

TECH NOTES

The Al-Si Phase Diagram

Introduction

Aluminum has a wide range of commercial applications due to its unique combination of good corrosion resistance, light weight, good mechanical properties, ease of fabrication and acceptable cost. Its density of $\sim 2.7 \text{ g/cm}^3$ makes it the lightest commercial metal other than magnesium ($\sim 1.74 \text{ g/cm}^3$) and beryllium ($\sim 1.85 \text{ g/cm}^3$). But, Al and its alloys have more versatility, fewer problems, and cost less than Mg or Be alloys. The range of melting points for both Al and Mg alloys are fairly similar, ~ 565 to 640°C (~ 1050 to 1185°F) for Al casting alloys and ~ 593 to 648°C (~ 1100 to 1198°F) for Mg casting alloys.

Metallographers and metallurgists can learn a great deal from the study of binary phase diagrams which map out the relationship between composition and phase occurrence as a function of temperature - but under "equilibrium" conditions. Equilibrium conditions involve very slow heating and cooling rates and metals production generally involves faster heating and cooling rates - non-equilibrium conditions. Despite this, the phase diagram is the starting point for our understanding of alloy systems. For example, the phase diagram teaches us about melting and solidification temperatures, the solidification sequence, equilibrium phases that can form, solubility limits for alloy or impurity additions and dissolution temperatures for second phases.

This Tech-Note is devoted to a study of the aluminum-silicon phase diagram, a diagram of considerable commercial significance. The binary diagram is the starting point for developing more complex alloys and for understanding their behavior. Elements such as Si and Fe are common impurities found in aluminum alloys, but silicon is also a deliberate alloying addition in both cast and wrought Al alloys. Cast Al alloys can contain Si in amounts from about 5 to 22 weight percent. At this level, Si improves the fluidity and castability of aluminum. The 3xx.x (Al-Si-Cu) and the 4xx.x (Al-Mg-Si) cast alloys (US designations of the Aluminum Association) are very popular commercially. Hypereutectic alloys (alloys with greater than 12.6% Si, the eutectic composition) contain primary Si particles that provide improved wear resistance. Such alloys may be used as engine blocks. A small addition of Mg to some of the 3xx.x cast alloys allows them to be age hardened and thus provide improved strength. Wrought 6xxx alloys are also Al-Si- Mg alloys that can be age hardened while some of the wrought 4xxx alloys cannot be age hardened and others can (Mg levels vary from <0.05 to as much as 2.0 wt. %). Si levels for the 4xxx wrought alloys vary between ~ 3.5 and 13.5 wt. % while the Si content of the 6xxx wrought alloys are much lower, ranging from ~ 0.2 to 1.8 wt. %.

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Casting Techniques

Al-Si alloys can be cast using a variety of techniques; the most commonly used techniques are sand casting, gravity die casting and injection mold casting. Each procedure has its strong points and weak points. Sand casting is the most versatile technique and permits manufacture of the largest castings - weights approaching 10,000 kg are possible. In fact, sand casting is best for larger castings and low production runs. The surfaces are the roughest of these methods and dimensional tolerances are the greatest. Die casting is the highest productivity method of the three. Molten metal is injected into a cavity made from heat treated tool steel under pressures up to $\sim 140 \text{ MPa}$ ($\sim 20 \text{ ksi}$). Castings are often smaller than $\sim 5 \text{ kg}$ ($\sim 10 \text{ lbs}$) but larger castings, up to $\sim 50 \text{ kg}$ ($\sim 100 \text{ lb.}$) are possible, depending upon the equipment available. Die cast parts have smooth surfaces and require little, if any, machining. Die casting permits production of thinner walls than the other methods. Permanent mold casting is performed using either gravity or pressure feeding of the liquid metal into a permanent mold. Casting sizes may be somewhat larger than for die casting. Surfaces are also quite smooth. Both die casting and permanent mold casting produce rapid solidification rates that yield fine microstructures and good properties.

