THE MODIFICATION OF Al-Si CASTING ALLOYS: IMPORTANT PRACTICAL AND THEORETICAL ASPECTS

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Abstract

A review is given of the modification of aluminum-silicon casting alloys. The mechanisms involved and important practical aspects are described. While a number of IA and IIA elements and several lanthanides produce a modified eutectic, only strontium and sodium have found significant commercial application. They react with and remove aluminum phosphide (AlP), an effective nucleant for silicon, and produce a fine fibrous eutectic. The resulting as-cast structure has improved ductility. In heat treated castings it is possible to reduce the solution time when a modifier is employed. The result is a significant cost saving—usually ten or more times the cost of the modifier addition. Modification may change the relative formation of porosity and shrinkage in a casting. This subject has been the subject of a great deal of controversy and confusion in the past, but recent research in Australia has clarified the mechanisms involved. This work is summarized and practical guidelines are offered for the foundryman. The modifiers strontium and sodium are poisoned by phosphorus, antimony and bismuth. Consequently, the levels of these impurities should be monitored carefully in secondary alloys.

Keywords: *modification, aluminum-silicon alloys, strontium, silicon particles, fibrous and eutectic.*

Introduction

Aluminum-silicon alloys are widely used in components where good strength and light weight are required, or where corrosion resistance and good castability are needed. However, the commercial application of these materials depends on the control of the structure of the silicon phase. This control is usually called 'modification'. Because of its commercial importance modification has been the subject of several hundred studies since its discovery in 1921 (1). This paper will not attempt to review the full extent of the available literature. Instead, the focus will be on aspects important for the commercial production of castings.

An examination of the literature shows that modification is a complex and controversial subject. Many conflicting theories have been proposed. Hence, this paper by necessity reflects the personal opinions and interpretations of the author. The reader desiring more information and other viewpoints on this fascinating subject is referred to a number of excellent surveys available in the literature (2-12).

This paper considers the modification process in hypoeutectic and eutectic alloys, which differ only in the relative volume fraction of primary aluminum and Al-Si eutectic. The refinement of hypereutectic alloys is not considered. In hypereutectic alloys phosphorus is added to produce finer primary silicon particles, but the eutectic is not modified. (3, 13-17)

An unmodified alloy contains large flakes of brittle silicon, which cause the casting to have poor ductility. Unmodified alloys often have elongations no more than a few percent and the fracture surface is primarily brittle. With a successful modification treatment the silicon assumes a fine, fibrous structure. These fibers appear to be small individual particles on a polished surface, but etching some of the aluminum from the surface shows that silicon is connected in a seaweed- or coral-like structure. The elongation of the modified alloy is improved significantly and an examination of the fracture surface reveals a 'dimpled' texture normally associated with ductile failure. Figures 1 and 2 show the structure of modified and non-modified A356 alloy, as observed on polished and deep-etched surfaces (18). Fracture surfaces can be seen in reference (19).

The effect of modification on as-cast tensile properties is given in Table 1 for several alloys. Modification has a significant effect on ductility. This is the basis for a test that 'old timers' sometimes use in the foundry. It is possible to pour a small bar casting. One end of the bar is clamped in a vise and the free end is hit with a hammer. The energy required to break the bar and the appearance of the fracture surface indicate when the alloy is modified.

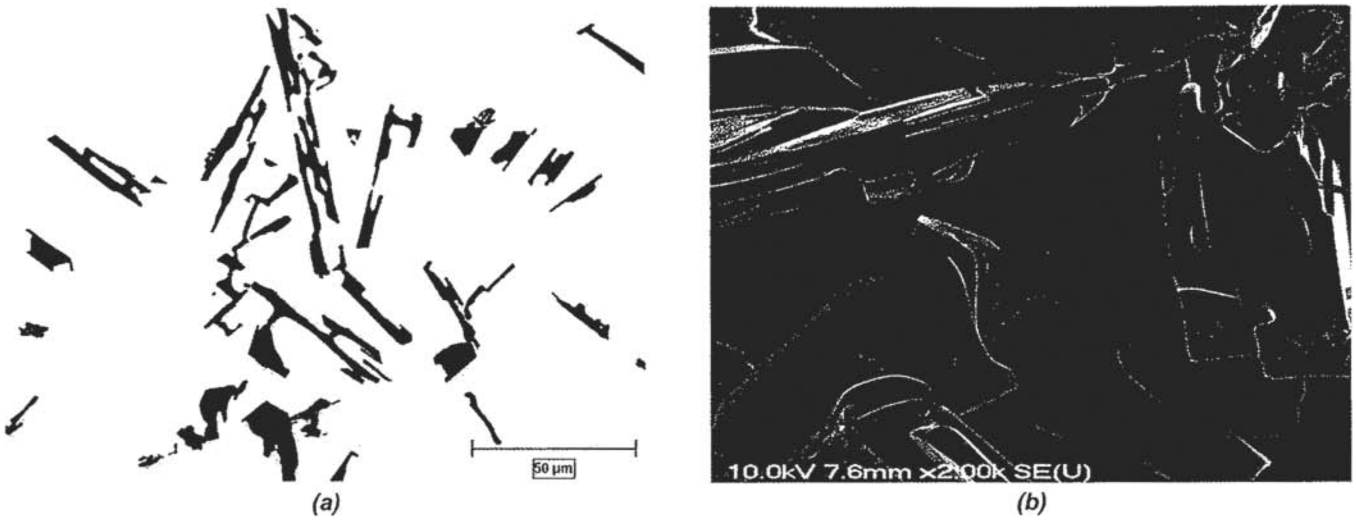


Figure 1. Structure of non-modified A356 alloy solidified at 1.5 to 2 °C/second (18) (a) polished surface, 400 x (b) deep etched surface, 1000x.

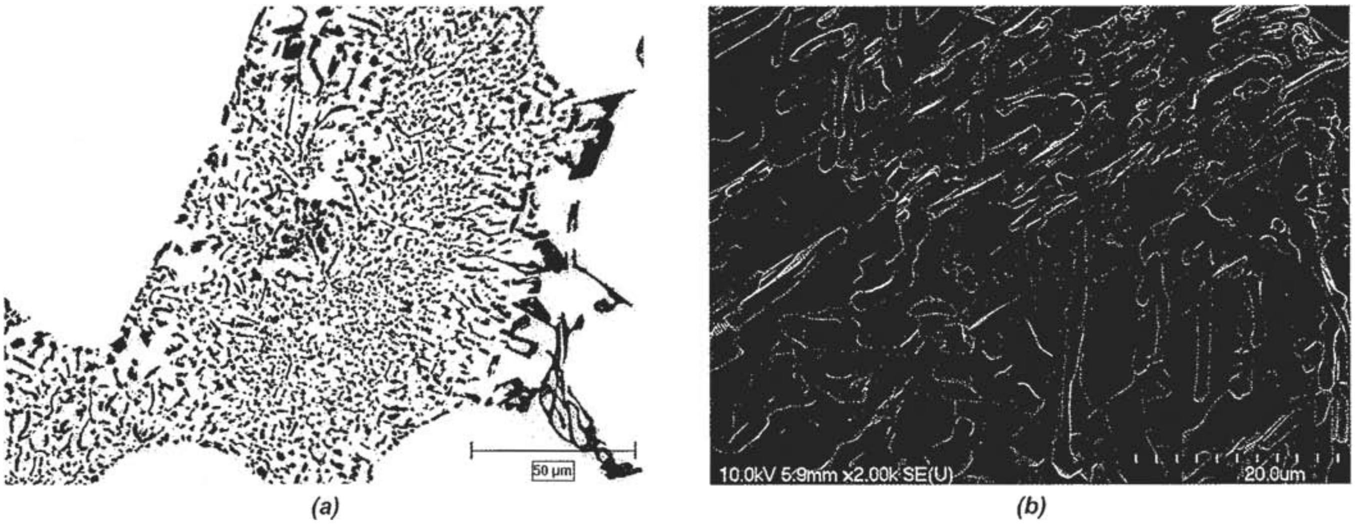


Figure 2. A356 alloy modified with 156 ppm Sr and solidified at 1.5 to 2 °C/second (18) (a) polished surface, 400x (b) deep etched surface, 1000x.

Table 1. Reported Mechanical Properties in the As-Cast Condition

Alloy	Cast Product	Modification	Yield (0.2%)*	UTS*	% Elongation	Reference
13% Si	sand cast test bar	none	---	124	2	(21)
		Na-modified	---	193	13	
13% Si	permanent mold test bar	none	---	193	3.6	(21)
		Na-modified	---	221	8	
359	permanent mold test bar	none	---	180	5.5	(22)
		0.007% Sr	---	210	12.0	
A413	sand cast test bar	none	112	137	1.8	(23)
		Sr modified	108	159	8.4	
A413	permanent mold test bar	none	125	168	6.0	(23)
		Sr modified	125	191	12.0	
A413	sample from auto wheel	0.06% Sr	126	193	12.8	(23)

* Units are MPa. To obtain ksi divide by 6.9.

Sodium was the modifier first used by foundrymen. It was employed for many years, especially in Al-Si alloys low in magnesium. These alloys provide good elongation with modest strength in the as-cast condition and were used in applications requiring reasonable ductility, such as automotive wheels. It is difficult to add sodium, however. It has low solubility in molten aluminum and a high vapor pressure, so its recovery is erratic. Sodium is also rapidly lost to oxidation after the addition (20). These problems made it difficult to control sodium modification. In the 1970s strontium began to replace sodium as the preferred modifier. Strontium is easily added via master alloys with nearly 100% recovery and its loss to oxidation is slow (20). With strontium the control of microstructure is easier and the mechanical properties in castings are more consistent (24, 25). Today the use of sodium as a modifier has almost completely disappeared. For this reason, the primary focus of this review will be on strontium modification.

Heat Treated Castings

An examination of Figures 1-2 and Table 1 make it abundantly clear that the mechanical properties of castings depend strongly on the size and shape of silicon crystals. One way to improve ductility is to employ a 'chemical' modification, as described above, by adding a small amount of sodium or strontium. Another way is to employ a 'thermal' modification, by subjecting castings to heat treatment.

Few foundrymen understand that a 'thermal' modification is possible, or that 'standard' heat treatment schedules are designed for non-modified alloys. Consider the schedules recommended for the solution heat treatment of A356 alloy by the American Foundry Society (26):

> Permanent Mold Castings: 12 hours at 1000 F (538 C) for T6 temper; 6-12 hours for T61 temper
>
> Sand Castings: 12 hours at 1000 F (538 C) for T6 temper

A detailed study of the solution heat treatment process (27) has shown that only 60 minutes is needed to place the Mg and Si in solution in permanent mold castings. The additional eleven hours recommended for the T6 solution heat treatment is used to 'modify' (spheroidize) the shape of silicon crystals. The practical consequence is important: When Al-Si alloys are chemically modified with sodium or strontium, the solution heat treatment time may be reduced.

This observation was first noted by Levy in 1978 (28), who described steps undertaken at Reynolds Metals to increase ductility in low pressure diecast aluminum wheels. Prior to this time most aluminum wheels in the U.S. were sold to the automotive aftermarket. The OEMs wanted an elongation of 10%, whereas 4% was the typical value in cast wheels. Levy found that 10% elongation could be achieved by:

- maintaining a low iron content in the metal
- modifying the metal (first with sodium, then later with strontium)
- using a shorter aging time

These procedures are now standard practice and aluminum castings are used extensively for wheels in new automobiles. Levy also noted that the solution time with modified metal could be reduced from 8 to 4 hours. The reduced solution time possible with strontium-modification is now also a common practice.

These considerations led to detailed studies (27, 29) on the solution heat treatment of non-modified and strontium-modified A356 alloy castings. Some of these results are plotted in Figure 3 for permanent mold (ASTM B108) and sand mold test bar castings. The mechanical properties of the castings in Figure 3 have been characterized by the Quality Index developed empirically by Drouzy, Jacob and Richard (30):

$$Q = UTS + 150 \log (E_f) \qquad \text{equation 1}$$

where the quality (Q) and the ultimate tensile strength (UTS) are in MPa and E_f is the elongation to fracture in a tensile test. The data points for Quality Index follow a straight line when plotted against the inverse of the cube root of solution time (minutes). The corresponding solution time (in hours) is also indicated at the top of Figure 3.

It is useful to consider what happens to the silicon phase during solution heat treatment and how the change in structure influences the quality of aluminum castings. A study of non-modified alloys under a hot stage microscope (31) showed that silicon plates (in the as-cast material) first break up into smaller pieces. This break-up happens rapidly, in an hour or two. There then follows a period where the small Si pieces gradually coarsen and become more spherical. The same process occurs in modified alloys (27, 29). Boeing engineers conducted extensive studies of high quality, aerospace castings. They examined the effect of solution heat treatment time along with other process variables. They finally concluded (32) that the quality of A357 alloy castings was well represented by the equation:

$$Q = 101 \cdot N^{0.5} - 129\frac{N^{0.5}}{AR} + \frac{1100}{AR} - 98 \cdot P^{0.5} - 570 \qquad \text{equation 2}$$

where Q is the quality index (in MPa), N is the cell count (aluminum cells per 0.0001 square inches), AR is the average aspect ratio of the silicon particles, and P is the area percent of porosity found on the polished surface of test specimens. The magnitude of the coefficient of the third term (1100 MPa) shows the importance of silicon particle shape (AR) on casting quality, and gives credence to theoretical studies which suggest that cracking of silicon particles controls tensile elongation and quality in Al-Si alloy castings (33).

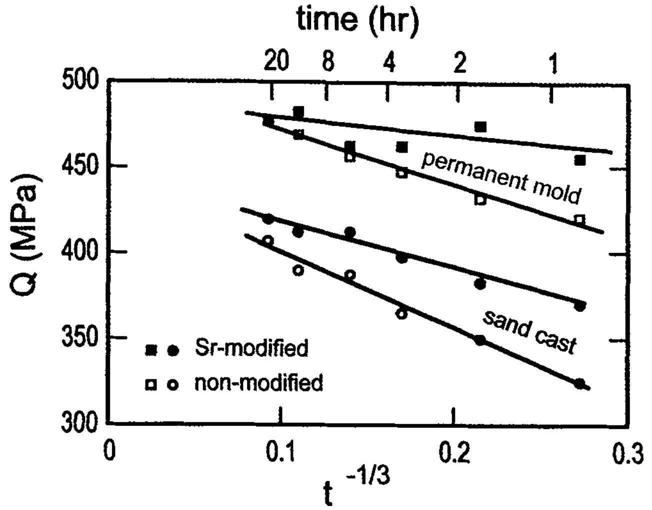


Figure 3. Mechanical properties versus solution time in A356-T6 alloy castings (27).

