicon.[12]

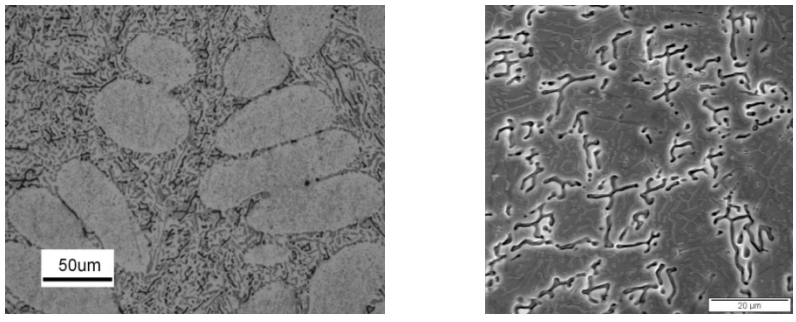


(a) (b)

Fig. 4. Optical micrographs showing the morphology of the Mg_2Si phase in an Al-14Si-0.2Fe-3Mg alloy modified with (a) 0.25 wt% Ce, and (b) 1 wt% Ce.

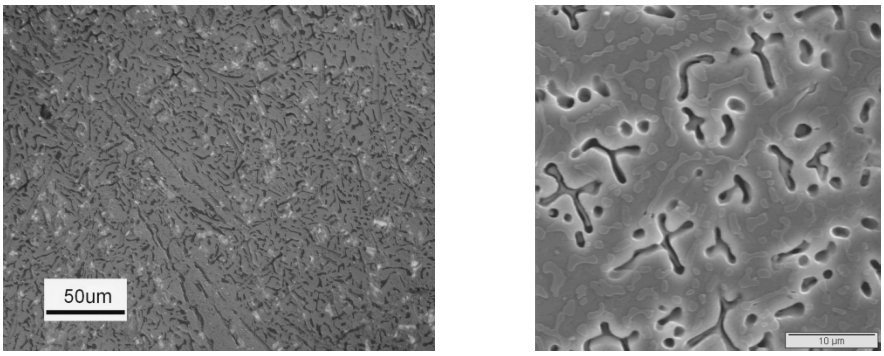
Sr has a similar effect to that of Ce on the morphology of the Mg_2Si phase; however, the effect occurs at much lower Sr levels. At 0.025 and 0.050 wt%, the eutectic silicon and the Mg_2Si phase are significantly modified. Figure 5(a) shows that addition of 0.025wt% Sr alters the morphology of the Mg_2Si phase and also refines it. The modified morphology of the Mg_2Si phase is evident in the SEM micrograph of Fig 5(b).

Addition of Ce (0.25%) + Sr (0.025%) result in a more uniform microstructure than either element alone. This may be due to the different modifying action of each element. While the Mg_2Si phase is effectively modified by both Ce and Sr, the eutectic Si is modified only by Sr. The morphology of the Mg_2Si phase is changed from the typical Chinese script to various other morphologies as seen in Fig. 6.



(a) (b)

Figg. 5. The morphology of Mg_2Si in Al-14Si-0.2Fe-3Mg-0.025Sr alloy. (a) Optical, and (b) SEM micrograph.

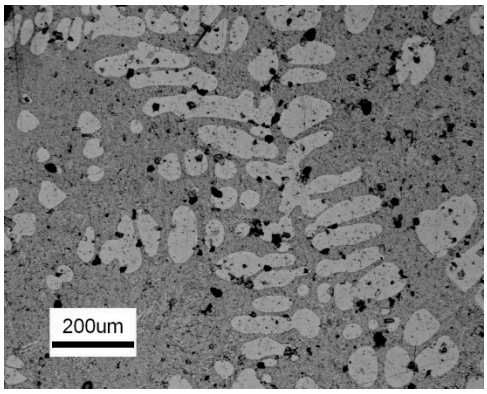


(a) (b)

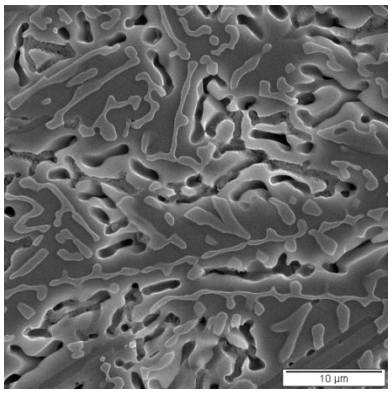
Fig. 6. The morphology of Mg_2Si in Al-14Si-0.2Fe-3Mg-0.25Ce-0.025Sr alloy. (a) Optical, and (b) SEM micrograph.