Intermetallic Phase Due to Si and Fe Additions

In the absence of other elements, Si additions to Al produce elemental Si particles and an Al-rich solid-solution phase. The solubility of Si in Al is quite low. In commercial alloys, it is quite common to have small amounts of iron present as an impurity of the refining and smelting processes. At low Fe impurity contents, most of the Fe remains in solid solution until the eutectic reaction occurs yielding a solid solution of $\alpha\text{-Al}$ and Al_3Fe intermediate (also called intermetallic) particles with a monoclinic crystal structure. If Mn is also present, and depending upon the solidification rate, Al_6Fe may precipitate instead. The maximum solubility of Fe in Al is 0.05 wt. %; however, the solubility is lower in commercial alloys. Commercial Al-Si alloys containing Fe impurities may form two types of intermetallic phases by a eutectic reaction (a eutectic reaction is where a liquid transforms to two different solid phases at a specific composition and temperature on cooling and the reverse on heating). For alloys with a low Si content, the Fe is present as Al_3Fe while at higher Si levels, first $\alpha\text{-Al}_{12}\text{Fe}_3\text{Si}$ (cubic crystal structure) and at still higher Si levels $\beta\text{-Al}_9\text{Fe}_2\text{Si}$ (monoclinic crystal structure) will form.

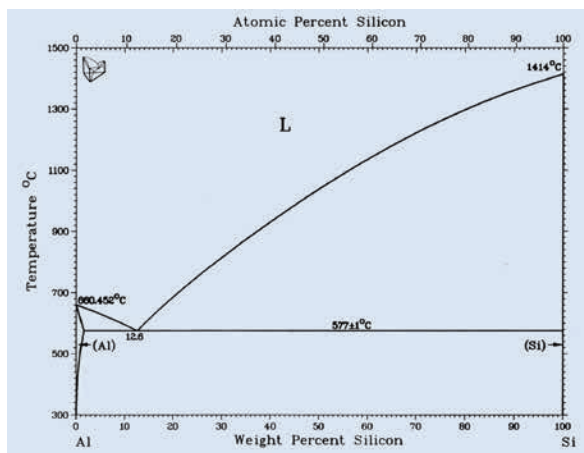


Figure 1. Al-Si binary phase diagram based upon Murray and McAlister (1) from (2).

Table 2. Etchants for Aluminum Used in this Tech Note

Name	Composition	Use
Aqueous 0.5% HF	99.5mL water (Note 1) 0.5 mL HF	Swab or immerse until structure is revealed
Keller's Reagent	95mL water, 2.5mL HNO ₃ , 1.5mL HCl, 1mL HF	Immerse specimen until structure is revealed. Brings up grain boundaries in 2xxx and 7xxx wrought alloys.
Si Blue Etch	90mL water, 4mL HF, 4mL H ₂ SO ₄ , 2 g CrO ₃	Immerse specimen about 10 s until structure is revealed.
Barker's Reagent	200mL water, 4 to 10mL HBF ₄	Use electrolytically at 20-40 V dc at 20 °C (Note 2) with an Al, Pb or stainless steel cathode
Weck's Reagent	100mL water, 4 g KMnO ₄ , 1 g NaOH	Use only by immersion, generally 10-20 s, until the surface is colored (brown).

Note 1. Always use distilled water and reagent grade chemicals for etchants.

Note 2. After using Barker's reagent, the structure must be examined with polarized light; adding a sensitive tint filter (1st order red filter) produces color contrast. HBF₄ has historically been called fluoboric acid but is now called fluoroboric acid.

Table 1. Preparation Method for Al and Alloys

Surface	Abrasive	Time, (min:s)
CarbiMet® PSA Grinding Paper	240grit SiC, water cooled, contra rotation, 5lbs [22N] per specimen	Until plane
UltraPol™ Silk Cloth	9µm diamond, contra, 5lb/specimen, with MetaDi® Fluid lubricant	5
TriDent™ Polyester Cloth	3µm diamond, contra, 5lb/specimen, with MetaDi® Fluid lubricant	5
TriDent™ Polyester Cloth (optional step - difficult specimens)	1µm diamond, contra, 5lb/specimen, with MetaDi® Fluid lubricant	3
MicroCloth® Synthetic Suede Cloth	0.05µm MasterMet® Colloidal Silica, comp., 5lbs/specimen	2-3
MicroCloth® Synthetic Suede Cloth (optional step - difficult specimens or for EBSD work)	0.05µm MasterMet® Colloidal Silica on the VibroMet® 2 Vibratory Polisher	0.5 to 3 h