Studies made by the author establish that the cost for solution heat treatment is about 0.5 cents/lb-hour. With strontium modification the solution time required can be cut in half. For permanent mold castings this represents a saving of at least four hours, or two cents a pound. This amount is significant in today's competitive market and is nearly ten times the cost of the strontium addition. Moreover, halving the solution time doubles the throughput of heat treatment furnaces, removing a production bottleneck in many foundries. These are important benefits, which often justify the modification of heat treated castings.

The above results show that, when long solution times are employed, non- and Sr-modified permanent mold castings have almost the same tensile properties. In fact, looking at the microstructure of castings subjected to a 'standard' solution heat treatment, it is difficult to distinguish any difference in the silicon phase. (Consider, for example, Figure 1 of reference (8) or Figure 10 of reference (29).) Hence, one may ask: "Why modify with strontium?" One answer is that modification usually changes the distribution of porosity and shrinkage in a casting, so that strontium additions may 'cure' shrinkage problems. This topic has been the subject of a great deal of controversy over the years, and is considered in detail below.

Porosity and Shrinkage Formation

In most aluminum foundries one-half to three quarters of all scrap is caused by the undesirable formation of porosity or shrinkage, or by problems directly related to these defects. Lack of pressure tightness, poor quality on machined surfaces, low elongation and loss of tensile strength, and poor fatigue strength are problems related to porosity and/or shrinkage formation. Unfortunately, there is no single 'recipe' that foundrymen can use to produce good castings. A number of factors must be considered and controlled, and the 'balance point' or 'sweet spot' that produces best results in one casting may give poor results in another. The situation is complex and poorly understood, and subject to a good deal of controversy. We first consider porosity and how modification changes porosity formation in a casting. We will then consider shrinkage and how modification changes feeding and shrinkage formation.

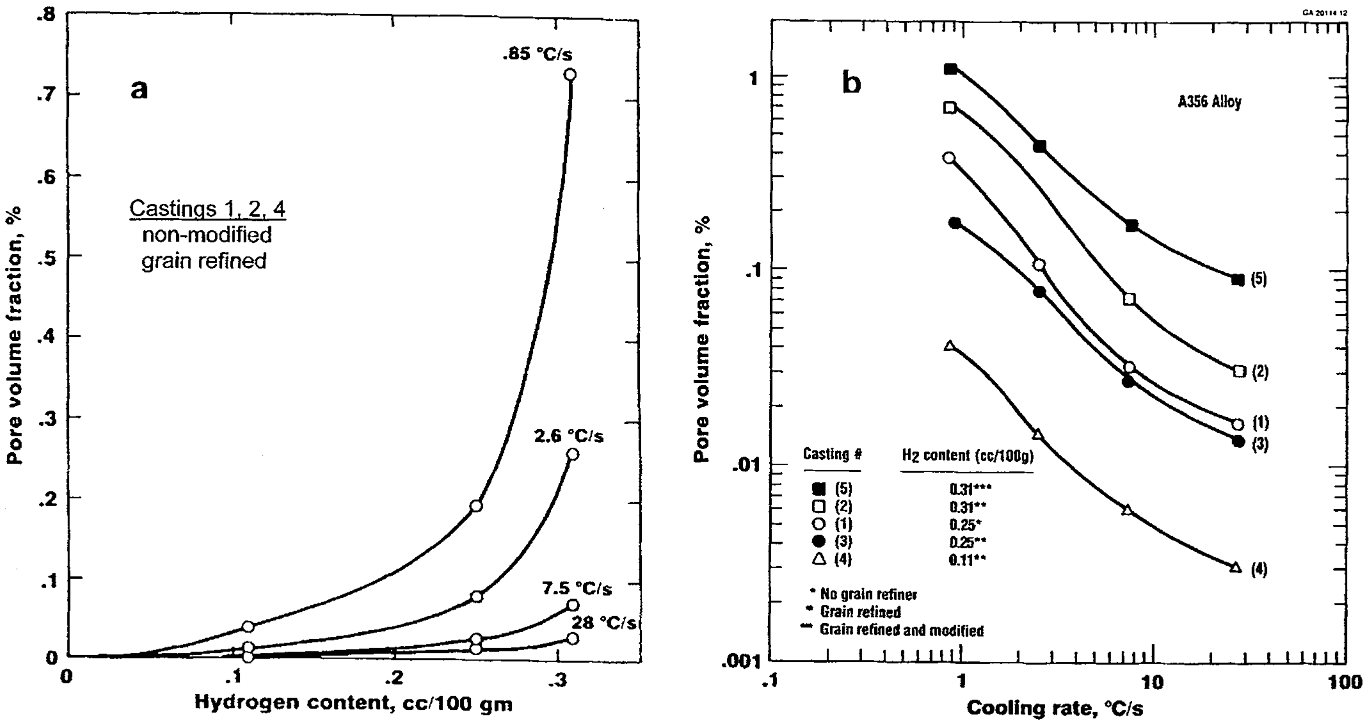


Figure 4. Pore volume fraction in A356 alloy castings (34).

The amount of porosity in a casting depends on several factors. These are listed below:

- solidification rate
- gas content
- metal cleanliness
- modification
- grain refinement
- pressure in the casting

Four of the above factors were studied by Fang and Granger (34). They poured directionally solidified castings of A356 alloy, which had a water-cooled copper chill at the bottom and were solidified directionally upwards from this chill. Because of the directional solidification, these castings had more than adequate feeding and shrinkage formation was not an issue. The amount of porosity and the average size of the pores were measured by quantitative metallography at various distances from the chill. The solidification rate at these locations was determined by thermocouples placed in the mold during solidification. The gas content of the molten metal was measured directly by the Telegas instrument prior to solidification. The porosity of the castings produced as a function of solidification rate and gas content is plotted in Figure 4.

Several important observations can be made from these results. They are:

1. *Solidification rate* has an overriding influence on the amount of porosity in a casting. Castings which freeze quickly can tolerate high contents of hydrogen gas. Slowly cooled castings, however, easily form significant amounts of porosity. This is why low gas levels are needed for best quality in large sand castings, but gas is sometimes added to permanent mold castings.
2. *Grain refinement* tends to reduce the amount of porosity. (Compare the results for castings 1 and 3 on the right hand side of Figure 4.) Grain refinement also reduces the size of pores. This occurs because hydrogen gas pressure does not usually become sufficiently high for pores to form until the last 5-10 percent of solidification. Hence, pores must fit into the spaces left between primary aluminum grains. Smaller pores produce a beneficial effect on fatigue life.
3. *Modification* tends to increase the amount of porosity formed, at least at the relatively high levels of gas (0.31 cc/100g) present in this study. (Compare the results for castings 2 and 5 on the right hand side of Figure 4.)

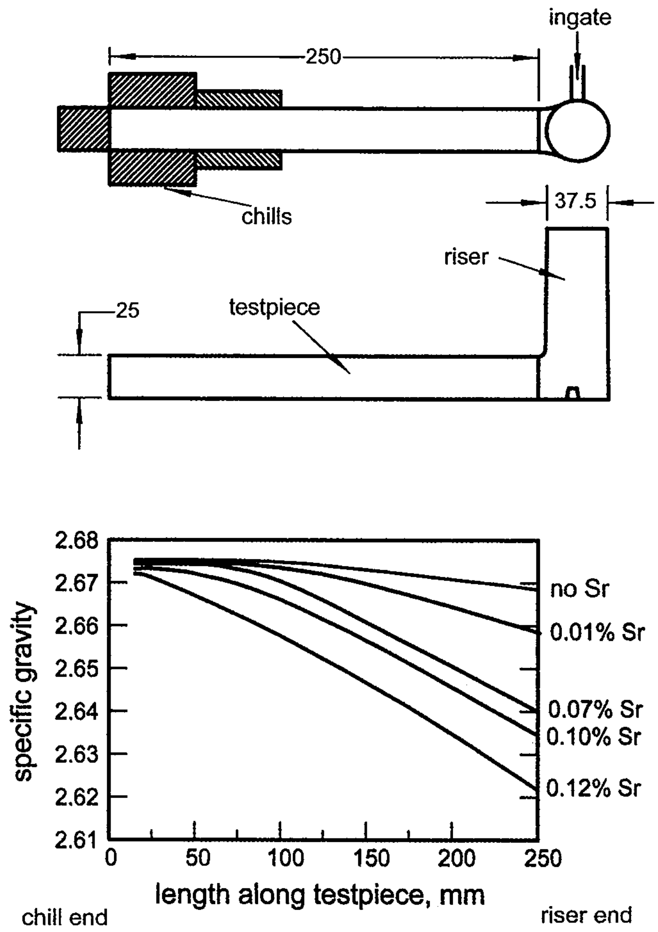


Figure 5. Distribution of porosity in an end-chilled sand casting (Reproduced from reference 25).

The question of porosity distribution in Na- and Sr-modified castings was studied by Pechiney and Montupet engineers (25). As part of their study they poured an end-chilled sand mold bar casting. The design of the casting is shown below in Figure 5. The porosity was determined in this bar by measuring the density (specific gravity) in sections cut along its length. These measurements were made in Na-, Sr- and non-modified A356 alloys. In the Na- and Sr-modified alloys there was an increased amount of porosity near the riser. The results for the Sr-modified alloy are shown below in Figure 5. (The results for Na-modified alloys were similar, but are not duplicated here.) The increase in porosity is most pronounced at higher addition levels of strontium. In practice, this means that we want to use the minimum amount of strontium needed to produce an acceptable level of modification. This is generally about 0.008 to 0.012 % or 80-120 ppm Sr.

There are a number of actions that foundrymen can take to minimize the increase in porosity associated with Sr-modification. Aside from keeping strontium levels at a minimum, one should consider:

1. *Lower gas* in the metal reduces the amount of porosity. Longer degassing times and low metal temperatures will help. The influence of gas content is illustrated well in a recent paper by Emadi and Gruzleski (35). They produced directionally solidified castings (similar to Fang and Granger in Figure 4) Some of their results have been reproduced in Figure 6. At a low gas content (0.13 cc/100 g) the increase in porosity with modification is negligible, except at the slowest cooling rates. (Compare curves 1 and 2.) At a higher gas content (0.26 cc/100g), there is a significant increase in porosity when strontium is added. (Curves 3 and 4.) The importance of foundry degassing practices should be obvious from these results.
2. *Increasing solidification rate* always reduces porosity, but this is especially true for strontium-modified alloys. If excessive porosity is found in part of a casting, this can often be removed by using chills in sand castings or conductive die coatings (or increased water cooling) in permanent mold castings.
3. *Grain refinement* is beneficial and tends to counteract the porosity formation caused by strontium additions. For this reason it is a good idea to use grain refinement in combination with strontium modification. Grain refinement is best accomplished by an addition of 10-20 ppm B in the form of 5%Ti-1%B or 3%Ti-1%B rod.

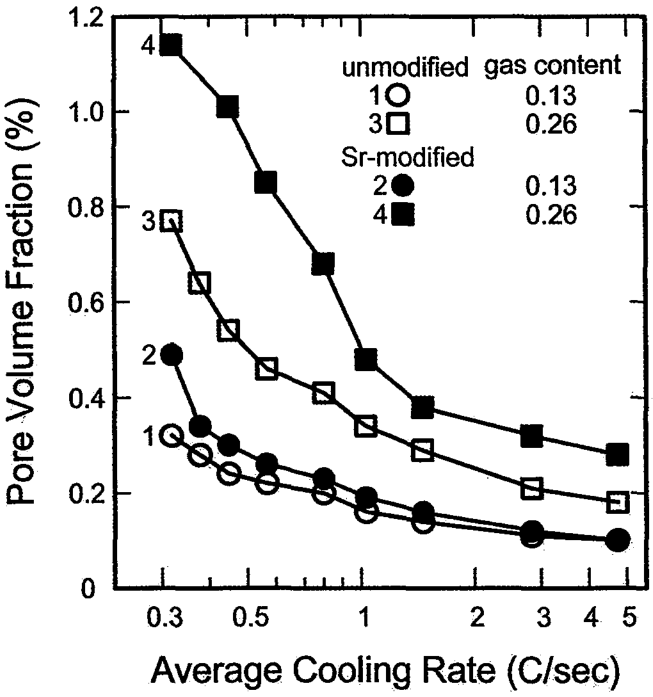


Figure 6. Porosity versus freezing rate in an A356 alloy (35).

4. *Mold Design* is also an important consideration in new castings. It is important to keep sources of heat away from areas where porosity is not desired. For example, in a wheel casting one would not want to gate metal into an area that will be machined to a high polish and coated. With the increased availability of powerful casting simulation programs, it is possible to determine with great precision where porosity might form before machining patterns or molds. In fact, when a casting is designed properly, an x-ray examination will show that the increased porosity formed by strontium additions is located in the base of the riser(s). This represents the ideal case.
5. *Filtration* will remove inclusions, making it more difficult for gas pores to nucleate during solidification.

Modification Mechanisms

At this point it will be useful to consider the mechanisms responsible for silicon modification and which cause the changes in porosity noted above. When these mechanisms are understood, it is easier to see how strontium-modification produces other effects:

- improved feeding from risers
- a changed distribution of shrinkage in castings
- increased segregation of iron compounds
- increased segregation of Cu as 'blocky' $CuAl_2$ in copper-containing alloys

We shall begin with cooling curves recorded during the solidification of Al-Si casting alloys. Generally these curves are obtained by pouring a liquid metal sample into a small crucible or sand cup, into which a thermocouple is placed. The interpretation of the temperature profile recorded during freezing is called thermal analysis. Thermal analysis can be a powerful tool, because the cooling curve of the alloy acts like a 'fingerprint' to identify the phases forming during solidification.