Adding 1wt% misch metal (which is equivalent to adding 0.53 wt% Ce) to the base alloy result in the formation of needle-like rare-earth particles that are very stable and do not dissolve into the matrix during a typical T6 solution heat treatment. Moreover, it did not affect the morphology of the Mg_2Si phase. This could be attributed to the short reaction time and/or the low temperature used. Hence, a systematic investigation was performed in order to determine the effect of reaction temperature and time on the morphology of the Mg_2Si phase. In this investigation, the base alloy, namely Al-14Si-3Mg, with different amounts of misch metal was melted at the different temperatures for the different reaction times that are shown in Table 3, and then it was solidified in sand molds. It was found that: (a) At a reaction temperature of 750°C, there is no significant change in the morphology and size of the Mg_2Si phase even after a reaction time of 4 hours. It seems that the dissolution kinetics of misch metal into the alloy at this temperature is very slow. (b) At a reaction temperature of 850°C, the Mg_2Si phase and the eutectic silicon are significantly refined even after a reaction time of only 1 hour - Figure 7(a). (c) Holding the melt for more than 2 hours at 850°C causes the Mg_2Si particles to coarsen - Fig. 7(b). (d) More rare earth particles form when the reaction temperature is increased from 750°C to 850°C. Fig. 7(c) clearly shows the morphology of the eutectic Si and the Mg_2Si phase, and Fig. 7(d) shows that the rare earth particles have a faceted morphology. The chemical composition of the particles was confirmed by EDX analysis[h] on several particles - Fig. 7(e). The atomic ratio of the rare earth elements is such that Ce : La : Pr : Nd = 8 : 7 : 5 : 6.

[h] Model KEVEX SIGMA



(a)



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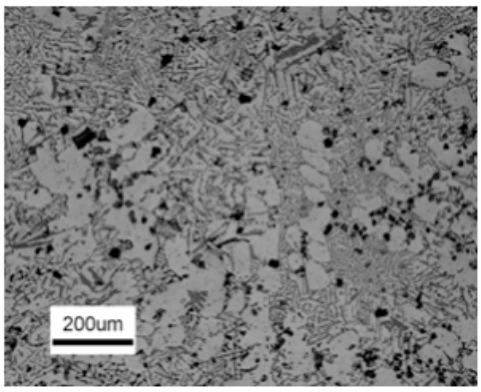
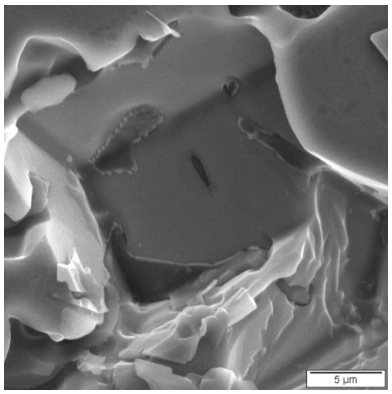
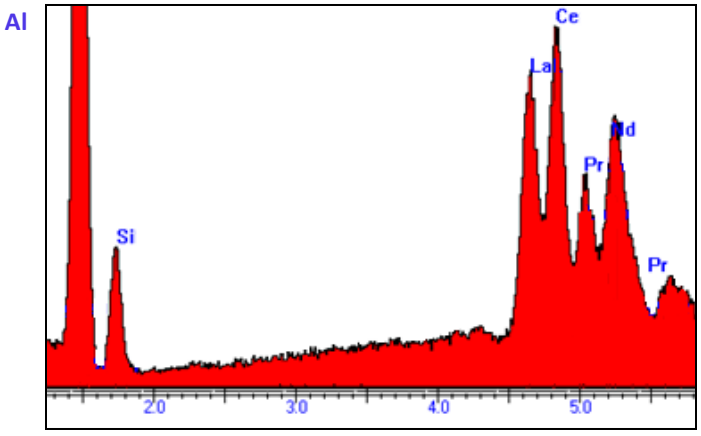