The Al-Si Phase Diagram

The binary Al-Si phase diagram was initially studied by Fraenkel of Germany in 1908. It is a relatively simple binary diagram where there is very little solubility at room temperature for Si in Al and for Al in Si. Thus, the terminal solid solutions are nearly pure Al and Si under equilibrium conditions. The currently accepted diagram, Figure 1, is

based on the study by Murray and McAlister¹ in 1984. The melting points of Al and Si are, respectively, 660.45 and 1414 °C, while the eutectic reaction occurs at 12.6 wt. % Si and 577 ± 1 °C². The maximum solubility of Si in Al occurs at the eutectic temperature and is 1.65 wt. %. At least up to the late 1950's, the eutectic was believed to be at 11.6 wt. % Si. Modification of the eutectic by very small Na additions has been known since the 1920s³⁻⁵. Modifiers like Na shift the eutectic to a higher silicon content, around 14 wt. %, preventing precipitation of proeutectic Si while refining the structure of the eutectic. This increases both strength and ductility substantially. Of course, increasing the solidification rate also has the same effect, hence the popularity of pressure die casting and permanent mold casting. Both create much finer grain structures and eutectic dispersions and better properties. For hypereutectic Al-Si alloys, phosphorus has been found to be the most effective addition to modify the proeutectic silicon phase, reducing the particle size and amount.

Table 1 lists our procedure for preparing aluminum alloys with several options, depending upon the degree of difficulty in preparing the specimens, or the need for absolute freedom from any remnant damage from sectioning and preparation, e.g., for EBSD or nano-indentation testing. Other polishing cloths can be substituted, generally based on personal preference. Table 2 lists the composition of the etchants used in this Tech Note.

Let's first examine the microstructure of high-purity Al. Figure 2 shows the recrystallized grain structure of a "super pure" specimen of Al electrolytically etched with Barker's reagent and viewed with polarized light plus a sensitive tint filter. This specimen actually has a small amount of impurities and visible second phases (some of the spots in the micrograph are where the etchant has attacked these precipitates). Figure 3 shows three views of the structure of an Al - 1% Si - 0.45% Mg wrought specimen containing grain boundary Si films and fine patches of the α - Al - Si eutectic, generally at grain boundary triple points. Etching with aqueous 0.5% HF outlines the second-phase Si particles. The "Si-Blue Etch" colors the Si preferentially. Weck's color etch for Al reveals the regions around the Si phase which has been denuded of Si, details that cannot be revealed with "black and white" etchants.

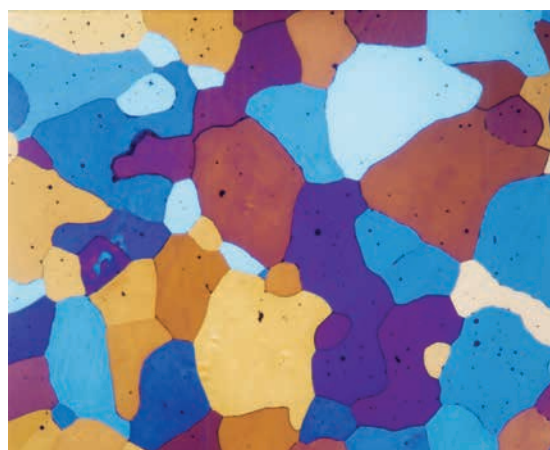


Figure 2. "Super-pure" aluminum electrolytically etched with Barker's reagent and viewed with polarized light plus a sensitive tint filter revealing an equiaxed, recrystallized grain structure. There are some fine impurity precipitates in this specimen, however, that cannot be seen with this etch and magnification (50x).