Thermal analysis has a long history as a laboratory tool for the study of Al-Si alloys. Two outstanding early examples are the 1950 work by Thall and Chalmers (21) and the 1966 paper by Crossley and Mondolfo (3). The latter experiments, in particular, helped to lay the foundation for our present understanding of Al-Si alloys. In the early 1980s two versions of commercial thermal analysis equipment became available (36-37), one of which was subsequently used widely as a foundry tool to evaluate grain refinement and modification treatments in the cast shop (24, 37). Unfortunately, no improvements have been made since that time and the tool has fallen into disuse. It is rare to see thermal analysis equipment operating today in foundries. Also, researchers have proposed a number of advanced analytical techniques to determine silicon modification (18, 36, 38-39), but none of these ideas has been transferred onto the foundry floor. There appears to be a useful opportunity for someone willing to convert this knowledge into a modern, inexpensive and easy-to-use computer-based thermal analysis system.

We now consider results of a recent study by researchers in Australia. They poured castings with a base Al-Si-Mg alloy and then made additions of strontium and phosphorus to the same metal (40). Thermal analysis curves for the three alloys are given in Figure 7. Important clues to operating mechanisms are available from these curves. Before extracting the information, however, it is necessary to introduce a few definitions and some basic concepts. For this purpose we employ the cooling curve for a modified A356 alloy, as shown in Figure 8 (41). To the left is the full curve. T_C is the temperature at the center of a small crucible during freezing. dT/dt is the first derivative of the cooling curve, T_C, and shows the instantaneous cooling rate in degrees per second. (The scale for the dT/dt curve appears on the right hand side of this figure.) The right hand side of Figure 8 shows an enlarged version of the cooling curves for the solidification of the Al-Si eutectic. (This is the area inside the box outlined by dashed lines on the left hand side of the figure.)

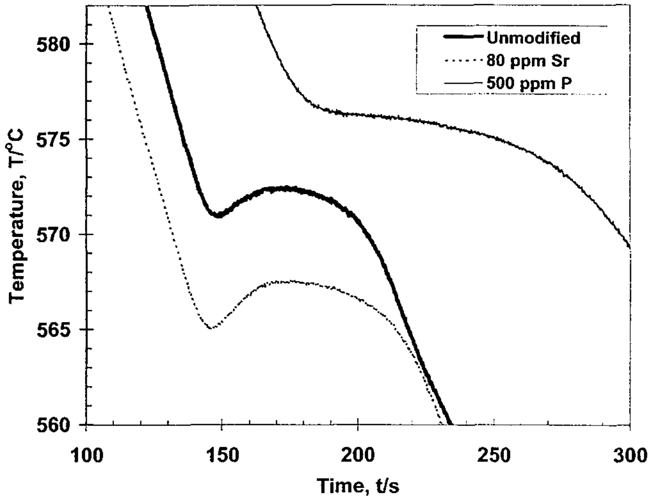


Figure 7. Effect of Sr and P on cooling curves.

In Figure 8 we see that, before the first eutectic forms, the cooling rate (dT/dt) is nearly constant at -0.6 C/sec. At a temperature of about 570 C the first derivative starts to increase. This happens because the Al-Si eutectic has begun to freeze, releasing latent heat into the sample. This point is called the eutectic nucleation temperature, T_N. As more eutectic grains form and grow, the amount of the latent heat released becomes larger, until the cooling stops and a minimum temperature occurs, T_{Min}. The sample then begins to heat up. (This is called recalescence.) The sample continues to heat until the steady-state growth temperature for the eutectic, T_G.

Looking once again at Figure 7, we find that strontium additions produce the following effects:

- The eutectic nucleation temperature (T_N) is reduced
- The eutectic growth temperature (T_G) is reduced
- The nucleation temperature is lowered with respect to the growth temperature (that is, $T_N \leq T_G$)

Phosphorus additions can be seen to have the opposite effects to those produced by strontium.

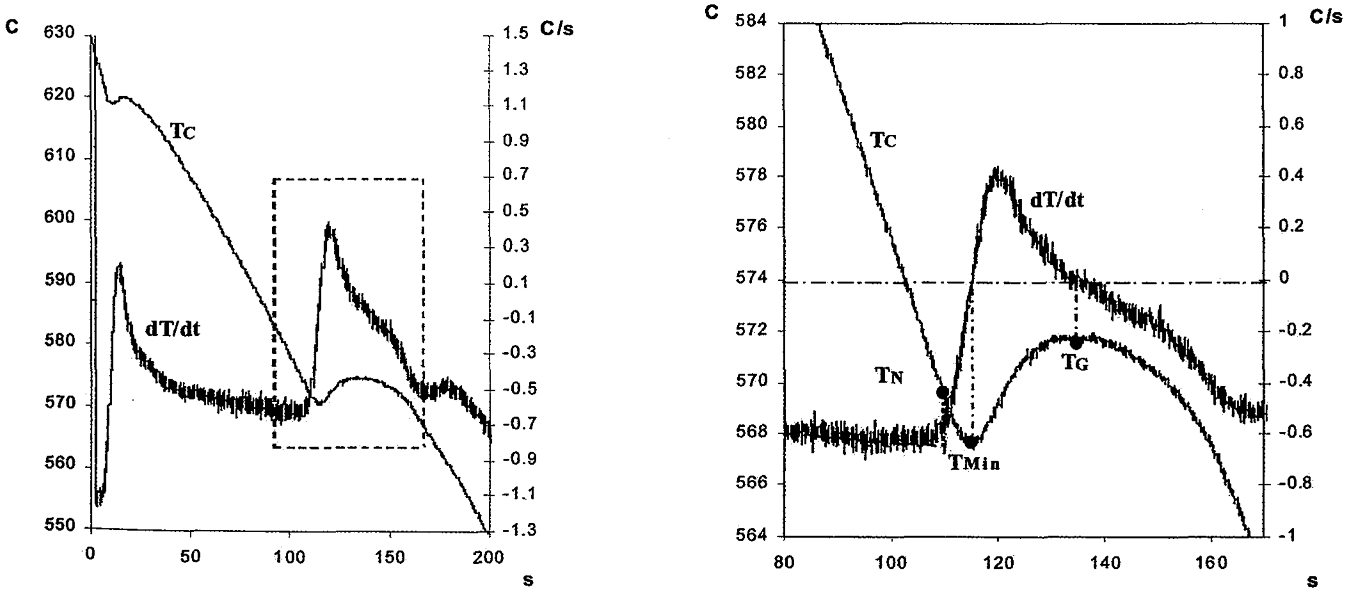


Figure 8. Thermal indicators in eutectic solidification (41) in an A356 alloy (40).

Eutectic Nucleation

How does an addition of a few ppm of Sr (or Na) change the nucleation of the silicon eutectic? This is an interesting and controversial question, which has been the subject of dozens of research papers and academic theses. In the author's opinion, the most likely explanation is that strontium (and other modifiers) react with to remove or somehow 'neutralize' AlP, which is an effective nucleant for the silicon phase. The supporting evidence for this hypothesis is outlined briefly below.

1. *Phosphorus is added to hypereutectic alloys* to reduce (or refine) the size of primary silicon. In 1966 Crossley and Mondolfo (3) found phosphorus-containing particles inside primary silicon crystals. Based on crystallographic data, they proposed that AlP has an epitaxial relationship with silicon and would be an effective nucleus.
2. *AlP nucleates silicon* in hypoeutectic alloys. This has been observed by a number of researchers. An example is shown in Figure 9. This particle was observed in a non-modified Al-10% Si alloy. The sample was quenched from the semi-solid state. The fine eutectic surrounding the larger Si crystals formed during this quench. (The dashed lines in Figure 9 indicate the outline of primary dendrites forming prior to eutectic solidification.) Some researchers have reported finding Al-P-O particles, but this observation appears to be an artifact. AlP is a reactive compound that combines readily with oxygen in the air, and perhaps with water used in polishing media. The oxygen is therefore the result of contamination. This was shown by elegant (and complicated) ion milling techniques, used to remove the contaminated oxygen-containing layers. The same study (43) also showed there is a definite epitaxial crystallographic relationship between AlP and the silicon crystal.
3. *Modifiers react with phosphorus.* The elements which have been reported to produce modification (7, 41, 44-45) are indicated by the shaded areas in Figure 10. These are all reactive metals that form compounds with phosphorus. As a consequence, they all have the capability to neutralize AlP particles in aluminum melts. This interpretation appears to be supported by thermal analysis data (41, 44).
4. *Phosphorus additions 'poison' modification.* A number of researchers have shown that high P levels make it difficult to modify Al-Si alloys. Some of the 'maps' produced by these studies will be shown later, when we discuss the effects of elemental additions on the modification process. One example of this poisoning effect is shown in Figure 11.
5. *Strontium poisons AlP in hypereutectic alloys.* The interaction between AlP and strontium is reciprocal, and also occurs in hypereutectic alloys. In these alloys phosphorus is normally added to nucleate and refine primary silicon. When strontium is added in sufficient quantities, and some time is allowed for the reaction between AlP and strontium to occur, the size of primary silicon increases significantly and the number of primary silicon particles is reduced (47, 48).
6. *Modifier additions change eutectic grain size.* When a modifier is added nucleants for the silicon eutectic are removed. The most significant consequence is a larger eutectic grain size and the change in porosity distribution discussed above. Owing to the importance of this subject, it is worthy of discussion in a separate section.

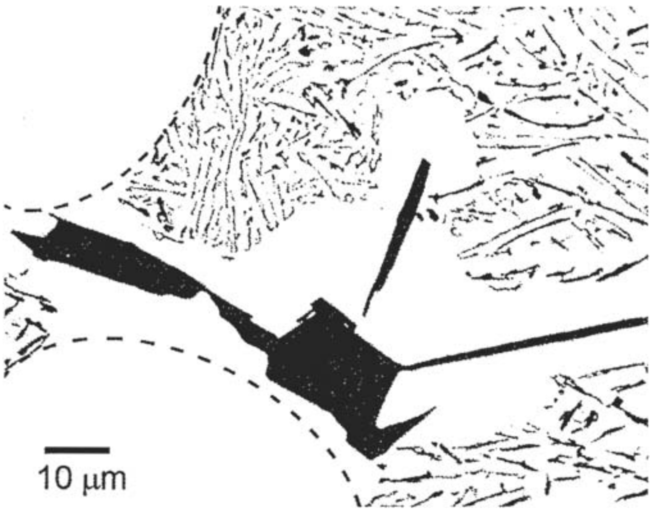


Figure 9. Phosphorus-rich particle inside silicon crystal in an Al-10% Si alloy (42).

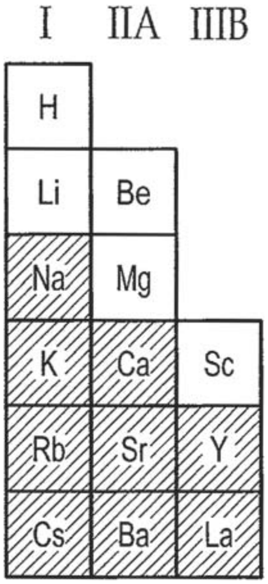


Figure 10. Elements which have been observed to produce modification in Al-Si alloys.

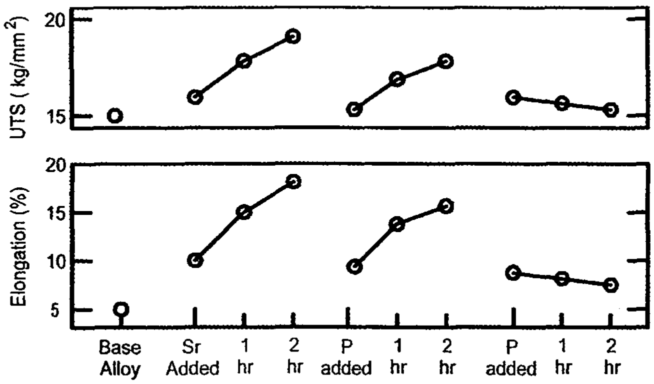


Figure 11. Effect of strontium and phosphorus additions and holding time (46) (Mechanical properties are for an as-cast Al-12%Si alloy).

Most popular casting alloys are hypoeutectic. For example, A356 alloy contains 7% Si, compared to the eutectic composition of 12.7% Si. Consequently, the as-cast structure contains 50-60% primary aluminum grains surrounded by a layer of Al-Si eutectic. It is difficult to discern the eutectic grain structure in this material by simple metallographic observation.

One way to observe eutectic grains is to partially solidify the alloy and subject a sample to a rapid quench. This procedure is usually called an interrupted quench. (That is, solidification is interrupted by a rapid quench.) This procedure was used in the 1963 research paper by Kim and Heine (45). It is possible that they were the first to observe the change in the eutectic grain structure of Al-Si alloys that occurs with modification. Unfortunately, their observation was not connected with the important issues at hand (porosity and shrinkage distribution in castings) and it was forgotten.

In 1981 Flood and Hunt used interrupted quench experiments to study sodium-modification of eutectic alloys (49). Their results showed clearly that sodium prevented the nucleation of eutectic grains. Figure 12 below is taken from their study. The left hand side (Figure 12a) shows the structure of the non-modified alloy. The lighter (white) portion of the ingot was allowed to solidify normally. The darker gray areas were quenched after about one-third of solidification was completed. It can be seen that numerous eutectic grains nucleated in this non-modified alloy and grew into small spherical 'colonies' of silicon crystals. The arrows in this figure show some of these eutectic grains. It is noteworthy that these grains are 'isolated', or completely surrounded by liquid metal. The sodium-modified alloy is on the right hand side of the figure (Figure 12b). In this case no silicon eutectic grains nucleated in the liquid. Instead, the eutectic first formed at the outside of the casting (in contact with the mold) and grew towards the center as a planar solidification front.