(c)



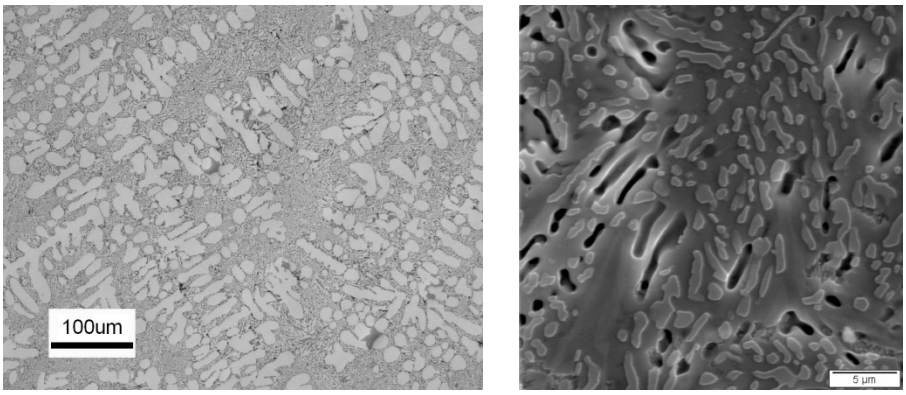
(d)



(e)

Fig. 7. Micrographs of Al-14Si-0.2Fe-3Mg-1MM alloy held at 850°C for (a) and (b) 2 hr, and (c) 4 hr. (d) Photomicrograph of a typical rare earth particle in the Al-14Si-0.2Fe-3Mg-1MM alloy held at 850°C for 2 hr, and (e) EDX spectrum obtained from the particle in (d).

Based on the preceding, it was decided that a reaction temperature of 800°C and a reaction time of 90 minutes are optimum for obtaining a refined Si and Mg_2Si morphology. Fig. 8 shows the as-cast microstructure of the optimized alloy (Al-14Si-3Mg + 1 wt% misch metal + 0.025 wt% Sr) processed with these optimum conditions. These samples were cast in a steel mold. The microstructure consists of α-Al dendrites, very fine eutectic silicon and Mg_2Si particles. Notice that the rare earth particles which were present in the alloy when it was slowly cooled in sand molds are almost absent from the alloy that is cast in steel molds.



(a) (b)

Fig. 8. Photomicrographs of Al-14Si-0.2Fe-3Mg-1MM-0.025Sr alloy (a) Optical and (b) SEM photomicrograph.

Fig. 9 shows the microstructure of these samples after they were solutionized at 540°C for 8 hours, and Fig. 10 shows the microstructure after the solutionized samples were aged. Two aging temperatures (170°C and 200°C) and two aging times (4 hours and 8 hours) were used. Fig 10 shows that both the silicon and Mg_2Si particles are almost completely spheroidised by the T6 (170°C, 8h) heat treatment. Table 4 shows the room temperature tensile properties and hardness of the alloy when heat treated to different conditions. The maximum yield strength (~ 49 ksi) is obtained when the alloy is aged at 170°C for 8 hours. The maximum hardness (HRB 78) is also obtained when the alloy is aged at 170°C for 8 hours. The measurements indicate that ageing at the higher temperature is detrimental to the hardness of the alloy.

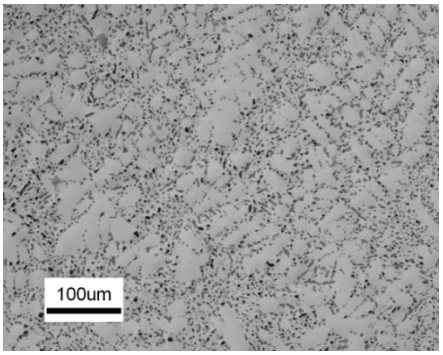


Fig. 9. Photomicrograph of Al-14Si-0.2Fe-3Mg-1MM-0.025Sr alloy after solution treatment at 540°C for 8 hours.