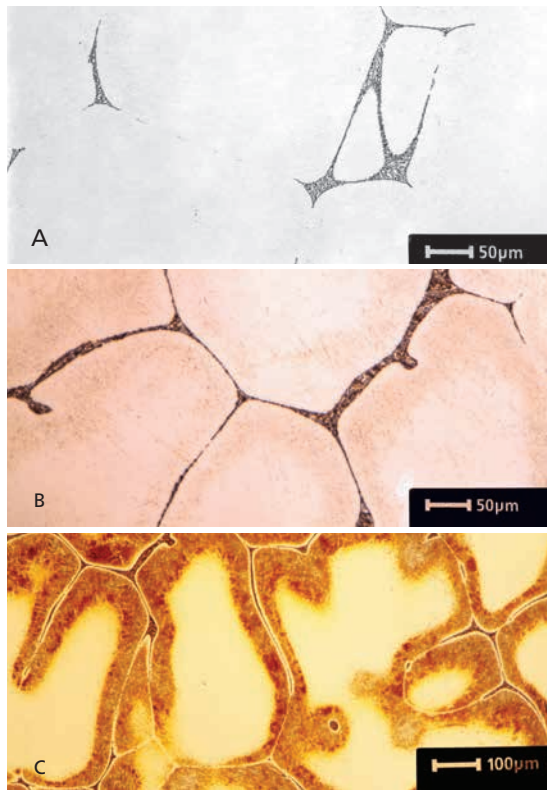


Figure 3. Microstructure of Al - 1% Si - 0.45% Mg revealed using (a) aqueous 0.5% HF, with (b) the Si Blue Etch; and (c) with Weck's color etch for Al, which revealed segregation around the grain boundary Si films and the eutectic (bright field illumination).

Figure 4 shows the microstructure of as-cast Al - 7.12% Si using the Si-blue etch and Weck's color etch for Al. Figure 4a shows that the Si particles are small and uniform in shape. Weck's reagent, Figure 4b, brings out the shape of the α -Al dendrites. In the center of the field of view, we can see a large primary dendrite with many smaller secondary dendrite arms perpendicular to the primary axis. Note that this etchant also reveals segregation within the dendrites, which would be more easily seen at a higher magnification. Figure 5 shows a similar Si level alloy, but with addition of 0.45% Mg. Note that the eutectic particles have a different shape in this alloy, being more elongated. Again, Weck's reagent brings out the shape of the α -Al dendrites. However, to really evaluate such differences, we must be sure that the plane of polish in each case is the same (it is best to use a plane parallel to the growth direction to see the dendrites properly and make spacing measurements).

Figure 6 shows two views of the as-cast microstructure of an Al 11.7% Si near-eutectic alloy. At low magnification, we can see the dendritic nature of the fine solidification structure. At high magnification, this is not observed; instead we see the fine eutectic and what appears to be randomly oriented α -Al grains. Figure 7 shows the as-cast microstructure of Al - 12% Si with long, fibrous Si in the eutectic. Compare Figure 7 to Figure 8 where sodium has been added to the same Al - 12% Si alloy which markedly refined the shape of the eutectic Si and produced proeutectic α -Al.

Figure 9 shows the cast structure of Al - 13% Si - 0.045% Mg, again with fibrous eutectic Si. Figure 10 shows the cast structure of Al - 19.85% Si with large primary Si particles. Note how Weck's reagent brought out the eutectic cells around these primary Si particles. Figure 11 shows the as cast structure of Al - 25% Si - 1.4% Fe. In Figure 11a, we can see the long β -AlFeSi needles. Figure 12 shows

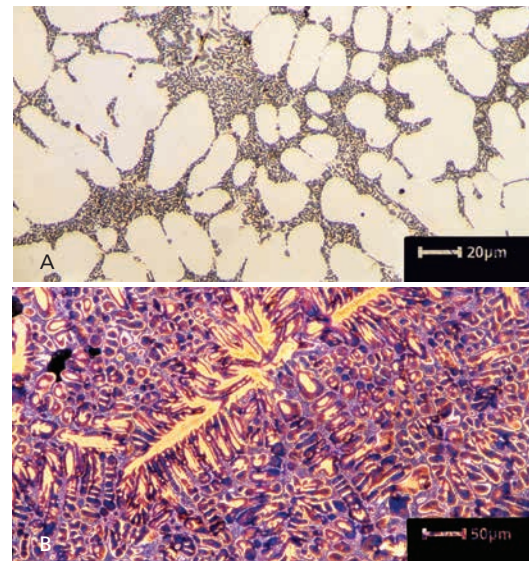


Figure 4. Cast microstructure of Al 7.12% Si revealing (a) the Si particles in the eutectic at high magnification with the Si Blue etch, and (b) the α -Al dendrites (the eutectic is too fine to resolve at this magnification) with Weck's reagent (viewed with polarized light and a sensitive tint filter).