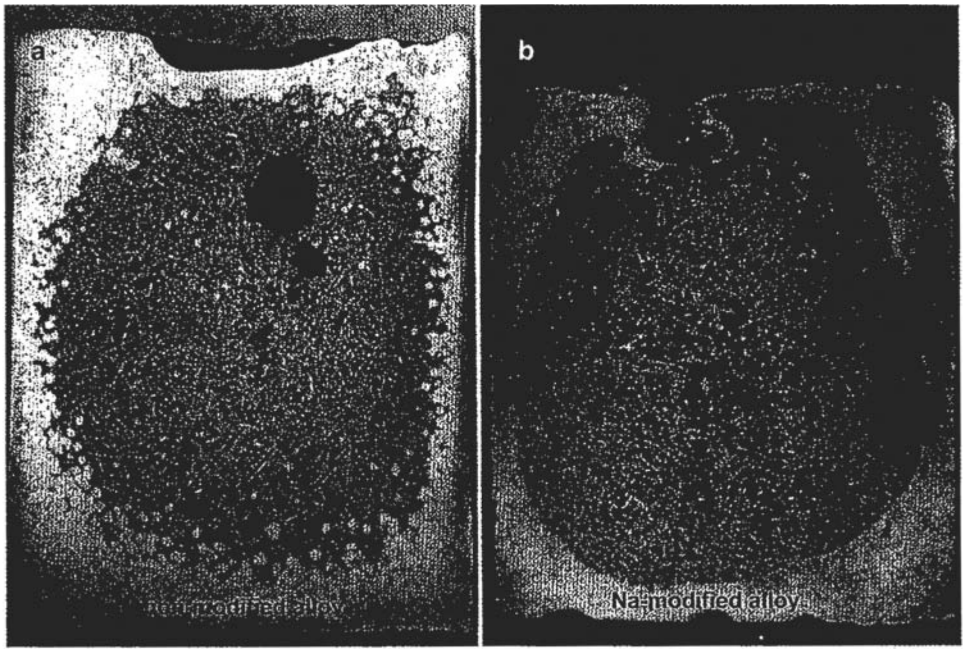


Figure 12. Structure of Al-Si eutectic alloy observed by an interrupted quench (49) (Arrows show individual eutectic grains).

Unfortunately, no thermal analysis was conducted in this study. From the structures observed, however, it would be reasonable to assume that for non-modified alloys the eutectic nucleation temperature is greater than the growth temperature (that is, $T_N > T_G$). This may be inferred from the appearance of eutectic grains in the liquid phase ahead of the solid/liquid interface. Conversely, for Na-modified alloys the nucleation temperature is lower than the growth temperature ($T_N < T_G$). As we shall see below, these differences have an important effect on the formation of porosity and shrinkage.

Inferences can also be made about the eutectic grain structure by anodizing a polished surface and looking at the sample in a microscope with polarized light. This procedure reveals the grain structure (size and relative orientation) of the aluminum phase in the eutectic. This procedure was used in the 1975 study by Jenkinson and Hogan (50).

More recently a number of studies have been undertaken by researchers in Australia. They developed special techniques to see eutectic grains in Al-Si alloy castings. For the researcher interested in experimental detail, the new procedures are reviewed in (51-52). For the purpose of this paper, however, it will be sufficient to extract the most important observations which have practical significance for foundrymen.

The eutectic structures observed in Al-Si alloy castings (42, 51-56) are summarized in Figure 13. This figure shows schematically the structure of three Al-7%Si alloy castings at a point during solidification when the primary aluminum grains have formed and the eutectic solidification is just beginning. On the left hand side of the figure is the non-modified structure (Figure 13a). The black areas indicate regions where Al-Si eutectic has solidified. There is a shell of eutectic in contact with the mold wall, and numerous small solid grains of eutectic are in contact with primary aluminum. In this case eutectic grains nucleate and grow on existing aluminum dendrites.

Figure 13b shows the strontium-modified alloy. In this case, the number of eutectic grains is smaller and the eutectic grain size is much larger. In experiments conducted by McDonald *et al.* (54-56) the eutectic grain size increased by an order of magnitude when strontium was added. The eutectic grains were a few hundred microns in diameter in non-modified alloys, and a few thousand microns in strontium-modified castings. Note also that the solid shell of eutectic is thinner when strontium is present. In fact, in large sand or investment castings there may be little solidified eutectic at portions of the mold surface. These changes have important ramifications for shrinkage formation.

On the right is the structure found in sodium-modified alloys. In this case no nucleation occurs in the liquid, and eutectic growth is from the mold walls towards the center. (This case was also shown in Figure 12b for an alloy of eutectic composition.)

In our discussion of Figure 4 we noted that grain refinement (of the primary aluminum phase) had a beneficial effect on the amount of porosity. The size of the pores was also reduced. From Figure 13 above we can now see that strontium additions have the opposite effect: The size of eutectic grains is increased. This change is almost certainly responsible for the increase in porosity found in most modified castings.

To one familiar with the technical literature in this area, this simple conclusion may be surprising. There has been a good deal of controversy over the last 25 years, and nearly a dozen theories have been proposed to account for the change in porosity observed in modified alloys. Surprisingly, eutectic grain size was never identified as a possibility, presumably because no one could measure it. For those interested in the scientific history and background, the other theories and the literature are reviewed elsewhere (53, 55, 57-59).

It may be useful to present a simple calculation. Fuoco and co-workers (60) duplicated the experiments of the Pechiney researchers summarized in Figure 5 and also conducted interrupted quench experiments in small crucibles. Their melts were maintained at a gas content of 0.13 cc/100g (STP). When strontium was added as a modifier the amount of porosity increased, and the pore size increased to an average diameter of 300 microns. Now, the question is this: From what volume of liquid metal (eutectic grain size) did this pore receive its hydrogen gas?

We begin by assuming that all of the gas originally present in the melt finds its way into a pore during solidification. If this is true, how much porosity forms? One hundred grams of metal, at a liquid density of 2.35 g/cc, has a volume of 43 cm^3. The gas volume at standard temperature and pressure is 0.13 cc. But at the eutectic temperature (and one atmosphere pressure) this gas will have a volume of 0.13 cc x (843/273) = 0.4 cc. Thus, the amount of porosity that corresponds to a gas content of 0.13 cc/100g (at STP) is approximately:

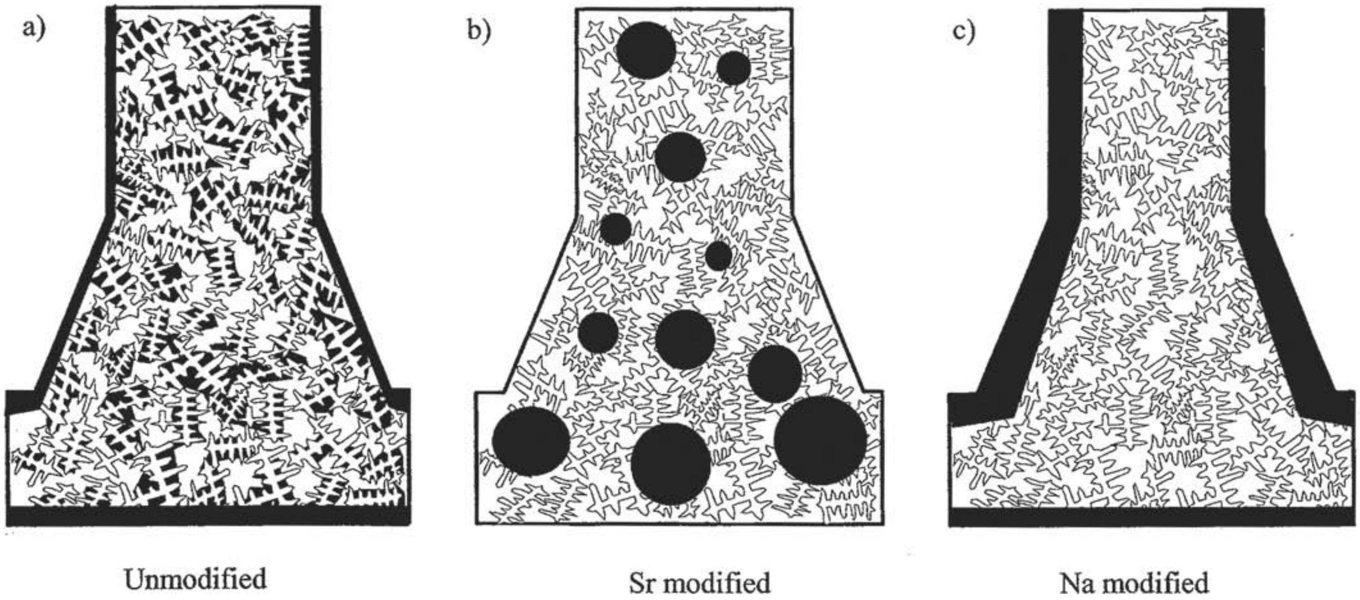


Figure 13. Structure of Al-Si eutectic grains in three semi-solid Al-7%Si alloys (42).

% Porosity = volume of gas/volume of metal = 0.4 cc/43 cc = 0.0093 or 0.93 % equation 3

For the material to have that amount of porosity, each pore must be surrounded by a volume of solid (pore-free) metal having an average size 107 times larger than the pore. ((1-.0093)/0.0093 = 107) From this we find that:

$$\frac{D_{grain}}{D_{pore}} \cong \sqrt[3]{107} \text{ or } 4.75\text{, thus } D_{grain} \cong 1425 \text{ microns} \qquad \text{equation 4}$$

In non-modified alloys the eutectic grains are about 250 microns in size. Using the same calculation as in equation (4), we find that the pore size is much smaller – about 50 microns. From this simple calculation one can see how a large eutectic grain size in modified alloys might contribute to a larger pore size in castings.

The above calculation assumed all hydrogen was able to diffuse to the pore, and corresponds to the case of slow solidification. During rapid freezing much of the hydrogen is 'frozen' or 'trapped' in the solid metal. In this case the amount of porosity is less and the pores are smaller.

Unfortunately, this simple picture is not the complete story. The experiments of Fuoco (60) and Anson (57-58) show that, at medium to high gas levels, pores nucleate or form earlier during the solidification process when strontium is present. The change in eutectic grain size cannot account for this observation. One possibility is a different nucleus for the pores. It is well known that oxide films nucleate porosity in aluminum castings (61-62). Strontium additions have been observed to change the composition of the oxide on the surface of a eutectic Al-Si alloy and to increase the oxidation rate of the melt (63). Strontium-containing oxides have also been observed to nucleate pores in Sr-modified castings (64-65). So, it is possible that a Sr-containing oxide film is a better nucleant for porosity.

We now pass on to other important changes that occur when an Al-Si alloy is modified.

Feeding and Shrinkage Formation

Considering once more the structures indicated in Figure 13, it is evident that relatively large channels of liquid eutectic will exist in the semi-solid, strontium-modified castings. These open channels change the feeding patterns. Because there is a thin shell of eutectic at the surface, these channels sometimes come to the surface. I have seen large Sr-modified sand castings which exhibited a 'worm hole' on the surface. These holes may go deep into the casting where an unfed thick section 'sucked' liquid away from the surface. This left an empty hole where the eutectic feeding channel was located. More common is the problem of a rough surface, usually called an 'orange peel' defect, sometimes seen in investment castings. Here again, poor feeding in a thick section pulls liquid away from the surface, leaving a rough surface of exposed, 'dry' aluminum dendrites. This defect has been described in the literature (66). Strontium has also been shown to promote 'surface slumping' in unfed sections of permanent mold castings (53, 75). Sodium-modified castings did not exhibit surface slumping, presumably because the solid outer shell of solidified eutectic is thicker.

The literature on the effect of modifiers on feeding is contradictory. Iwahori and co-workers (67) conducted an elegant series of experiments that showed feeding stopped in non-modified alloys when the Al-Si eutectic began to freeze. Looking at the left hand side of Figure 13, it is tempting to say that the many small eutectic grains in this structure act to 'close off' liquid feeding paths between aluminum dendrites. Iwahori and his colleagues later (68) repeated the same experiments in modified alloys. Sodium modified alloys fed longer (later into solidification) which meant that smaller risers could be employed without creating shrinkage in their casting. On the other hand, strontium modified alloys were observed to behave the same as non-modified melts. Unfortunately, these experiments were conducted with 1.7 kg (3.7 lb) melts, so the results cannot be scaled-up directly to melt practices found in operating foundries. A third study (69) reported that strontium made feeding worse in a simple bar casting, whereas three other papers (70-72) reported that strontium modification improved feeding.

In the early 1980s I began to work for a company that made and sold Al-Sr master alloys. During my first year I visited a foundry that was trying to make lost foam cylinder heads in a 319-type alloy. They were having problems with shrinkage located on the machined deck face. When they modified the alloy with strontium, the shrinkage defect disappeared. Since that time I have seen the same thing occur in many other castings, and others (42, 73-75) have reported the same effect of strontium on shrinkage. An example of the change possible is given in Figure 14. This shows the internal structure at a 'hot spot' in a permanent mold casting. In the non-modified alloy (Figure 14a) a large concentrated shrink is found. When strontium is added (Figure 14b and 14c) the shrink disappears and is replaced by dispersed microporosity.

My own belief is that strontium helps to 'cure' shrinkage by a combination of better feeding and increased porosity. Both tend to displace shrinkage. If you look carefully at the tops of risers during solidification, it will become apparent that feeding usually improves when strontium is used as a modifier. (The shape of the cavity at the riser top changes, showing that feeding occurs longer when the metal is modified.) Grain refinement also assists feeding, which is another reason to use it in combination with strontium.

In the Na-modified casting (Figure 14d) there is found a concentrated shrink. However, it is smaller in size than in the non-modified alloy. Perhaps the shrink was reduced by improved feeding.

