Introduction

It is common practice in the foundry industry to treat certain molten alloys with chemical inoculants prior to casting in order to modify the microstructure upon solidification. For example, when magnesium is added to molten gray iron, the resulting cast microstructure will contain graphite in the form of nodules instead of flakes. A modification treatment is also used to spheroidize sulfide inclusions in steel castings. Here the morphology of the sulfide inclusions is changed from stringers to spheres with additions of cerium. In the case of aluminum-silicon alloys, an inoculation treatment with sodium changes the morphology of eutectic silicon crystals from a plate to a fibrous form.

In each of these examples, the morphology of a particular phase constituent is changed from an angular shape to a rounded shape. Angular constituents are deleterious, because they serve as sites for crack initiation and they provide preferential fracture paths. Thus modification treatments generally result in improved toughness.

Although modification treatments have long proven to be of great value in foundry applications, their application in welding processes has been neglected. Recently, Davila et al. (Ref. 1) have shown that when welding ductile iron, the weld metal can be modified with ferromagnesium additions to the weld pool. In essence, they demonstrated the feasibility of applying a foundry practice to welding.

The rapid cooling rate associated with the welding process, 10 to 100 times greater than most castings, gives rise to many unique solidification characteristics. Since the shape, size, and distribution of any phase in a solidified microstructure is determined by nucleation and growth rates, which are both influenced by cooling rate, it can be appreciated why welded and cast microstructures may differ.

An aluminum-silicon (Al-Si) eutectic alloy was chosen for this investigation of weld metal modification. Al-Si alloys are widely used in both foundry and joining industries in applications such as casting of automobile engine blocks, dip-brazing of automobile radiators, and braze-welding of dissimilar metals. However, only the foundry industry has utilized a modification treatment. In the foundry industry, modified Al-Si alloys have been used since 1921 when Pacz (Ref. 2) discovered that a treatment with sodium salts produced an improvement in strength and ductility.

The problem addressed here is whether or not additions of sodium to the weld pool will also result in a modified microstructure. A major question related to this problem is how might sodium be introduced to the weld pool and, if it can be introduced, will it remain in solution long enough to interact with solidification mechanisms. A large amount of sodium may be required to compensate for a high attrition rate during welding. Another question of concern is how the rapid cooling rate, characteristic to welding, will influence modification mechanisms.

A systematic study was made of the microstructural changes which occur in the weld metal of an Al-Si eutectic alloy treated with sodium. This study involved a correlation of both cooling rates and sodium additions with weld metal microstructure. Experimental results are examined in light of modification theory and correlations are discussed. First, however, a description of both normal and modified microstructures is presented followed by a review of modification theory.

Microstructure of Al-Si Alloys

The Al-Si binary system has a simple eutectic occurring at approximately 12.5 wt-% silicon and 557°C (1035°F) (Ref. 3) as shown in Fig. 1. Note that aluminum and silicon have negligible solubility for one another in solid solution. For this reason, the alpha and beta phases will henceforth be referred to as aluminum and silicon respectively. The exact composition of the eutectic has been a controversial subject due to the tendency to form primary aluminum at moderate cooling rates. Values for the eutectic composition have been reported ranging from 11.7 to 12.7 wt-% silicon. For example, the eutectic point will shift approximately 2 wt-% to a higher silicon concentration in a die cast Al-Si eutectic alloy due to the formation of primary aluminum. The supercooling associated with this shift is reported to be on the order of 10°C (50°F) (Ref. 4).