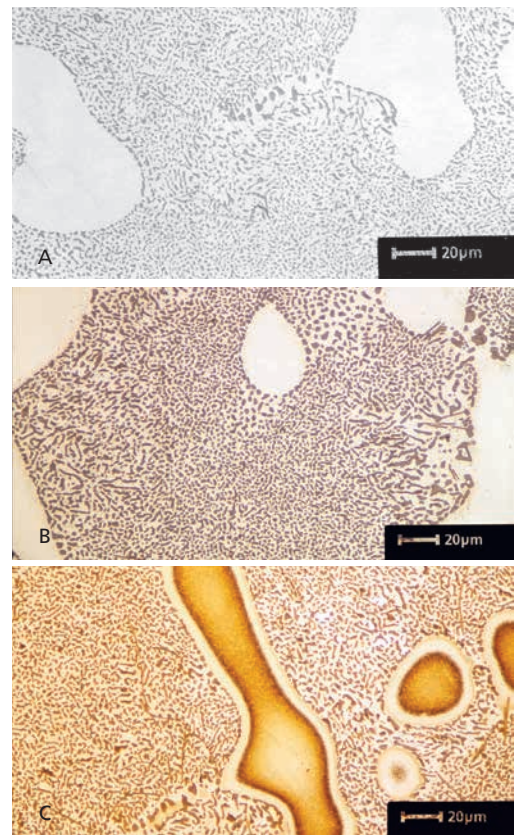


Figure 5. Microstructure of as-cast Al - 7% Si - 0.45% Mg revealed (a) using aqueous 0.5% HF, with the (b) Si Blue Etch; and, (c) with Weck's etch (bright field illumination) which revealed the segregation within the α -Al dendrites.

the cast Fe. In Figure 11a, we can see the long β -AlFeSi needles. Figure 12 shows the cast structure of Al - 50% Si. Note the massive brittle primary Si particles, most of which are cracked.

Figures 13 to 16 show the structure of Al - 12.9% Si gravity die cast specimens. The specimen in Figure 13 was not modified. It contains some large primary proeutectic Si particles. Compare the microstructure of this specimen to that of: Figure 14, refined with 0.03% Ti; Figure 15, modified with 0.045% Sr; and, Figure 16, modified with 0.05% Sr and refined by 0.05% Ti. Note that the heats modified with Ti contain some elongated needles. The heat refined with 0.03% Ti (Figure 14) contained a few small primary proeutectic Si particles, while the heats modified with Sr did not contain primary Si particles.

Conclusions

Al-Si alloys have considerable commercial importance as casting alloys. Hypoeutectic alloys with ~7% Si are widely used in automotive applications. Near-eutectic alloys, generally containing eutectic modifiers, are also widely used, particularly by die casting. Hypereutectic alloys containing large primary Si particles are used in applications requiring wear resistance. The Al-Si binary phase diagram is the basis for understanding the microstructure of these alloys.

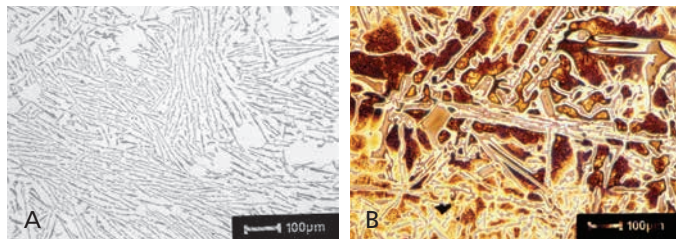


Figure 9. As-cast microstructure of Al - 13% Si - 0.45% Mg etched with (a) 0.5% HF and (b) Weck's reagent.