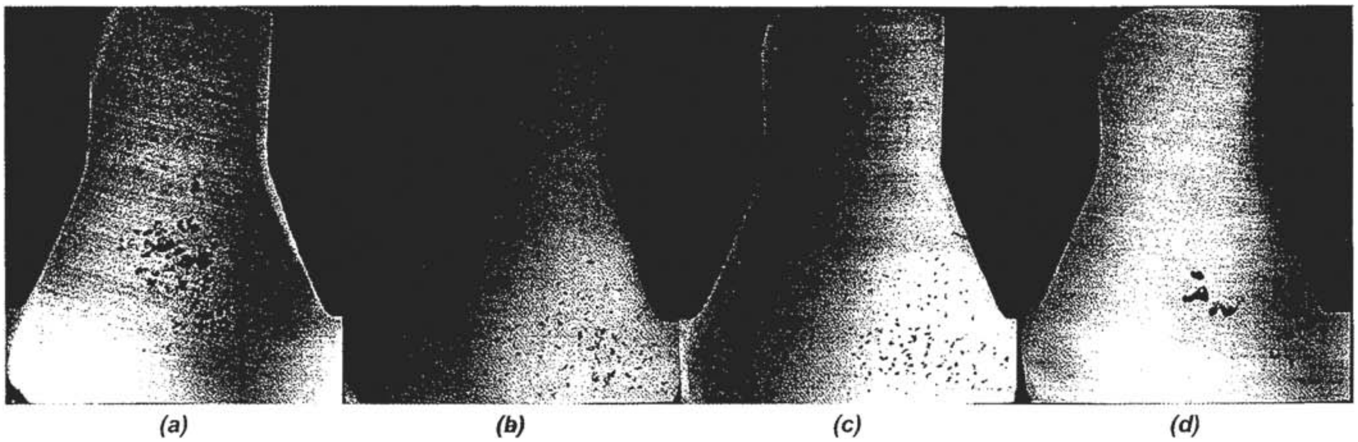
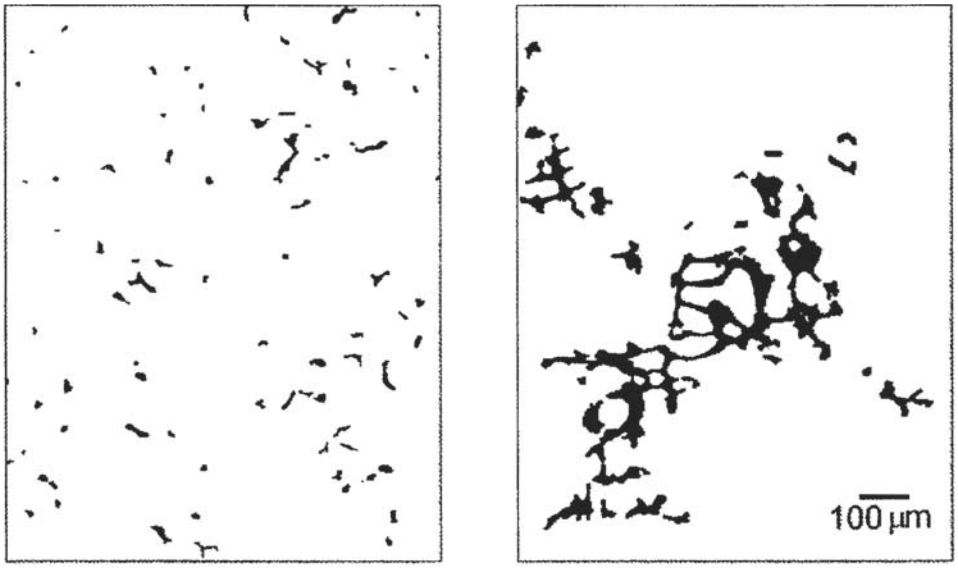


Figure 14. Cross section of hot-spot area (spoke-rim junction) of permanent mold Al-10%Si-Mg alloy casting (42) (a) Unmodified alloy (b) 50 ppm Sr (c) 100 ppm Sr (d) Na-modified.



(a) 2 wt% Cu, 0 ppm Sr

(b) 2 wt% Cu, 100 ppm Sr

Figure 15. Binary image showing distribution of $CuAl_2$ phase in an Al-10%Si alloy casting (56).

Figure 16. Distribution of β Phase in an Al-10%Si alloy (56) (Arrows show β plates located at eutectic grain boundaries).

Copper and Iron Segregation

The larger eutectic grain size in modified alloys tends to increase copper and iron segregation, in the same way it increases segregation of gas. Several studies have noted that strontium promotes the formation of large 'blocky' $CuAl_2$ particles (56, 76-78). These particles take longer to dissolve during solution heat treatment (76). There also is an observable change in the copper eutectic cooling curves (76, 78); so thermal analysis could be used to help control $CuAl_2$ morphology in modified Al-Si-Cu casting alloys. The effect of strontium on copper segregation in an Al-10%Si-2%Cu Alloys is shown below in Figure 15.

Grain refinement of the primary aluminum phase helps to disperse the blocky $CuAl_2$ particles (76).

A similar segregation effect may also occur with iron intermetallic compounds, depending on the iron content of the alloy. Figure 16 shows the distribution of β plates in an Al-10%Si alloy which contains 0.11% Fe and 140 ppm Sr. The iron-containing plates are found at the boundaries of the eutectic grains.

Recommended Foundry Practices

We now consider how strontium is best used in the foundry. Each process step is considered individually.

Adding Sr

Making additions of strontium is relatively easy. There are several master alloy compositions and different products available for this purpose. Their recovery and speed of dissolution have been studied in detail (24, 79-82). Waffle products tend to be slow to dissolve. Higher metal temperatures generally promote more rapid dissolution and higher recoveries. The exception is the 90Sr-10Al product, which is exothermic and goes into solution best when the melt temperature is low. Strontium recoveries are generally high with all products, 90 percent or more.

In past years an Al-14Sr-10Si master alloy was marketed by some companies, but this was a terrible product. It was hard to dissolve, and it always 'gassed' the metal. This is perhaps because the product contained high levels of Ca and Ba (79). This master alloy has not been available in North America for many years, but I was told recently that an overseas company is once again making this product. Foundrymen should be aware of potential problems with this strontium-silicon master alloy.

Several workers have noted that strontium is slow acting showing an 'incubation time' of one or two hours (10, 24, 46, 72, and 81). Modification was observed to improve with time after the addition, even though part of the added strontium may be lost to oxidation. An example of this effect was shown in Figure 11. More recent research has established that most of the delay is caused by the time needed for intermetallic particles in waffle products to dissolve. Strontium-containing rod products usually have small particles of $SrAl_4$ and are fast dissolving and fast acting (24, 81). With strontium master alloy rod additions no more than about 10-15 minutes is needed to reach full modification.

The melt loss of strontium is slow (20), so it will be convenient for many foundrymen to have strontium added to their alloys by their ingot supplier.

How Much to Add

It is generally accepted that the best silicon modification in A356 alloy occurs at a level of about 0.012% Sr, or 120 ppm. An example of how mechanical properties have been observed to vary with strontium content is shown in Figure 17 (82). This plot shows the quality index of A356 alloy at three different cooling rates. In practice, however, good modification can be obtained at significantly lower concentrations, depending on the purity of the alloy. In primary metal the phosphorus level is usually below 10 ppm and other 'bad' impurities are absent, so full modification can be obtained with strontium contents as low as 60-70 ppm. Good modification can also be obtained at higher levels of strontium, although this tends to result in more porosity. The reason for the small drop in quality, as strontium becomes more than about 0.03%, is that higher levels result in coarser silicon particles (18, 83).

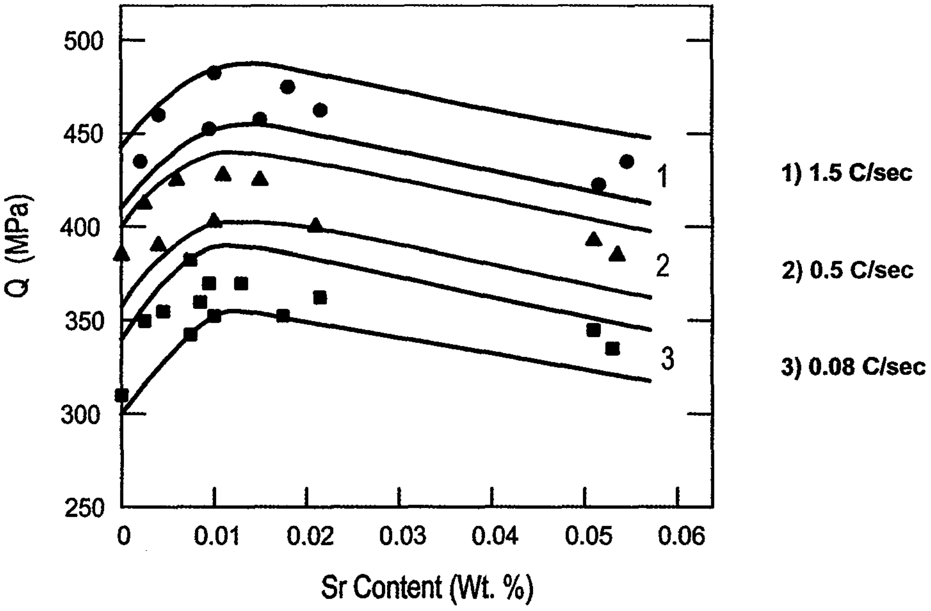


Figure 17. Quality index of A356-T6 alloy castings at three cooling rates (82).

Gas Pickup and Degassing

It is generally agreed that adding strontium does not result in any appreciable gas pickup (84, 85). Sodium additions, however, do add gas to the melt (86). The evidence regarding the effect of modifiers on gas pickup from the atmosphere is less clear, however. Experiments with small melts held under atmospheres having a controlled humidity (63) show that strontium additions do increase the gas, by changing the composition of the oxide on the melt surface. Other laboratory experiments (85) suggest that strontium has no effect. My experience in the foundry is in agreement with the observations offered by Hurley and Atkinson (24). As long as large strontium additions and high melt temperatures (> 1400 F or 760 C) are avoided, there is no significant increase in gas pickup from the atmosphere.

Degassing of modified melts should be done using nitrogen or argon, preferably with a rotary impeller. No chlorine or other reactive gas (nor salts or fluxes) should be employed, as these will tend to 'burn out' dissolved Sr. Contrary to an observed loss of sodium (86), degassing with inert gases does not result in a significant loss of strontium.

Quality Control Testing

Under normal conditions a spectrographic analysis for Sr is sufficient to control modification in a foundry using primary metal. As we shall see below, however, some elements can 'poison' the effect of modifiers. These may become a concern when secondary metals or scrap are incorporated into the furnace charge. In this case it would be wise to check modification levels by the routine use of thermal analysis. This measurement technique has been found to be an acceptable quality assurance tool (24, 37).

Mold Reactions

The addition of strontium has been observed to increase hydrogen gas pickup in green sand mold castings (86-87). This can become a serious problem in large, complicated castings. To a certain extent, this gas pickup can be avoided by careful gate and runner design, and by use of mold coatings.

Growth of SILICON Eutectic

A careful examination of the literature makes it evident that the crystallization of silicon in Al-Si alloys is an exceedingly complex affair. In particular, the presence (or absence) of impurity elements has a significant effect on the structure formed. In our earlier discussion of cooling curves, we noted that modifiers change the *nucleation* of silicon. This effect was considered in some detail, to explain effects ancillary to silicon modification (changes in porosity formation, feeding, etc.). There is also, however, a change in the *growth* of the silicon phase during chemical modification with sodium or strontium. This is evidenced by a 6-10 C depression in the eutectic growth temperature, T_G.

The formation of silicon crystals in liquid Al-Si melts is influenced by the high latent heat (and entropy) associated with freezing of silicon (88). This complicates the kinetics of the silicon crystals growing from the melt. In fact, depending on the impurities present and the solidification conditions, silicon can form an amazing range of structures. The papers by Fredriksson (89) and Day and Hellawell (90) show the many chameleon-like forms that silicon can assume.

A number of theoretical and experimental studies have been offered to explain the mysterious growth of silicon. A detailed review of this work is beyond the scope of this paper, whose focus is on practical aspects of modification. Instead, the reader is referred to a number of key papers and reviews, which provide an introduction to this field of inquiry (9, 11, 12, 56, 88-94). There are also directional solidification studies, which show how the Al-Si eutectic grows from liquid melts (50, 95-96).

Nearly 20 years ago a committee of foundrymen (within AFS) considered the range of silicon structures commonly observed in commercial castings. They established a modification rating system (97). It is available as a wall chart which may be purchased from AFS. A number from one to six is assigned, depending on the silicon structure observed.

For the sake of discussion here an abbreviated form of the rating system is given in Figure 18. Each micrograph in Figure 18 is for a polished, unetched sample of A356 alloy. The silicon phase has a dark grey color. Iron-containing intermetallic phases are light grey, and aluminum is white. Below is a brief description of each rating.

Non-Modified Structure (#1)

The fully non-modified Al-Si eutectic consists of large, acicular silicon flakes. This is the structure observed in normal commercial alloys when no modifiers are present. However, very rapid solidification can produce some refinement and a structure similar to rating number 2 or 3.

Lamellar Structure (#2)

Small amounts of strontium produce some refinement of the large, acicular plates, so that fine lamellae of silicon are present in the eutectic. This structure is preferable to (1), since sufficiently long solution heat treatments break up the lamellae and produce rounded silicon particles.

Transitional Lamellar Structure (#3)

At slightly higher strontium levels the lamellar plates of silicon become even finer, and start to break down into smaller segments. The arrows in Figure 18(3) indicate two plates that are starting to transform into an aligned row of individual fibers. The reason for this change in structure is perhaps best seen in studies of directionally solidified Al-Si alloys (50, 95-96). In non-modified alloys the silicon plates grow faster than aluminum, so that new cells of aluminum nucleate on the protruding silicon plates. As strontium is added the growth of Si is retarded, until the aluminum phase starts to 'overgrow' the silicon. (The discussion by Major (96) on this point is particularly lucid.) This 'overgrowth' is starting to occur in this structure, as indicated by the arrows. The result is that some of the lamellar silicon plates are starting to break down into smaller, fibrous segments.

Mostly Modified Structure (#4)

At this point sufficient strontium has been added to completely transform the silicon from acicular/lamellar forms into a modified, fibrous structure. However, some larger silicon crystals are still found in the structure, as indicated by the arrows in Figure 18.4. The larger silicon crystals in this micrograph appear to have formed at a location where two eutectic grains have 'collided'. Between two eutectic cells the local growth rate will slow considerably, and when the strontium level is marginal, there will be a local loss of modification. (See the modification 'maps' in (50) and (54, 56) for a more detailed explanation.)

Fully Modified Structure (#5)

Here we have the fibrous silicon that is normally considered to be the fully modified structure.