In any hypo-eutectic or rapidly cooled eutectic Al-Si alloy, primary aluminum will be present in the form of dendrites. To explain how primary aluminum can form in an eutectic alloy under non-equilibrium conditions (i.e. rapid cooling), Kumar et al. (Ref. 5) proposed that the molten eutectic be regarded as a colloidal dispersion of Al-Si clusters in a matrix of monatomic aluminum atoms. In essence, the aluminum atoms not associated with Al-Si clusters will tend to behave in a manner similar to pure supercooled aluminum and will solidify in a dendritic manner leaving behind the Al-Si clusters still in a molten state. They verified this concept by examining the chemical variation in a test sample which was quenched from
In hyper-eutectic Al-Si alloys, primary silicon is observed in the form of octahedral crystals with (111) facets. Silicon has a diamond cubic crystal structure which is similar to a face-centered-cubic structure in that the (111) planes are closest packed. A hexagonal polygon is revealed whenever planar metallography bisects one of these crystals parallel to a (111) plane.

The structure of the eutectic, the last constituent to solidify, can take various forms depending upon the thermal gradient and growth rate. In directional growth experiments performed by Day and Hellawell (Ref. 6), the structure of the Al-Si eutectic was studied at slow growth rates (less than 0.001 mm/s). The silicon was found to grow in a rod-like form with growth occurring on closest packed (111) planes with a <100> growth direction. This is a common binary eutectic form (Ref. 7) where the microstructure consists of colonies containing parallel rods of one phase embedded in a matrix of the other phase. The distance between alternating phases is determined by the ability of atoms to diffuse at the liquid-solid interface. Both Jackson and Chalmers (Ref. 8) and Tiller (Ref. 9) have shown that this phase spacing is proportional to the inverse square-root of the growth rate. Day and Hellawell (Ref. 6) have confirmed that this relationship does apply to the rod type of structure observed in the Al-Si system.

For typical foundry castings, where growth rates are higher (0.001 to 1 mm/s), the Al-Si eutectic microstructure differs from the rod type. Here the microstructure may be subdivided into many individual colonies each of which contain silicon crystals in the form of lenticular plates with (111) habit planes. In any one colony, these plates radiate outward from one common nucleation site and are surrounded by a continuous matrix of aluminum. During early investigations of Al-Si cast alloys, the eutectic was mistakenly thought to consist of independently nucleated (divorced) crystals of silicon due to their random orientation and discontinuous nature when observed in planar cross-section. More recently, however, Holmanova (Ref. 10) and Day and Hellawell (Ref. 11) have examined the eutectic microstructure with scanning electron microscopy (SEM) using deep-etch techniques and have determined that eutectic silicon is in a continuous, interconnected form.

A growth mode proposed by Wagner (Ref. 12) and Hamilton and Seidensicker (Ref. 13) for diamond-cubic germanium crystals may help to explain the unique eutectic structure observed in Al-Si foundry castings. Under equilibrium conditions, a diamond-cubic crystal should grow primarily on (111) facets. However, with multiple twinning observed on (111) planes, it is possible to have rapid growth in <121> directions. This growth is made possible by the reentrant grooves formed by twinning. These reentrant grooves provide locations where atoms may be easily deposited. Hellawell (Ref. 14) suggests that the change in growth mode of an Al-Si eutectic, in going from a rod to a plate morphology, may be explained by a shift to this twinning mechanism of growth.

**Modified Microstructure**

The addition of a modifying element to a molten Al-Si alloy will alter the solidification process and will result in a change in microstructural morphology. The rapid cooling of a molten Al-Si alloy, as in die casting, has been observed to have a similar effect. This morphology change occurs in the eutectic silicon. Instead of assuming their normal plate-like form, the eutectic silicon crystals become fibrous. The modifying elements most commonly used include sodium, antimony, and strontium. However, only the use of sodium was considered here; the use of other modifiers has basically the same effect on microstructure even though the degree of modification and the relative amounts added may be different.

Similar to the misbelief discussed previously that the normal eutectic consisted of discontinuous plates of silicon, a modification treatment was thought to refine and spheroidize these silicon plates. This was attributed to the circular shaped silicon crystals observed in planar metallographic cross-sections. However, the deep-etch SEM work discussed earlier (Ref. 10,11) again revealed that modified eutectic silicon crystals are actually in a continuous fibrous form. A comparison between the normal and fibrous (modified) form of eutectic silicon, as conceived by Holmanova and Klaban (Ref. 15), is depicted in Fig. 2.