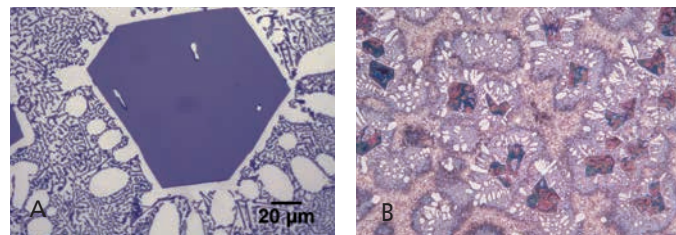


Figure 10. As-cast microstructure of Al - 19.85% Si etched with (a) the Si Blue reagent revealing proeutectic primary Si particles surrounded by the Al - Si eutectic (500x); and, with (b) Weck's reagent showing the eutectic cell structure (200x).

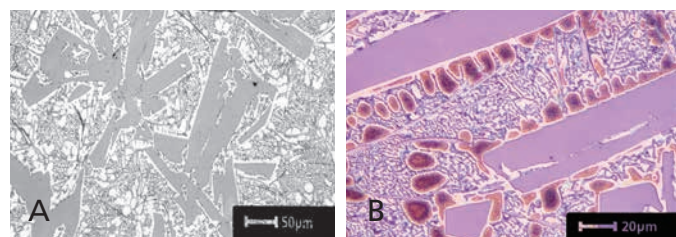


Figure 11. As-cast microstructure of Al - 25% Si - 1.4% Fe etched with (a) aqueous 0.5% HF; and with (b) Weck's reagent showing large primary proeutectic Si particles surrounded by the Al - Si eutectic.

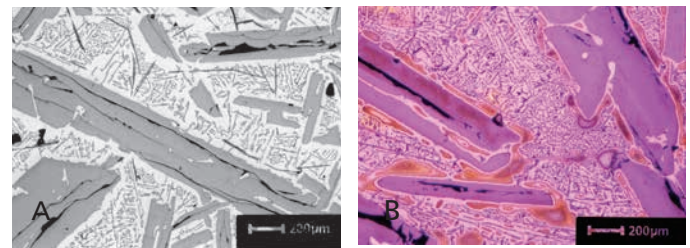


Figure 12. As-cast microstructure of Al - 50% Si etched with (a) aqueous 05% HF; and, with (b) Weck's reagent revealing very large, brittle primary Si particles surrounded by the α Al - Si eutectic.

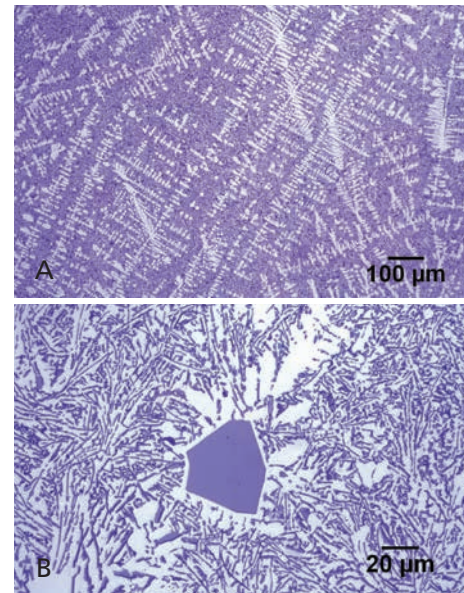


Figure 13. Gravity die cast Al - 12.9% Si (unmodified) etched with the Si Blue reagent. Note the primary Si and that the Si in the eutectic is fibrous in shape.