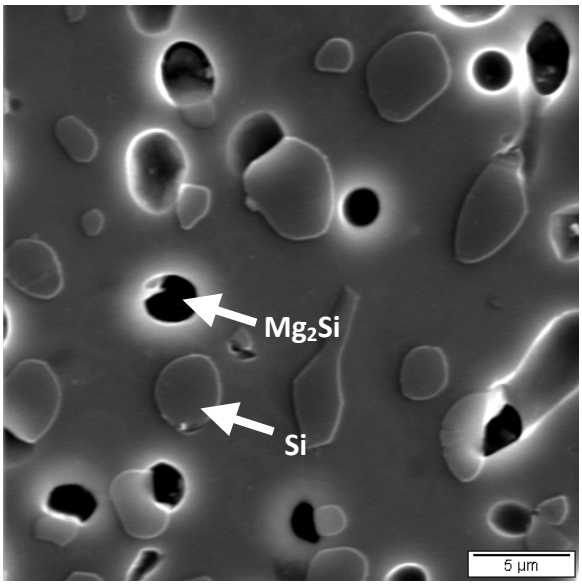


Fig. 10. SEM photomicrograph of Al-14Si-0.2Fe-3Mg-1MM-0.025Sr alloy after T6 (170°C, 8 hr) heat treatment.

Table 4 Room temperature tensile properties and hardness of Al-14Si-0.2Fe-3Mg-1MM-0.025Sr.

Temper	Condition	UTS (MPa)	YS (MPa)	El (%)	Modulus of Elasticity (GPa)	Hardness (HRB)
As-cast	-	220.6	145.5	2.29	73	40
T4	1 day	280.6	209.6	2.46	76	60
T6	170°C 4 hrs.	339.9	308.2	0.94	91	74
	170°C 8 hrs.	346.8	337.2	0.67	92	78
T6	200°C 4 hrs.	349.6	335.1	0.73	89	75
	200°C 8 hrs.	321.9	299.9	0.79	85	70

Summary and Conclusions

Adding about 3 wt% Mg to hypereutectic Al-Si alloys completely suppresses the formation of primary silicon particles and significantly refines the eutectic Si. However, it leads to formation of large Mg_2Si particles that have Chinese script morphology. Adding optimum amounts of misch metal and strontium to the hypereutectic Al-Si-3Mg alloy modifies and refines both the eutectic Si and the Mg_2Si phase. A reaction temperature of about 800^{o}C and a reaction time of about 90 minutes are optimum for complete dissolution of the misch metal in the alloy and

attainment of the refined microstructure in cast parts. Higher temperatures and longer times cause excessive coalescence of the Mg_2Si and Si phases. T6 heat treatment of tensile bars cast from these alloys in steel molds yields room temperature tensile properties that are comparable to those of conventional A390 alloy.