Fredrikson et al. (Ref. 16) observed that additions of sodium will also affect the morphology of primary silicon crystals. Instead of assuming their normal octahedral shape with (111) facets, they assume more of a spherical shape owing to the development of (100) facets. Kobayashi et al. (Ref. 17), discovered that the crystallographic orientation relationships between a primary silicon crystal and the aluminum matrix is different for a sodium treated alloy. This indicates that a different primary silicon facet is serving to nucleate the eutectic microstructure.

**Modification Theory**

At one time it was believed that the observed supercooling and refinement of a modified Al-Si eutectic might be the result of nuclei poisoning. During the nucleation process, enough silicon atoms must cluster together to form a critical embryo before nucleation and growth may proceed. If sodium atoms were to adsorb onto embryos and prevent them from reaching their critical size, nucleation would not occur and supercooling would result. Since the critical embryo size needed for nucleation will decrease with temperature, a sufficient degree of supercooling would eventually be reached at which point nucleation would occur. This would result in a refinement of colony size because of the larger number of critical nuclei of the smaller size.
This theory was supported by the observation that supercooling increases with an increase in sodium content (Ref. 18). However, when Day (Ref. 19) studied the size of eutectic colonies using copper alloy additions to help outline colony boundaries, he discovered that sodium did not affect the total number of colonies formed. This observation disproved the nucleation theory for modification.

Another modification theory involves interfacial energy. According to Thall and Chalmers (Ref. 20), there should be a tendency for the aluminum to solidify at a faster rate than the silicon due to its higher thermal conductivity and lower latent heat of fusion. Were it not for the high interfacial energy which develops between the solid aluminum and silicon phases, the aluminum phase would overgrow the silicon phase and eventually envelop it. Davies and West (Ref. 21) subsequently determined experimentally that sodium does reduce the interfacial energy between the two solid phases by a small amount. Whether capillary behavior influenced by sodium is the controlling factor for modification is still not certain.

The cooperative growth of the aluminum and silicon phases at the liquid-solid interface must also be dependent upon the ability of atoms to diffuse to their respective solid phases. If, for example, the presence of sodium were to hinder the mobility of silicon atoms at the liquid-solid interface, the aluminum phase could again overgrow and envelop the silicon phase. Diffusion experiments performed by Davies and West (Ref. 22) indicate that sodium does hinder diffusion of silicon in the molten eutectic. However, they also discovered that a slowly cooled eutectic could not be modified by sodium, indicating that diffusion hindrance cannot be an important consideration for slow growth rates.

In conjunction with the effect of sodium on interfacial energy and diffusion, a growth poisoning theory proposed by Davies and West (Ref. 22) helps to explain why sodium causes modification. They propose that sodium atoms are adsorbed on the reentrant twinning grooves of silicon plates thus disrupting or "poisoning" growth.

The concept of poisoning may best be explained by reference to the "terrace-kink-ledge" model for surfaces (Ref. 23). Here it is assumed that the retention of a surface atom after deposition is dependent upon the number of bonds it makes with neighboring atoms. It is also assumed that the total number of bonds that a deposited atom makes is determined by the number of sides it has in contact with the surface. Therefore, an atom deposited in a kink position should have a higher probability of retention than an atom deposited in a ledge position. Similarly, a terrace position should have the least likelihood of atom retention.

The reentrant twinning grooves in silicon crystals, discussed earlier, provide a large number of kink and ledge positions to facilitate rapid growth. Now, if sodium atoms were to adsorb on these reentrant twinning grooves, silicon atoms would be forced to deposit on terrace positions which would decrease the growth rate. This poisoning would result in the aluminum phase overgrowing the silicon. If there were localized regions where overgrowth did not occur, this would lead to the out-growth of silicon fibers. This same reasoning may be applied to explain modification caused by rapid cooling. With rapid cooling, the kinetics of atom deposition would restrict the silicon growth rate which would again allow the aluminum phase to overgrow the silicon. The concept of poisoning may also be used to explain the change in morphology of primary silicon crystals. If sodium atoms were to adsorb on kink or ledge positions on primary (111) growth planes, secondary growth planes, such as (100), would become activated as a result of the subsequent supercooling.