'Super' Modified Structure (#6)

On rare occasions an extremely fine fibrous eutectic was observed. The individual fibers are so small that they cannot be seen in an optical micrograph. (This photo is shown at c. 800x magnification.) They are, however, distinguishable with a scanning electron microscope at higher magnifications.

Overall Ratings

It is fairly common to find a mix of structures in a casting. The usual way to assign a rating to a mixed structure is to multiply the area percentage of each structure by the rating number and average the values. For example, suppose we have a casting that is approximately 20% rating (Figure 18.3) and 80% rating (Figure 18.4). The overall rating for this casting would be:

Similarly, a casting that is 50% structure (Figure 18.4) and 50% structure (Figure 18.5) would have an overall modification rating number equal to 4.5.

Effect of Other Elements

A number of elements have a significant effect on the silicon structure, even when present in small quantities. These effects are not usually of concern in primary alloys. For the foundry using secondary alloys, however, it is important that impurity elements be considered. Each element is briefly considered below.

Phosphorus

Phosphorus is present in most primary alloys at a level of 5-10 ppm. Even this very small amount has a significant effect on the silicon structure in foundry alloys. Studies have been made with very high purity alloys (4, 98). A zone refined alloy containing 0.6 ppm P exhibited a refined eutectic structure similar to a Sr-modified alloy (4), whereas an alloy containing 6 ppm P had the normal non-modified structure shown in Figure 18(1). Directional solidification studies by Major (96) showed that phosphorus changes the relative growth kinetics of aluminum and silicon during eutectic solidification, and the morphology of the solid/liquid interface. A number of other researchers have considered the effect of phosphorus in aluminum alloys (4, 23, 40, 43, 98-102). It is well known that phosphorus 'poisons' the modifying effect of strontium (4, 23, 99, 102) and sodium (4, 101, 102). The effect of phosphorus on strontium modification is shown in Figure 19. This figure is a 'map' of the Sr-P interaction in A356 alloy sand castings. "F" represents the fibrous or fully modified structure. "L" represents the region where lamellar silicon is found, and "A" stands for acicular, non-modified silicon. From the results in this figure we find that, for each 10 ppm increase in P, one must increase the Sr by 30 ppm to offset the poisoning effect of phosphorus.

Antimony

Antimony additions will produce a lamellar structure similar to the one indicated in Figure 18(2). This was the basis for the 'Calypso' series of antimony-modified foundry alloys developed by Pechiney about thirty years ago (4, 25). Antimony does not increase porosity, as strontium and sodium sometimes do. (See Figure 5) For many years antimony was added to Al-Si casting alloys by French and Japanese wheel makers to produce a partial refinement (lamellar structure). For this reason antimony sometimes turns up in secondary alloys made from scrap wheels.

Antimony resides underneath phosphorus in group VA of the periodic table, so its chemical properties are similar in many respects. A number of researchers have documented that antimony poisons the modification effect of both strontium and sodium (102-107). The deleterious effects of antimony can often be counteracted with increased levels of strontium, as shown in Figure 20. Unfortunately, once antimony is added it remains in the scrap cycle. It cannot be removed by oxidation with oxygen or chlorine.

Improved properties and shorter solution times are possible with strontium. The widespread use of rotary impellor degassers now make it easy to obtain a low hydrogen content in our melts.

Antimony is a heavy metal and many are concerned about possible health risks associated with its use in the foundry. For all of these reasons antimony is now rarely used.

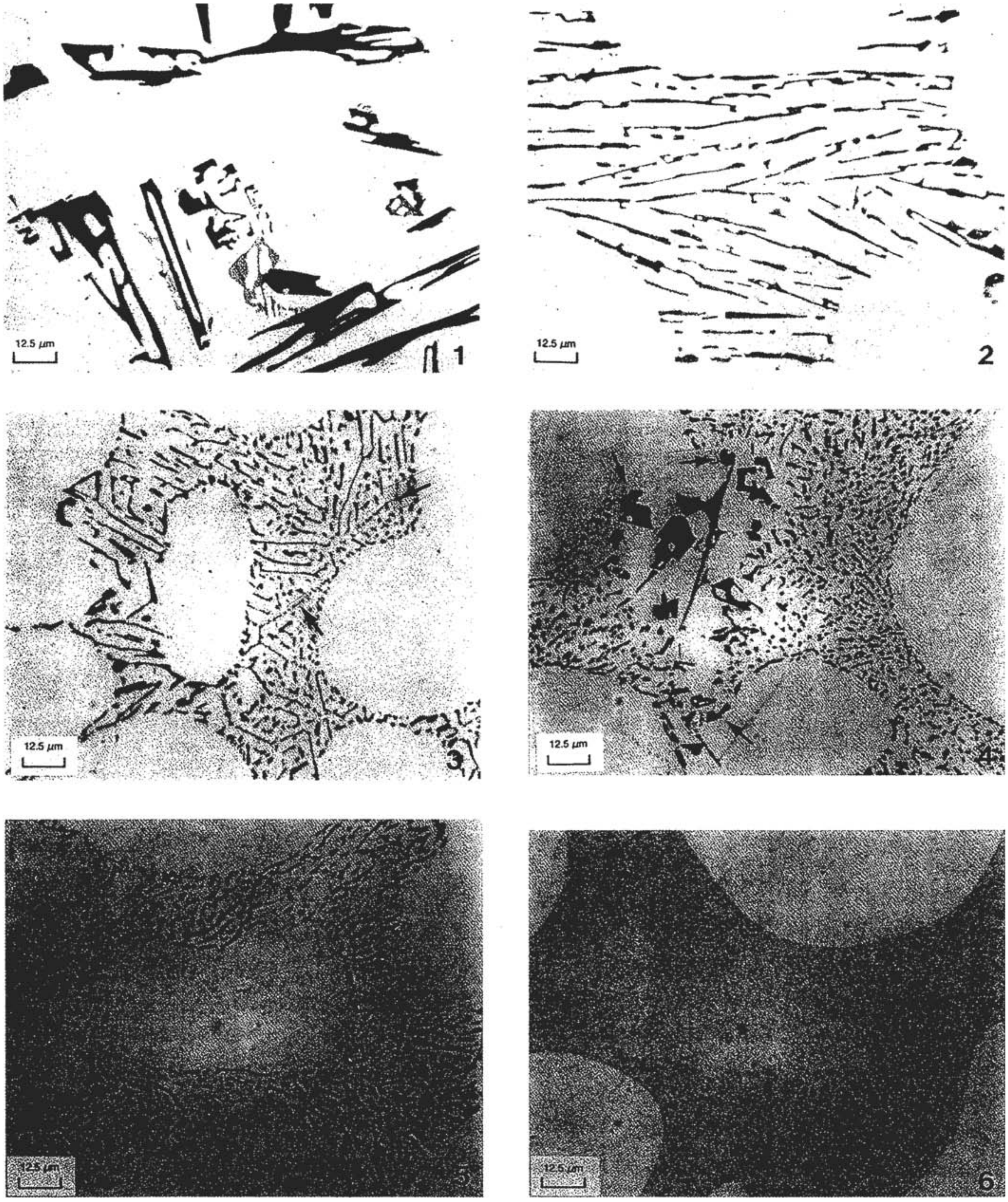


Figure 18. Modification rating system proposed by American Foundry Society (97)
(See text for explanations of rating system).

Bismuth

Bismuth is an element that is added to free machining alloys. This scrap sometimes finds its way into secondary alloys like 319. Because it is also a group VA element, it poisons the effect of Sr-modification when present in significant quantities (99, 108-109). Researchers and foundrymen agree that the Sr:Bi ratio must be greater than 0.45 in order to produce a fully modified silicon eutectic in 319 alloy.

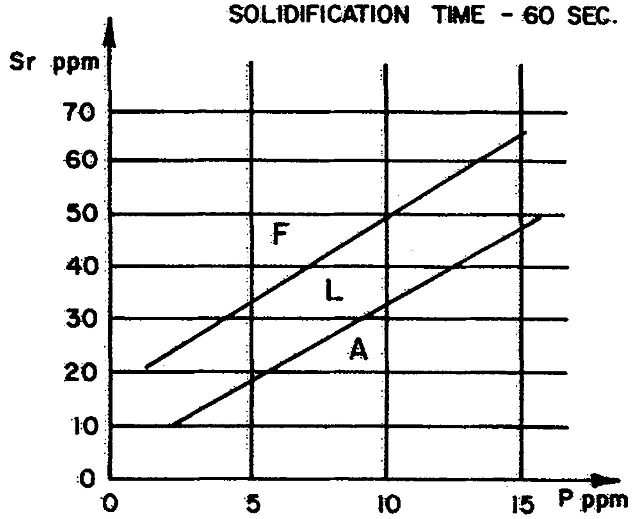


Figure 19. Sr-P interaction in sand cast A356 alloy (102).

Magnesium

When magnesium is added to Al-Si alloys, there is a coarsening of the Si eutectic (4, 110). This is perhaps because Mg changes the phase relationships to produce a eutectic 'mushy zone'.

Boron

Some researchers have experimented with boron additions to grain refine Al-Si alloys. Boron forms the compound AlB_2, which is an effective nucleant in foundry alloys, but boron also forms the compound SrB_6. Thus, boron additions interfere with Sr-modification (111). For this reason, grain refinement is best accomplished by additions of TiB_2, via Al-Ti-B master alloys.

Calcium

There have been many studies on the use of calcium as a modifier (44-45, 63, 108, 112-113), either alone or in combination with sodium or strontium. When calcium is added to Sr-modified melts, there is a coarsening of the silicon eutectic, similar to that which occurs with magnesium or excess quantities of strontium. The action of calcium is similar to strontium as a modifier, except calcium does not work as well at slow cooling rates. Calcium changes the surface oxide when dissolved in aluminum melts, making the metal extremely susceptible to gas pickup. Calcium sometimes finds its way into the foundry via silicon additions used to make up the alloy. It is best to keep calcium less than about 30 ppm to avoid excessive gas pickup. When necessary, calcium is easily removed by additions of reactive salts, or by degassing with a few percent of chlorine in the inert gas. Salts and chlorine also remove strontium, however, so it is best to first remove calcium, skim the melt to remove any reactive salts, and then make the strontium master alloy addition.

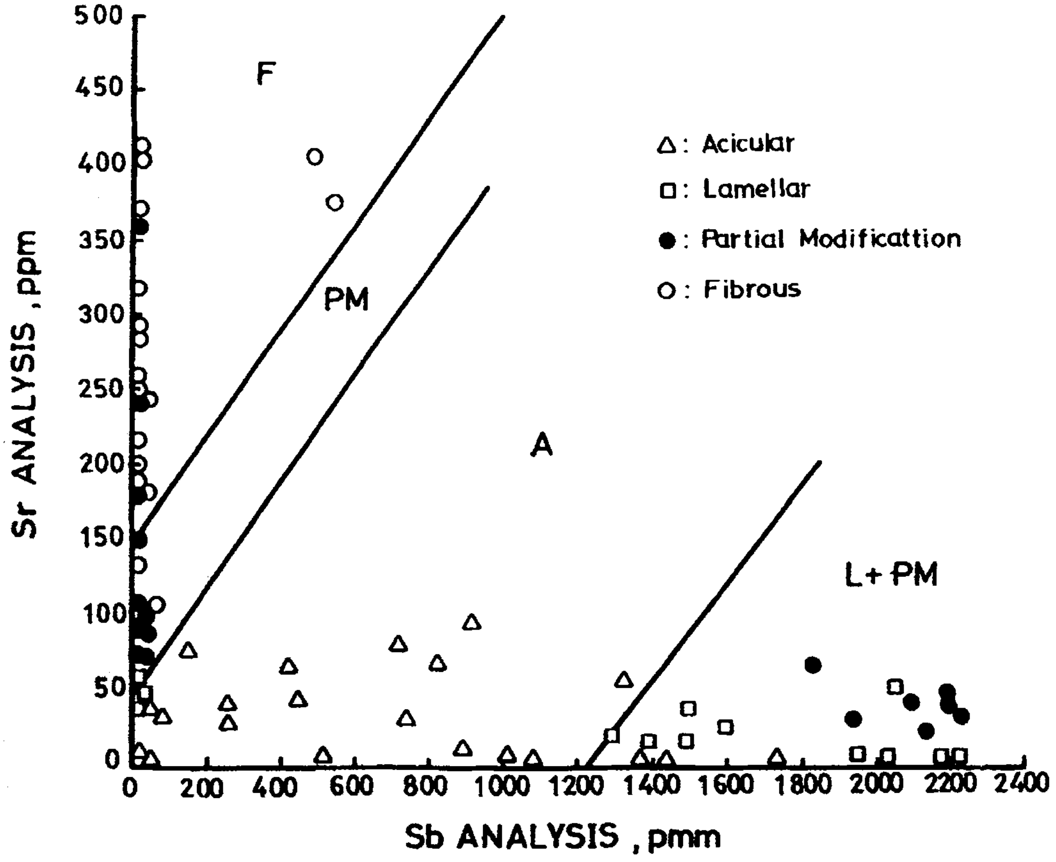


Figure 20. Sr-Sb interactions in A356 alloy (104).

Concluding Remarks

In conducting this review I was amazed by the volume of information available in the technical literature. I was also struck by the relative paucity of information in some areas, and tantalized by possible future advances in two areas of modification technology. For these reasons, a few suggestions will be made for areas where future research and development appear to be useful.

There have been studies on the effect of phosphorus or strontium additions on the formation of iron-containing compounds in foundry alloys (114-117). Unfortunately, the available information is contradictory. Since iron is always a problem in aluminum castings, it would be worth exploring any method that offers promise of controlling, or limiting, the loss of elongation and tensile strength normally associated with higher iron contents. A detailed fundamental study would be extremely useful. Perhaps the best way to develop better information would be with directional solidification experiments. Careful thermal analysis studies may also be helpful, and studying the effect of freezing rate on particle formation would also be informative.