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APPENDIX B

Heat Treatment of HPDC Alloys

Heat Treatment of HPDC A380 Alloy

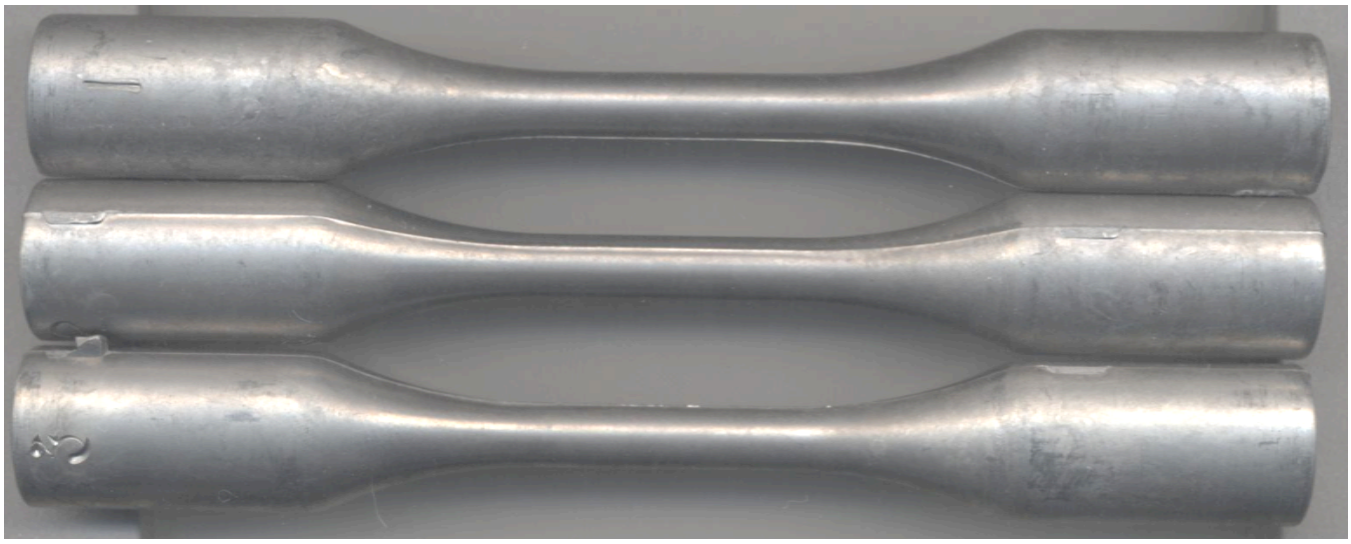
Preliminary heat treatment experiments were performed using three variants of A380 alloy, the chemical compositions of which are summarized in Table I. The alloys were die-cast to produce ASTM standard tensile specimens. The tensile specimen were subjected to solution treatment at different temperatures and visually examined for the occurrence of "blisters". Solution treatment was performed in an air-circulating furnace for 30 minutes at temperatures ranging from 465-505^{o}C and the samples were then quenched in water.

- At 475^{o}C, blisters did not occur (Figure 1a).
- At 485^{o}C, blisters did not occur (Figure 1b).
- Occasional blisters were observed at 495^{o}C as indicated by arrows in Figure 1c.
- At 505^{o}C, the specimens became completely discolored and many blisters were observed on the surface (Figure 1d).

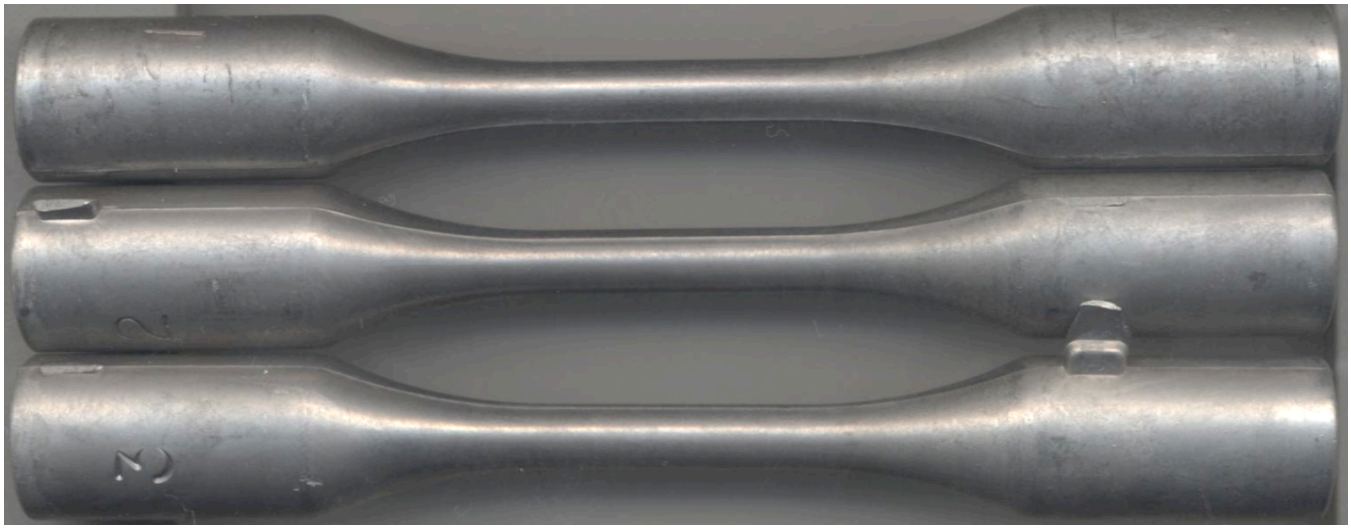
Solutionizing at 485^{o}C for 30 minutes seems to be optimum. Specimens that were solutionized at 485^{o}C were then aged for 8 hours at 165^{o}C and their room temperature tensile properties were measured. Table II lists these properties. After heat treatment, Sample #1 has the highest elongation, while Sample #3 has the highest ultimate and yield strengths. The alloys that contain Ti (Samples #2 and #3) show significant increase in yield stress upon heat treatment compared to the as cast condition.