One modification theory, not yet discussed, involves the formation of the ternary compound NaAlSi. It was once thought that the formation of this ternary compound might interfere with silicon growth. Molecules of this compound might poison preferred growth planes in a manner similar to sodium atoms. Newtorny and Schell (Ref. 24) have determined, however, that when NaAlSi is purposely added to an Al-Si alloy, modification will not occur. They concluded that it is the free sodium which is responsible for modification.

Even though the NaAlSi ternary compound is generally not thought to form in a typical modified structure, it has been observed in an "overmodified" structure. Whenever excessive amounts of sodium are added, above and beyond that amount necessary to poison the growth of silicon, a noted change in microstructure is observed.

The formation of this overmodified structure has been studied by Kobayashi et al. (Ref. 25) and Davies and West (Ref. 22). According to these investigators, the eutectic begins to solidify in a normal manner until the excess of sodium builds up at the liquid-solid interface. When a critical concentration of sodium is reached, NaAlSi nuclei form and disrupt continuous colony growth resulting in a characteristic banded structure. Bands of silicon tend to form a continuous network from one colony to another which has a deleterious effect on mechanical properties.

**Experimental Materials and Procedure**

Weld pool inoculation with sodium was achieved indirectly by inoculation of the base material prior to welding. The base metal was prepared by melting the Al-Si eutectic alloy #413 (refer to Table 1)
in a small steel crucible, inoculating the molten charge with metallic sodium, and then casting the treated alloy into rectangular stainless steel chill molds. All of this was performed in an argon protective atmosphere to minimize cross contamination and sodium attrition through oxidation. After casting, a light machining cut was made along the surface of the ingots to insure uniformity in smoothness. Ingot dimensions were 0.5 x 1.0 x 6.0 in. (13 x 25 x 152 mm).

The gas tungsten arc (GTA) welding process was used with a cover gas supply consisting of a mixture of 50% argon and 50% helium (by volume) at a flow rate of 20 ft³/h (9 L/min). Three different sets of welding parameters were investigated by holding the arc current constant at 200 amperes (A) and welding at three different travel speeds: 5, 10, and 15 ipm (2.1, 4.2, and 6.3 mm/s). Arc voltage was held constant at 24 volts (V) which corresponded to an electrode gap of 0.125 in. (3.18 mm) using a 0.125 in. (3.18 mm) diameter electrode. The use of these parameters resulted in the three heat inputs: 16, 24, and 48 kJ/in. (630, 946, and 1890 kJ/m). Weld fixturing consisted of a clamping device whereby an ingot could be tightly held between two copper plates. These copper plates were used as heat sinks to promote two dimensional heat flow. This clamping device was mounted on a variable speed, motor driven table and was positioned underneath the welding torch.

This study was divided into three phases. The first phase was designed to generate sodium-free weld samples to serve as a standard. The second phase was designed to determine the effect of variations on sodium content. Ingots treated with differing amounts of sodium (0.001, 0.020, and 0.070 wt-% Na) were prepared and welded. In the third phase, the effect of heat input on sodium modification was investigated. Here, ingots treated with 0.020 wt-% sodium were prepared and welded using three different heat inputs.

Once the welds were made, metallographic specimens were machined from the ingots transverse to the welding direction. These specimens were polished and then etched by swabbing with a 0.5 vol-% HF solution. Some specimens were deep etched prior to SEM observation using the technique developed by Holmanova (Ref. 10). This involved immersing the specimen for 5 min in a solution of 10 parts HF, 12 parts HCl, and 78 parts water (by volume). Following this, the specimen was immersed in a 25 vol-% HNO₃ solution for 2 min. This deep etch attacked only the aluminum and permitted a three dimensional view of the silicon crystals. All phase constituents were identified with electron microprobe analysis.