In Figure 18(6) a 'super' modified structure was shown. If it were possible to produce a structure like this consistently in commercial casting processes, this would be a significant advance in casting technology. The mechanical properties of the castings should be superior to anything we are able of producing today, and it may allow us to further reduce solution heat treatment times. Two recent laboratory studies suggest ways in which this might be accomplished. The first is the excellent study of Al-Si alloys produced by semi-solid metal (SSM) processing (18). In melts which were subjected to stirring during solidification, an extremely fine, 'super' modified eutectic was produced. In the second study (118) ultrasound produced the same structure. This question arises: What level of vibration or ultrasound (or metal movement) is required to produce a 'super' modified structure? It would be worth trying to answer this question. It also raises profound questions about the mechanisms operating to produce the modified structure.

There was only one paper (119) which studied the effect of modification practice on fatigue properties. This study suggested that best fatigue properties are obtained when a grain refiner is used in combination with strontium. In view of the importance of fatigue life, further study appears to be justified.

Likewise, there was only one paper on machinability (120). This paper suggested that Na- and Sr- modification improves surface finish and reduces tool wear. An increase in shear angle was recommended in modified alloys for best results. Machinability is another subject that merits further study.

Finally, there is the foundryman's equivalent of "I have a dream ..." Is it possible to somehow modify Al-Si alloys without the undesirable increase in porosity? This may be so. Researchers at CAST in Australia have been studying nucleants for the silicon eutectic in Al-Si alloys (52). In non-modified alloys they found AlP, but in Sr-modified alloys other nucleants were observed. These nucleants contained Ti and V. They then added Ti, V and B (in unspecified proportions) and were able to reduce the eutectic grain size. (Note Figure 6 of their paper.) This is an exciting result. If it could be translated into commercial practice, it would be the most significant advance in modification technology since strontium was introduced more than 30 years ago. It is to be hoped that this work will continue.

Acknowledgments

The author gratefully acknowledges Alcoa Primary Metals, whose support has made this study possible.

REFERENCES

1. A. Pacz: U.S. Patent 1,387,900, 16 August, 1921.
2. R.W. Smith: "Modification of Aluminum-Silicon Alloys," *Solidification of Metals*, pp. 224-237, Iron and Steel Inst., London, © 1968.
3. P.B. Crosley and L.F. Mondolfo: "The Modification of Aluminum-Silicon Alloys," *Modern Castings*, pp. 89-100 (March, 1966).
4. Serge Bercovici: "Control of Solidification Structures and Properties of Al-Si Alloys," Paper presented at the 45th. International Foundry Congress, Budapest (October, 1978).
5. R.J. Kissing and J.F. Wallace: "Refinement of Aluminum-Silicon Alloys," *Foundry*, Vol. 91(4), pp. 74-79 (April, 1963).
6. Shu-Zu Lu and A. Hellawell: "Modification of Al-Si Alloys: Microstructure, Thermal Analysis, and Mechanisms," *J. of Metals*, pp. 38-40 (February, 1995).
7. G.K. Sigworth: "Theoretical and Practical Aspects of the Modification of Al-Si Alloys," *AFS Transactions*, Vol. 91, pp. 7-16 (1983).
8. M. Adachi: "Modification of Hypo-eutectic and Eutectic Al-Si System Casting Alloys," *J. Japan Inst. Light Metals*, Vol. 34 (6), pp 361-373 (1984).
9. J.E. Gruzleski and B. Closset: *The Treatment of Aluminum-Silicon Alloys*, pp. 25-105, American Foundry Soc., Des Plaines, Illinois © 1990.
10. L. Backerud, G. Chai and J. Tamminen: *Solidification Characteristics of Aluminum Alloys—Volume 2: Foundry Alloys*, pp. 25-38, AFS/Skanaluminium © 1990.

11. J.E. Gruzleski: "The Art and Science of Modification: 25 Years of Progress," *AFS Transactions*, Vol. 100, pp. 673-683 (1992).
12. M.M. Makhlouf and H.V. Guthy: "The Al-Si Eutectic Reaction: Mechanisms and Crystallography," *J. Light Metals*, Vol. 1, pp. 199-218 (2001).
13. M. Adachi: "Modification of Hypereutectic Al-Si System Casting Alloys," *J. Japan Inst. Light Metals*, Vol. 34 (7), pp 430-436 (1984).
14. A.P. Bates: "Hypereutectic Aluminum-Silicon Alloys: A Review of Published Information," *Metallurgia*, Vol. 61 (364), pp. 70-79 (February, 1960).
15. J.L. Jorstad: "The Hypereutectic Al-Si Alloy Used to Cast the Vega Engine Block," *Modern Casting*, Vol. 60, pp. 59-64 (October, 1971).
16. Y.P. Telang: "Process Variables in Al-21 Si Alloys Refinement," *Modern Casting*, Vol. 43(5), pp. 232-240 (1963).
17. J.L. Jorstad and D. Apelian: "Hypereutectic Al-Si Alloys: Practical Processing Techniques," *Die Casting Engineer*, Vol. 48 (3), pp. 50-58, (May, 2004).
18. S. Nafisi and R. Ghomashchi: "Effects of Modification during Conventional and Semi-Solid Metal Processing of A356 Al-Si Alloy," *Materials Science and Engineering A*, Vol. 415, pp. 273-285 (2006).
19. M. Helmanova: "The Influence of Solidification Rate on the Spatial Distribution of Eutectic Silicon in Technical Silumins," *Praktische Metallographie*, Vol. 12, pp. 59-68 (1975).
20. J. Gobrecht: "The Influence of Alloying Elements on the Duration of Modification of Na and Sr in Al-Si Cast Alloys," *Giesserei*, Vol. 65, pp. 158-164 (1978).
21. B.M. Thall and B. Chalmers: "Modification in Aluminum-Silicon Alloys," *J. Inst. Metals*, Vol. 77, pp. 79-97 (1950).
22. Z. Poniewierski: "Effect of the Type of Modification on the Microstructure of Al-Si Eutectic," *Rev. Hautes Temp. et Refract.*, Vol. 14, pp. 253-260 (1977).
23. F. Fommei: "Modification Treatments of Al-Si Alloys," *Aluminio*, Vol. 46, pp. 121-135 (1977).
24. T.J. Hurley and R.G. Atkinson: "Effects of Modification Practice on Aluminum A356 Alloys," *AFS Transactions*, Vol. 93, pp. 291-196 (1985).
25. M. Garat, G. Laslay, S. Jacob, P. Meyer, P.H. Gaerin and R. Adam: "State of the Art Use of Sb-, Na- and Sr-modified Al-Si Casting Alloys," *AFS Transactions*, Vol. 100, pp. 821-832 (1992).
26. J.J. Jorstad and W.M. Rasmussen: *Aluminum Casting Technology*, 2^{nd}. Edition, pp. 76-77, American Foundry Society, © 1993.
27. S. Shivkumar, S. Ricci, B. Steenhoff, D. Apelian and G. Sigworth: "An Experimental Study to Optimize the Heat Treatment of A356 Alloy," *AFS Transactions*, Vol. 97, pp. 791-810 (1989).
28. S.A. Levy: "Techniques for Improving Ductility of Low Pressure Die Cast Aluminum Wheels," *AFS Transactions*, Vol. 86, pp. 135-138 (1978).
29. F. Paray and J.E. Grusleski: "Factors to Consider in Modification," *AFS Transactions*, Vol. 102, pp. 833-842 (1994).
30. M. Drouzy, S. Jacob and M. Richard: "Interpretation of Tensile Results by Means of a Quality Index," *AFS International Cast Metals Journal*, Vol. 5, pp 43-50 (1980).
31. P.Y. Zhu, Q.Y. Liu and T.X. Hon: "Spheroidization of Eutectic Silicon in Al-Si Alloys," *AFS Transactions*, Vol. 91, pp. 609-614 (1983).
32. D.L. McLellan and M.M. Tuttle: "Aluminum Castings – A Technical Approach," *AFS Transactions*, Vol. 91, pp. 243-252 (1983).
33. Q.C. Wang, C.H. Caceres, and J.R. Griffiths: "Damage by Eutectic Particle Cracking in Aluminum Casting Alloys A356/A357," *Met. Mater. Trans. A*, Vol. 34A, pp. 2901-2912 (2003).
34. Q.T. Fang and D.A. Granger: "Porosity Formation in Modified and Unmodified A356 Alloy Castings," *AFS Transactions*, Vol. 97, pp. 989-1000 (1989).
35. D. Emadi and J.E. Gruzleski: "Effects of Casting and Melt Variables on Porosity in Directionally Solidified Al-Si Alloys," *AFS Transactions*, Vol. 102, pp. 307-312 (1994).
36. J. Charbonnier: "Microprocessor Assisted Thermal Analysis Testing of Aluminum Alloy Structures," *AFS Transactions*, Vol. 92, pp. 907-922 (1984).
37. D. Apelian, G. K. Sigworth, and K. Whaler: "Assessment of Grain Refinement and Modification of Al-Si Foundry Alloys by Thermal Analysis," *AFS Transactions*, Vol. 92, pp. 297-305 (1984).
38. N. Tenekedjiev and J.E. Gruzleski: "Thermal Analysis of Strontium Treated Hypoeutectic and Eutectic Al-Si Casting Alloys," *AFS Transactions*, Vol. 99, pp. 1-6 (1991).
39. G. Chai and L. Bäckerud: "Factors Affecting Modification of Al-Si Alloys by Adding Sr-Containing Master Alloys," *AFS Transactions*, Vol. 100, pp. 847-854 (1992).
40. K. Nogita and A.K. Dahle: "Eutectic Growth Mode in Sr, Sb and P Modified Hypoeutectic Al-Si Foundry Alloys," *Materials Trans.*, Vol. 42(3), pp. 393-396 (2001).
41. A. Knuutinen , K. Nogita, S.D. McDonald and A.K. Dahle: "Modification of Al-Si Alloys Modified with Ba, Ca, Y and Yb," *J. Light Metals*, Vol. 1, pp. 229-240 (2001).
42. A.K. Dahle, S.D. McDonald and K. Nogita: "Eutectic Solidification in Hypoeutectic Al-Si Alloys and Its Effect on Porosity," *Advances in Aluminum Casting Technology*, pp. 1-10, M. Tiryakioglu and J. Campbell, editors, ASM International, Metals Park, Ohio, © 2002.
43. K. Nogita, S.D. McDonald, K. Tsujimoto, K. Yasuda and A.K. Dahle: "Aluminum Phosphide as a Eutectic Grain Nucleus in Hypoeutectic Al-Si Alloys," J. Electron Microscopy, Vol. 53(4), pp. 361-369 (2004).

44. A. Knuutinen, K. Nogita, S.D. McDonald and A.K. Dahle: "Modification of Al-Si Alloys with Ba, Ca, Y and Yb," *J. Light Metals*, Vol. 1, pp. 229-240 (2001).
45. C. B. Kim and R.W. Heine: "Fundamentals of Modification in the Aluminum-Silicon System," *J. Inst. Metals*, Vol. 92, pp. 367-376 (1963-1964).
46. Y. Tsumura, A. Sakakibara, K. Toyoda and M. Ishikawa: „The Mechanism of Incubation Period of Modification Effect of Al-Si Alloy," *J. Japan Inst Light Metals*, Vol. 30, pp. 239-245 (1980).
47. N. Tenekedjiev, D. Argo and J.E. Gruzleski: "Sodium, Strontium and Phosphorus Effects in Hypereutectic Al-Si Alloys," *AFS Transactions*, Vol. 97, pp. 127-136 (1989).
48. G. K. Sigworth: "Observations on the Refinement of Hypereutectic Al-Si Alloys," *AFS Transactions*, vol. 95, pp. 303-314 (1987).
49. S.C. Flood and J.D. Hunt: "Modification of Al-Si Eutectic Alloys with Na," *Metal Science*, Vol. 15, pp. 287-294 (1981).
50. D.C. Jenkinson and L.M. Hogan: "The Modification of Al-Si Alloys with Strontium," *J. Crystal Growth*, Vol. 28, pp. 171-187 (1975).
51. A.K. Dahle, K. Nogita, S.D. McDonald, C. Dinnis and L. Lu: "Eutectic Modification and Microstructural Development in Al-Si Alloys," *Materials Sci. Eng. A*, Vol. 413-414, pp. 243-248 (2005).
52. K. Nogita, S.D. McDonald and A.K. Dahle: "New Approaches to Understand Modification and Nucleation Mechanisms of Hypoeutectic Al-Si Alloys," *Shape Casting: 2nd. Internat. Symposium*, pp. 51-58, The Metals Society, Warrandale, Pennsylvania © 2007.
53. A.K. Dahle, J.A. Taylor and D.A. Graham: "The Role of Eutectic Growth Mode in Porosity Formation in Al-Si Alloys," *Aluminum Trans.*, Vol. 3(1), pp 17-30 (2000).
54. S.D. McDonald, A.K. Dahle, J.A. Taylor and D.H. StJohn: "Eutectic Grains in Unmodified and Strontium-Modified Hypoeutectic Al-Si Alloys," *Metall.Mater. Trans. A*, Vol. 35A, pp. 1829-1837 (2004).
55. S.D. McDonald, A.K. Dahle, J.A. Taylor and D.H. StJohn: "Modification-Related Porosity Formation in Hypoeutectic Al-Si Alloys," *Metall.Mater. Trans. B*, Vol. 35B, pp. 1097-1106 (2004).
56. S.D. McDonald: "Eutectic Solidification and Porosity Formation in Unmodified and Modified Hypoeutectic Al-Si Alloys," Ph.D. Thesis, Division of Materials Engineering, University of Queensland, Brisbane, Australia, July, 2002.
57. J.P. Anson, M. Stucky and J.E. Gruzleski: "Effect of Sr Modification on Nucleation and Growth of Microporosity During Solidification of Al-7% Si Foundry Alloy," *AFS Transactions*, Vol. 108, pp. 419-426 (2000).
58. J.P. Anson, M. Stucky and J.E. Gruzleski: "Effect of Sr Concentration on Microporosity Formation in A356 Aluminum Alloy," *AFS Transactions*, Vol. 109, pp. 1-16 (2001).
59. R. Fuoco, H. Goldenstein and J.E. Gruzleski: "Evaluation of Effect of Modification Induced Undercooling on Microporosity Formation in A356 Aluminum Alloy, *AFS Transactions*, Vol. 102, pp. 297-312 (1994).
60. R. Fuoco, E.R. Correa and A.V.O. Correa: "Effect of Modification on Microporosity Formation in 356 Aluminum Alloy," *AFS Transactions*, Vol. 103, pp. 379-386 (1995).
61. K.J. Brondyke and P.D. Hess: "Interpretation of Vacuum Gas Test Results for Aluminum Alloys," *Trans. TMS-AIME*, Vol. 230, pp. 1542-46 (1964).
62. E.L. Rooy and E.F. Fischer: "Control of Aluminum Casting Quality by Vacuum Solidification Tests," *AFS Transactions*, Vol. 76, pp. 237-240 (1963).
63. K.E. Höner and Z. Youling: "Influence of Ca ans Sr on the Hydrogen Pickup in Aluminum Alloy Melts by Example of G-AlSi12," Giesserei-Forschung, Vol. 39(11), pp. 34-48 (1987).
64. L. Liu, A.M. Samuel, F.H. Samuel, H.W. Doty and S. Valtierra: "Influence of Oxides on Porosity Formation of Sr-Treated Al-Si Casting Alloys," *J. Materials Sci.*, Vol. 38, pp 1255-67 (2003).
65. D. Emadi, J.E. Gruzleski and M. Pekguleryuz: "Melt Oxidation Behavior and Inclusion Content in Unmodified and Sr-Modified A356 Alloy—Their Role in Pore Nucleation," *AFS Transactions*, Vol. 104, pp. 763-768 (1996).
66. S. McDonald, M. Dargusch, G. Song and D. StJohn: "Unintentional Effects of Sr Additions in Al-Si Foundry Alloys," *Shape Casting: 2nd. Internat. Symposium*, pp. 59-66, The Metals Society, Warrandale, Pennsylvania © 2007.
67. H. Iwahori, K. Yonekura, Y. Sugiyama, Y. Yamamoto and M. Nakamura: "Behavior of Shrinkage Porosity Defects and Limiting Solid Fraction of Feeding on Al-Si Alloys," *AFS Transactions*, Vol. 93, pp. 443-451 (1985).
68. H. Iwahori, K. Yonekura, Y. Yamamoto and M. Nakamura: "Occurring Behavior of Porosity and Feeding Capabilities of Sodium- and Strontium-Modified Al-Si Alloys," *AFS Transactions*, Vol. 98, pp. 167-173 (1990).
69. R. Fuoco, E.R. Correa and H. Goldenstein: "Effect of Modification on Microporosity in 356 Aluminum Alloy," *AFS Transactions*, Vol. 104, pp. 1151-1157 (1996).
70. Ø. Nielsen and S.O. Olsen: "Experiment for Quantification of Feedability and Permeability in Industrial Aluminum Alloys," *Internat. J. Cast Metals Research*, Vol. 19(1), pp. 32-37 (2006).
71. J.M. Kim, H.W. Kwon and C.R. Loper, Jr.: "Feeding Behavior of Modified and Unmodified Al-Si Alloys," *AFS Transactions*, Vol. 104, pp. 743-749 (1996).
72. P.D. Hess and E.V. Blackmun: "Strontium as