Table I. Chemical composition of the A380 alloys.

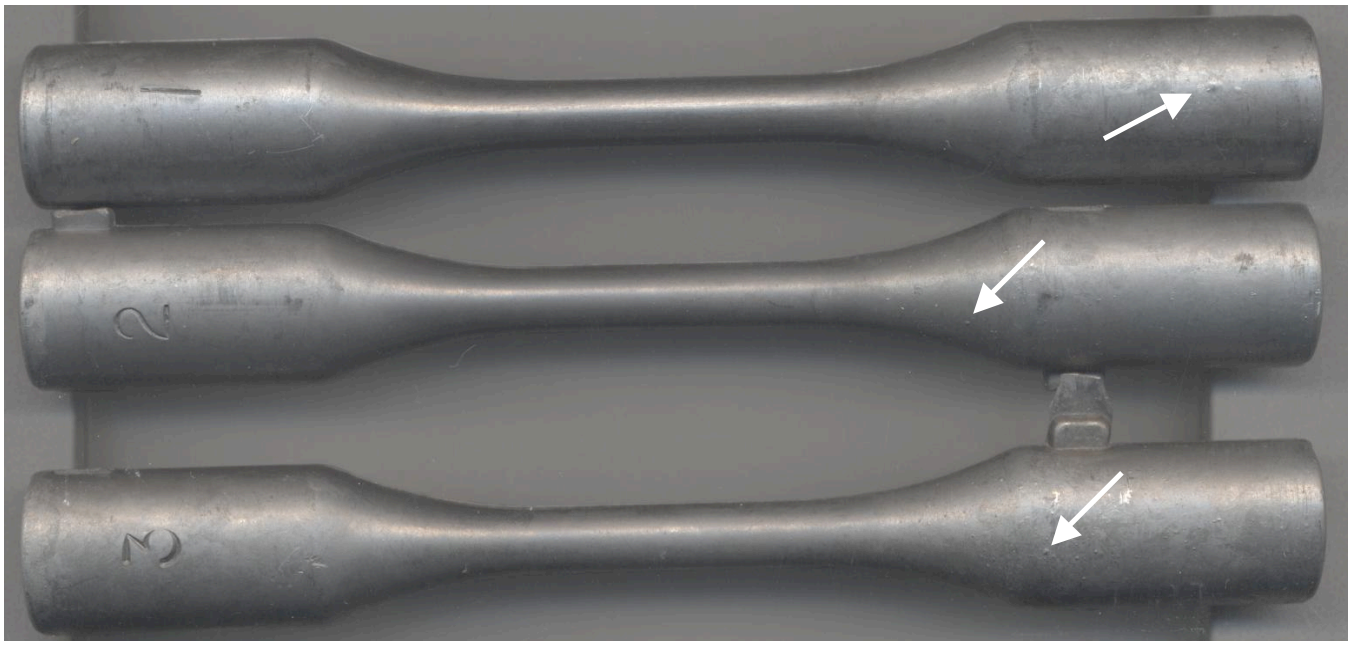
	Si	**Mg**	**Cu**	**Fe**	**Mn**	**Zn**	**Ni**	**Ti**	**Sr**
Sample # 1	9.08	0.050	3.11	1.05	0.27	1.80	0.076	0.053	-
Sample # 2	7.67	0.097	3.44	0.73	0.43	2.15	0.038	0.150	-
Sample # 3	9.45	0.330	3.00	0.61	0.55	1.89	0.027	0.220	0.035