**Results and Discussion**

A major microstructural difference was observed between sodium-free and sodium-treated ingots as shown in Fig. 3. The sodium-free microstructure consists of primary silicon (dark polyhedral), eutectic aluminum (light areas), and eutectic silicon (dark lenses). The sodium-treated microstructure consists of primary silicon (dark polyhedrons) and aluminum dendrites (light pools) clearly delineated by the modified eutectic structure. Note that the primary silicon crystals in the sodium-treated microstructure are more rounded than in the sodium-free microstructure. The dark lenses remaining in the sodium-treated microstructure are not silicon, but are plates of the iron compound Fe₂Si₂Al₃. This iron compound was also present in the sodium-free microstructure, but was indistinguishable from silicon crystals.

The effect of rapid cooling on microstructure can be seen in Fig. 4 where an ingot microstructure is compared with a weld metal microstructure using a planar etch. Neither of these samples was treated with sodium. Note that the silicon plates seen in the ingot microstructure are much more coarse than in the weld metal microstructure. Notice also the disappearance of primary silicon crystals in the weld metal microstructure. In Fig. 5 there is a comparison similar to Fig. 4 except that a deep etch has been used. Here it can be seen that the rapid cooling rate of welding has caused partial modification. In essence, silicon morphology has been modified from plates to subplates.

When welds were made on ingots containing sodium, the degree of modification was found to be increased above and beyond the modification provided by rapid cooling. This can be seen in Fig. 6 where both planar and deep etched
microstructures are shown of weld metal treated with sodium. Comparing Fig. 5B with Fig. 6B, the eutectic silicon is found to be more fibrous for the microstructure containing sodium. This change to fibers can only be attributed to the addition of sodium. A comparison of partial modification, caused by rapid cooling, and complete modification, caused by sodium additions, is given schematically in Fig. 7.

Variations in the amount of sodium added to the weld metal produced only a slight variation in the degree of modification for a given heat input. Sodium additions as low as 0.001 wt-% proved to enhance the degree of modification over that produced by rapid cooling. In essence, a certain critical concentration of sodium (some amount less than 0.001 wt-%) is required to achieve modification by poisoning. Also, with increasing amounts of sodium added, there was an increase in the amount of Fe$_2$Si$_2$Na present. A comparison of the results of three different sodium additions is shown in Fig. 8.

Variations in welding heat input caused only a slight change in the degree of modification as shown in Fig. 9 for microstructures treated with 0.020 wt-% sodium. Primary aluminum dendrite spacing was essentially the only microstructural feature which varied greatly with welding heat input as shown in Fig. 10. However, it should be noted that dendrite spacing must indirectly influence eutectic colony size. As the dendrites become closer spaced, the colony size must decrease. This means that even though dendrite spacing and colony size vary with welding heat input, the size and shape of eutectic silicon crystals remain about the same.

Considering the expression for dendrite spacings, as derived by Brown and Adams (Ref. 26) for three dimensional heat flow, and using heat flow relationships developed by Rosenthal (Ref. 27), Jarman and Jordan (Ref. 28) concluded that dendrite spacing should be directly proportional to heat input for two dimensional heat flow. The spacing between primary aluminum dendrites obtained from Fig. 10 was indeed found to be directly proportional to welding heat input as shown in Fig. 11.

A quantitative comparison of degree

![Fig. 11 - Linear relationship between primary aluminum dendrite spacing (D) and welding heat input (H)](image)

\[ \ln(D) = \ln(K) + m \ln(H) \]

![Fig. 12 - Definition of shape factor for eutectic silicon crystals](image)

\[ \phi = \frac{W}{L} \]
of modification can be made by assigning a shape factor to eutectic silicon crystals based upon their geometry. This was accomplished by defining a shape factor (Φ) to be the ratio of width (minor axis) to length (major axis) of a cross-sectional area taken perpendicular to the growth direction of a eutectic silicon crystal as shown in Fig. 12. For a plate-like microstructure, this ratio will approach zero. For a completely fibrous microstructure, the ratio will be unity.