Modifying Agent for Hypoeutectic Aluminum-Silicon Alloys," *AFS Transactions*, Vol. 92, pp. 87-90 (1975).

73. S.D. McDonald, K. Nogita, A.K. Dahle, J.A. Taylor and D.H. StJohn: "Eutectic Solidification and Porosity Formation in Al-Si Alloys: Role of Strontium," *AFS Transactions*, Vol. 108, pp. 463-470 (2000).
74. C.M. Dinnis, A.K. Dahle and J.A. Taylor: "Eutectic Morphology and Porosity in Unmodified and Sr-Modified Al-Si Alloys," *AFS Transactions*, Vol. 113, pp. 99-106 (2005).
75. D. Argo and J.E. Gruzleski: "Porosity in Modified Aluminum Alloy Castings," *AFS Transactions*, Vol. 96, pp. 65-74 (1988).
76. Z. Li, A.M. Samuel, F.H. Samuel, C. Ravrindran and S. Valtierra: "Effect of Alloying Elements on the Segregation and Dissolution of $CuAl_2$ Phase in Al-Si-Cu 319 Alloys," *J. Materials Sci.*, Vol. 38, pp. 1203-1218 (2003).
77. F.H. Samuel, A.M. Samuel and H.W. Doty: "Factors Controlling the Type and Morphology of Cu-Containing Phases in 319 Aluminum Alloy," *AFS Transactions*, Vol. 104, pp. 893-901 (1996).
78. M. Djurdjevic, T. Stockwell and J. Sokolowski: "Effect of Strontium on Microstructure of Al-Si and Al-Cu Eutectics in 319 Aluminum Alloy," *Internat. J. Cast Metals Res.*, Vol. 12, pp. 67-73 (1999).
79. B. Closset and S. Kitaoka: "Evaluation of Sr Modifiers for Al-Si Casting Alloys," *AFS Transactions*, Vol. 85, pp. 233-240 (1987).
80. M.O. Pekguleryuz and J.E. Gruzleski: "Conditions for Strontium Master Alloy Additions to A356 Melts," *AFS Transactions*, Vol. 96, pp. 55-64 (1988).
81. G. Chai and L. Bäckerud: "Factors Affecting Modification of Al-Si Alloys by Adding Sr-Containing Master Alloys, *AFS Transactions*, Vol. 100, pp. 847-854 (1992).
82. B. Closset and J.E. Gruzleski: "Mechanical Properties of A356 Alloy Modified with Pure Strontium," *AFS Transactions*, Vol. 90, pp. 453-464 (1982).
83. R. DasGupta, C.G. Brown and S. Marek: "Analysis of Overmodified 356 Aluminum Alloy," *AFS Transactions*, Vol. 96, pp. 297-310 (1988).
84. J. Gruzleski, N. Handiak, H. Campbell and B. Closset: "Hydrogen Measurement by Telegas in Sr-Treated A356 Melts," *AFS Transactions*, Vol. 94, pp. 147-154 (1986).
85. F.C. Dinayuga, N. Handiak and J.E. Gruzleski: "The Degassing and Regassing Behavior of Sr-Modified A356 Melts," *AFS Transactions*, Vol. 96, pp. 83-88 (1988).
86. X.-G. Chen, F.J. Klinkenberg, R. Ellerbrok and S. Engler: "Efficiency of Impeller Degassing and Regassing Phenomena in Aluminum Melts," *AFS Transactions*, Vol. 102, pp. 191-197 (1994).
87. G.K. Sigworth, C. Wang, H. Huang and J. T. Berry: "Porosity Formation in Modified and Unmodified Al-Si Alloy Castings," AFS Transactions, Vol. 102, pp. 245-261 (1994).
88. B. Gallois and G. K. Sigworth: "An Analysis of Silicon Eutectic Modification," Thermal Analysis of Molten Aluminum, pp. 101-119, Amer. Foundry Society, Des Plaines, IL, © 1985.
89. H. Fredriksson, M. Hillert and N. Lange: "Modification of Aluminum Silicon Alloys by Sodium," *J. Inst. Metals*, Vol. 101, pp 285-299 (1973).
90. M.G. Day and A. Hellawell: "The Microstructure and Crystallography of Aluminium-Silicon Eutectic Alloys," *Proc. Roy. Soc.*, Vol. 305A, pp. 473-491 (1968).
91. Shu-Zu Lu and A. Hellawell: "Mechanisms of Silicon Modification in Aluminum-Silicon Alloys: Impurity Induced Twinning," *Metall. Trans. A*, Vol. 18A, pp. 1721-1731 (1987).
92. A. Hellawell: "How Does a Modifier Work?," pp. 9-1 to 9-17, *Proc. 2nd. Internat. Conference on Molten Aluminum Processing*, American Foundry Soc., © 1989.
93. R. Elliott: *Eutectic Solidification Processing*, Butterworth, London, 1983.
94. R. Elliott: "Growth Kinetics in Aluminum Silicon Eutectic Alloys," pp. 10-1 to 10-24, *Proc. 2nd. Internat. Conference on Molten Aluminum Processing*, American Foundry Soc., © 1989.
95. L. Clapham and R.W. Smith: "Partial Modification in Unidirectionally Solidified Al-Si Eutectic Alloys," *Acta Metall.*, Vol. 37(1), pp. 303-311 (1989).
96. J.F. Major and J.W. Rutter: "Effect of Strontium and Phosphorus on Solid/Liquid Interface of Al-Si Eutectic," *Mater. Sci. Technol.*, Vol. 5(7), pp. 645-656 (1989).
97. G. K. Sigworth: "Determining Grain Size and Eutectic Modification in Aluminum Alloy Castings," *Modern Casting*, Vol. 77, pp. 23-25, July, 1987.
98. S.D. McDonald, K. Nogita and A.K. Dahle: "Eutectic Nucleation in Al-Si Alloys," *Acta Mater.*, Vol. 52, pp. 4273-4280 (2004).
99. C.R. Loper, Jr., H.-G. Seong and J.-I. Cho: "Interaction of Phosphorus and Bismuth (with Sr) in A356.2 Alloy," *AFS Transactions*, Vol. 109, pp. 1-13 (2001).
100. C.R. Loper, Jr. and J.-I. Cho: "Influence of Trace Amounts of Phosphorus in Aluminum Castings," *AFS Transactions*, Vol. 108, pp. 667-672 (2000).
101. B. Günther and H. Jürgens: "Influence of Minor Impurities on Mechanical Properties, Structure and Solidification Form of Eutectic on Near-Eutectic Al-Si Casting Alloys," *Giesserei*, Vol. 67, pp. 8-13 (1980).
102. S. Bercovici, M. Garat and R. Scalliet: "A Review of Recent French Casting Alloy Developments," Report 13691, April, 1978, Pechiney Ugine Kuhlmann, 125 Third Ave., N.Y., New York, 10022.
103. N. Handiak, J.E. Gruzleski and D. Argo: "Sodium, Strontium and Antimony Interactions During Modification of AS7G03 (A356) Alloys," *AFS Transactions*, Vol. 95, pp. 31-38 (1987).

104. E.N. Pan, Y.C. Cherng, C.A. Lin and H.S. Chiou: "Roles of Sr and Sb on Silicon Modification of A356 Aluminum Alloys, *AFS Transactions*, Vol. 102, pp. 609-629 (1994).

105. B.L. Tuttle, D Twarog and E. Daniels: "The Effect of Trace Amounts of Antimony on the Structure and Properties of Aluminum Alloy A356.2," *AFS Transactions*, Vol. 99, pp. 7-16 (1991).

106. W. Wang and J.E. Gruzleski: "Interactive Effects During Sodium or Strontium Treatment of Antimony-Containing A356 Alloy," *AFS Transactions*, Vol. 98, pp. 227-234 (1990).

107. Anon.: "Incompatibility of Sodium and Antimony in the Modification of Al-Si Alloys," *Fondeur D'aujord'hui*, Vol. 272, pp. 12-13 (1976).

108. S. El-Hadad, A.M. Samuel, F.H. Samuel, H. W. Doty and S. Valtierra: "Effect of Bi and Ca Additions on the Characteristics of Eutectic Silicon Particles in Sr-Modified 319 Alloys," *Internat. J. Cast Metals Res.*, Vol. 15, pp. 551-564 (2003).

109. C.J. Machovec, G.E. Byczynski, J.W. Zinel and L.A. Godlewski: "Effect of Bi-Sr Interactions on Si Morphology in a 319 Type Aluminum Alloy," *AFS Transactions*, Vol. 108, pp. 439-444 (2000).

110. G. Heiberg et al.: "Effect of Mg, Fe and Cu on Eutectic Solidification of Hypoeutectic Al-Si Alloys," *AFS Transactions*, Vol. 110, pp. 347-358 (2002).

111. B. Golhahar, A.M. Samuel, F.H. Samuel, H.W. Doty and S. Valtierra: "Effect of Grain Refiner-Modifier Interactions on the Microstructure and Mechanical Properties of A356 Alloys," *AFS Transactions*, Vol. 115, paper 07-012 (2007).

112. A. Abdollahi and J.E. Gruzleski: "Evaluation of Calcium as a Eutectic Modifier in A357 Alloy," *Internat. J. Cast Metals Res.*, Vol. 11, pp 145-155 (1998).

113. C.R. Loper, Jr. and J.-I. Cho: "Influence of Trace Amounts of Calcium in Aluminum Castings," *AFS Transactions*, Vol. 108, pp. 585-592 (2000).

114. L. Lu and A.K. Dahle: "Iron-Rich Intermetallic Phases and their Role in Casting Defect Formation in Hypoeutectic Al-Si Alloys," *Met. Mater. Trans. A*, Vol. 36A, pp. 819-835 (2005).

115. W. Kalifa, A.M. Samuel, F.H. Samuel, H.W. Doty and S.Valtierra: "Metallographic Observations of β-AlFeSi Phase and its Role in Porosity Formation in Al-7%Si Alloys," *Internat. J. Cast Metals Res.*, Vol. 19, pp. 156-166 (2006).

116. B. Kulunk, S.G. Shabestari and J.E. Gruzleski: "Beneficial Effects of Strontium in A380 Alloy," *AFS Transactions*, Vol. 104, pp. 1189-1193 (1996).

117. S.G. Shabestari and J.E. Gruzleski: "Modification of Iron Intermetallics by Strontium in 413 Aluminum Alloy," *AFS Transactions*, Vol. 103, pp. 285-293 (1995).

118. X. Jian, C. Xu, T. Meek and Q. Han: "Effect of Ultrasound Vibration on the Solidification Structure of A356 Alloy," *AFS Transactions*, Vol. 113, pp. 131-138 (2005).

119. P.D. Lee and T.C. Lindley: "The Influence of Sr and TiB_2 Additions on the Formation of Porosity in Aluminum Castings and Their Effect on Fatigue Properties," *Shape Casting: The J. Campbell Symposium*, pp. 225-234, The Metals Soc. © 2005.

120. E. Sato, T. Saga and S. Nagai: "Effects of Additional Elements on the Machinability of Al-Si Casting Alloys," *J. Japan. Inst. Light Metals*, Vol. 33(11), pp 649-654 (1983).