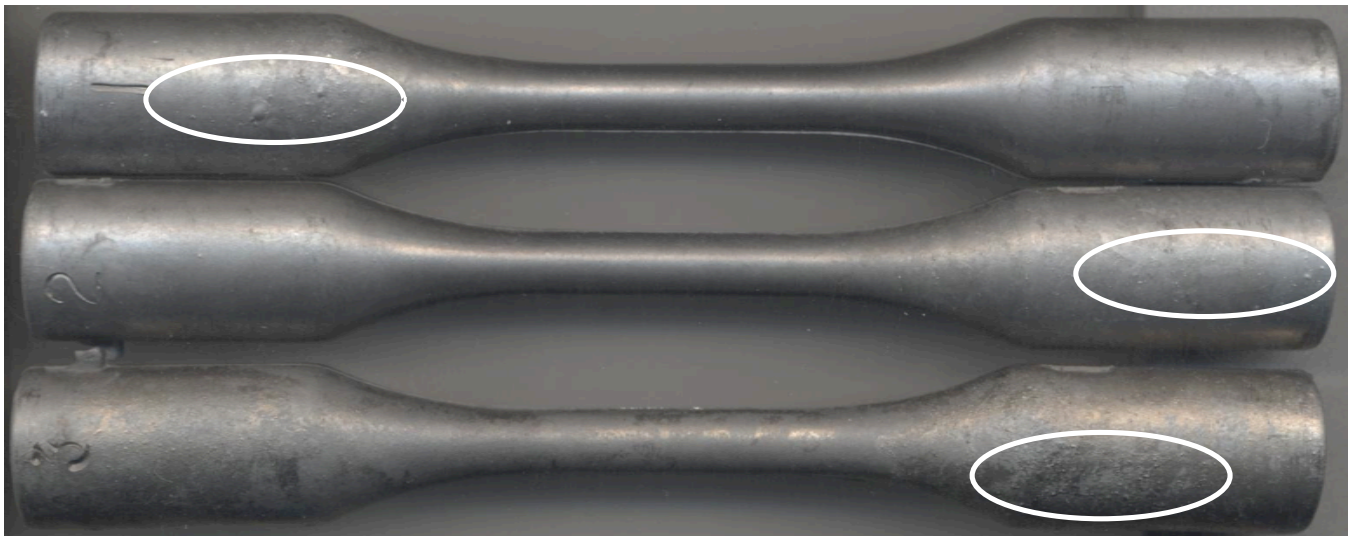
(a)



(b)



(c)



(d)

Figure 1. Surface appearance of the alloy A380 solutionised for 30 min. at (a) 475°C, (b) 485°C, and (c) 495°C (d) 505°C

Table II. Tensile properties of die cast specimens of the A380 alloys shown in Table I.

	Temper	UTS (ksi)	YS (ksi)	EL (%)	Modulus (GPa)	Hardness (RHB)
Sample # 1	As-cast	46.4	28.3	4.0	70	45
	T6	45.2	26.0	6.8	67	40
Sample # 2	As-cast	43.2	27.0	3.3	82	43
	T6	52.0	40.7	3.0	85	48
Sample # 3	As-cast	50.1	38.4	3.2	83	49
	T6	57.0	45.3	3.6	84	49

Summary

This preliminary study shows that high pressure die-cast A380 alloys can be subjected to a T6 heat treatment without causing any surface blistering. This is achieved by solution treating the parts for much shorter times and at lower temperatures than those used for heat treating parts that were cast in permanent molds.

Solutionizing at 485^{o}C for 30 minutes ensures a blister-free sample and the tensile properties are significantly improved.

The findings from this study provide guidelines for heat treating the die casting alloy that is being developed in this project.