Besides characterizing the crystals by their shape, they must also be characterized by size which is conveniently done by comparing cross-sectional widths. In essence, modification involves both a shape change and a size change. When a plot is made of plate width versus shape factor, as shown in Fig. 13, a relative degree of modification can be ascertained for various microstructures. Note that the sodium-free ingot microstructure represents the lowest degree of modification whereas the sodium-treated weld metal microstructure represents the highest degree of modification.

Comparing the sodium-free ingot microstructure with the sodium-free weld metal microstructure, it can be seen that the increase in cooling rate caused marked refinement, not so much by a shape change, but by a decrease in plate (or fiber) spacing. Note also that the refinement of the weld metal microstructure treated with sodium was due primarily to a shape change.

Primary aluminum dendrites were observed in all microstructures that were in a modified condition. The presence of primary aluminum may be explained by considering the coagulation concept discussed earlier. This effect should be even more pronounced for rapid (non-equilibrium) cooling. This explains why primary aluminum is present in weld metal microstructures, but is absent in sodium-free ingot microstructures.

The reason why sodium additions promote primary aluminum formation is not clear. Kumar et al. (Ref 15) found that sodium additions weakened the Al-Si bond and eliminated clustering. The addition of sodium should, therefore, decrease the tendency to form primary aluminum. This was not found to be the case in this study.

In considering the effect of rapid cooling rate on silicon plate (or fiber) spacing, the relationship discovered by Day and Hellowell (Ref. 6) can be extrapolated to faster growth rates as shown in Fig. 14. If the plate spacing in the weld metal is taken to be 1 μm, this will correspond to a growth rate of 300 μm/s (from Fig. 14).

It is assumed that the total distance a silicon plate may grow is on the order of half the dendrite spacing (approximately 10 μm), then the eutectic solidification time at a 300 μm/s grow rate will be 0.03 s. If it is further assumed that the eutectic solidifies within one degree of temperature, this will correspond to a cooling rate of approximately 30 °C/s (54 °F/s); this is within reason for a welding operation. It appears as though the inverse square-root relationship for eutectic plate spacing can be applied to weld metal solidification.

It is interesting to note that the addition of sodium did not affect primary aluminum dendrite spacing. Implicit to this discovery is the condition that supercooling preceding dendrite formation must be independent of sodium content. The amount of primary aluminum formed in all cases remained constant at approximately 28 vol.-%. This corresponds to a shifting of the eutectic point to approximately 16 wt-% silicon which is much more than the 2 wt-% shift reported for die casting. The reason behind the formation of a constant amount of primary aluminum is uncertain. It may be that eutectic colonies will always begin to nucleate on primary aluminum dendrites after a certain degree of supercooling has been reached as determined by the latent heat of fusion released during dendrite formation.

In order to determine whether or not the weld metal treated with 0.070 wt-% sodium was in an overmodified condition, electron microprobe mappings of silicon, iron and sodium were made to check for a banded structure. There were several regions containing excessive amounts of sodium which were randomly distributed, but no banded structure was observed.

While Fe2SiAl9 plates were observed in all of the microstructures examined, the weld metal treated with 0.070 wt-% sodium contained an exceptionally large number of plates — Fig. 8C. It appears as though excess sodium serves to increase the nucleation of this compound. Due to its shape and continuity in structure, the presence of Fe2SiAl9 is extremely detrimental to fracture toughness.

Conclusions

1. The rapid cooling associated with welding causes partial modification of Al-Si eutectic weld metal microstructure.

2. The presence of sodium in the weld pool of an Al-Si eutectic alloy will cause the weld metal microstructure to become fully modified. In essence, sodium enhances the degree of modification beyond that caused by rapid cooling.

3. A common foundry technique for controlling cast microstructure in Al-Si alloys can successfully be applied to a welding operation.

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