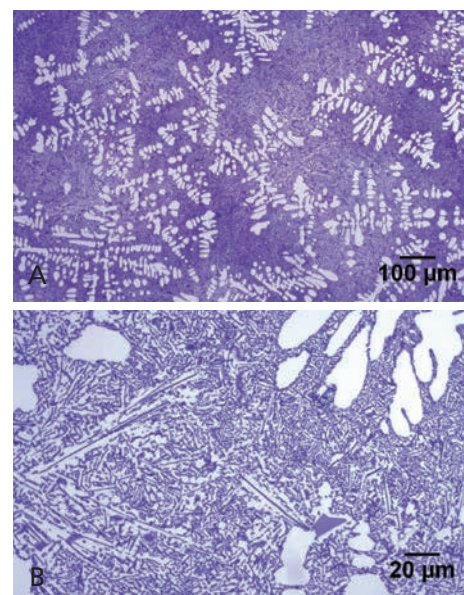


Figure 14. Gravity die cast Al - 12.9% Si with 0.03% Ti added to refine the size of the Si in the eutectic (Si Blue Etch).

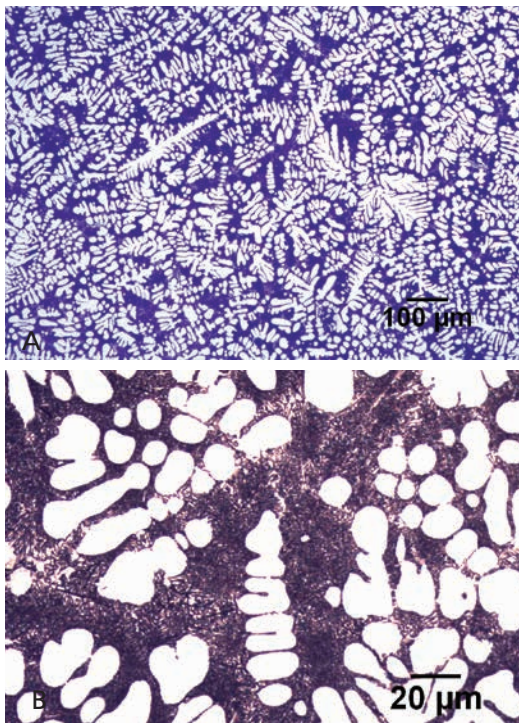


Figure 15. Gravity die cast Al - 12.9% Si with an addition of 0.045% Sr to modify the eutectic (Si Blue Etch). No primary Si particles were observed.

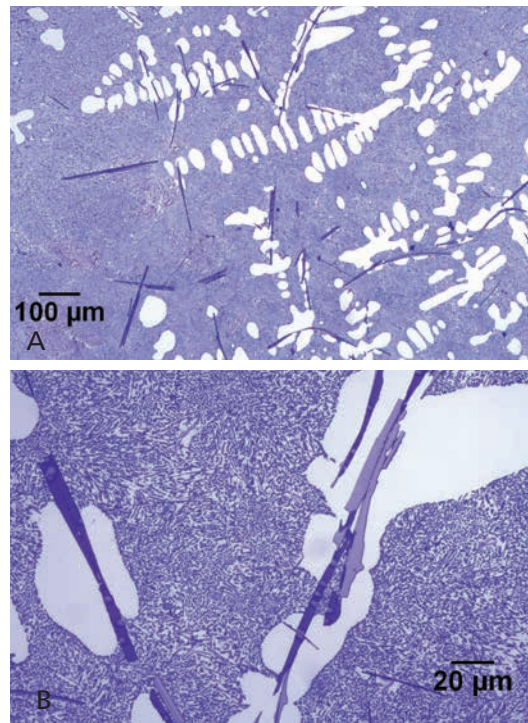


Figure 16. Gravity die cast Al - 12.9% Si with additions of 0.05 % Sr and 0.05% Ti. Note how fine the eutectic is. The long needle-like particles are β -AlFeSi that form due to the addition of Fe in the die cast heats to prevent "soldering" of the cast part to the tool steel dies.

References

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Biography

Dr. Juan Asensio, Lecturer at The School of Mines, Oviedo University (Spain), teaches Engineering Materials at The Department of Materials Science and Metallurgical Engineering. He has worked on Al-Si alloys in cooperation with several companies in the field located in northern Spain, such as Thyssen- Krupp Güss, Alusigma, Fundiser, Fagor- Ederland, among others. Contact Juan at: jasensio@etsimo.uniovi.es; fax: +34 985 104 302.

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