The Effects of Sodium on the Growth Velocity and Growth Morphology of Silicon in Al-Si Alloys

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The effects of sodium additions to Al-Si alloys have been studied by determining the coupled zone for normal and "modified" alloys. Sodium slows the growth rate of silicon with respect to aluminum, and changes the morphology of the silicon. These effects were observed to be independent of growth temperature. A hypothesis that sodium adsorbs on the fast-growing faces of silicon can explain all observations.

THE addition of minute quantities of sodium (or any other alkali metal) results in a beneficial change in the mechanical properties of Al-Si alloys. For an Al-12 pct Si alloy, the ultimate tensile strength is 22,000 psi and the elongation is 6 pct. The addition of sodium increases the ultimate tensile strength to 28,000 psi and an elongation of 14 pct.[1] The amount of sodium added is ~0.01 pct. There are three general effects noted on addition of sodium:

1) A lowered arrest temperature on cooling.
2) A much finer eutectic structure.
3) An alteration of primary silicon.

The equilibrium eutectic temperature as reported by Hansen[2] is 577°C. Under normal cooling rates Al-Si alloys without sodium freeze within 2°C of this temperature. Al-Si alloys to which sodium has been added freeze at lower temperatures; around 567°C for normal laboratory cooling rates, (10 to 100°C/min), however, the alloy melts at the equilibrium eutectic temperature.[3-5]

The microstructure of the Al-Si eutectic without sodium additions is that of random acicular silicon in an aluminum matrix. On etching and observation with a scanning electron microscope, the silicon is found to be interconnected {111} platelets,[6] the apparent randomness due to extensive twinning of the silicon.

The eutectic microstructure of Al-Si alloys with sodium is that of very fine bundles of fibers.[6,7] At very low growth rates, alloys without sodium assume a ⟨100⟩ fiber texture.[6,8] Until electron microscopy the structure of the sodium-treated alloy had been identified as globular.

The growth of primary silicon in alloys without sodium is by the twin-plane-reentrant-edge mechanism.[9-14] The silicon grows in a faceted manner, requiring nucleation and then growth of atomic layers. The atomic cluster required for growth on a {111} plane is 3. If the silicon is twinned, with a reentrant groove, it may be less. Thus, there is more frequent nucleation at twins. If there is a set of parallel twins, the crystal can grow with there always being a reentrant edge in which nucleation of another atomic layer can take place.

The addition of sodium to Al-Si alloys changes pri-

mary silicon crystals from {111} faceting to {100}.[15] The primary silicon appears as equant blocks.

PREVIOUS WORK ON Al-Si ALLOYS

There are two chief schools of thought concerning the effects of sodium. Sodium is thought to either cause the growth of silicon to be restricted or to have some effect on the nucleation of silicon from the melt.

Thall and Chalmers,[4] Ghosh and Kondic,[16,17] and Plumb and Lewis[5] identify the eutectic silicon as globular, and they regard the major action of sodium as a restriction on the growth of silicon.

Thall and Chalmers[4] obtained cooling curves for Al-Si alloys and showed that the eutectic cooling arrest temperature was lowered with sodium additions. This was explained as sodium lowering the interfacial energy, and as the eutectic grows, the aluminum continually pinches off the silicon, forcing it to renucleate. The arrest temperature is determined by that temperature at which the nucleation of silicon is high enough to produce continual growth.

Ghosh and Kondic[16] observed that at very slow cooling rates, even sodium-treated alloys of Al-Si would solidify at the equilibrium eutectic temperature. The Al-Si alloys with sodium, in general, did not tend to undercool. The freezing arrest temperature was felt to be a function of cooling rate, with sodium-treated alloys having the lowest arrest temperature for a given cooling rate. The effect of sodium was held to be that of slowing the growth rate of the eutectic silicon by slowing the diffusion of silicon in the melt. Undercooled below the eutectic temperature, the nucleation frequency of silicon is high, and this, coupled to the low diffusion rate of silicon, produces a fine dispersion of globules.[16,17]

Plumb and Lewis,[5] as mentioned above, regard that another major effect of sodium is to alter the nucleation behavior of the silicon. Kim and Heine,[18] Crosley and Mondolfo,[19] Davies and West,[20] and Chadwick[21] also regard a major effect of sodium as altering the nucleation behavior of silicon. Crosley and Mondolfo[19] and Davies and West[20] note that sodium alters the growth of silicon as well as allowing the silicon to undercool.

Kim and Heine,[18] observing that sodium-treated samples solidify at a lower temperature, proposed that the silicon morphology is growth-temperature dependent. At temperatures above 570°C the growth morphology of silicon is acicular, at temperatures about 560°C the growth form is globular. The action of sodium is to

allow the liquid to undercool to temperatures where the growth form of silicon is globular.

Crosley and Mondolfo[19] ascribe a dual effect to sodium. Sodium first eliminates nucleants for silicon, allowing silicon to undercool, and also changes the eutectic growth form from one in which silicon leads the interface into the liquid to one in which aluminum leads. The aluminum in the sodium-treated alloy then cuts off the silicon and forces it to renucleate at the temperature at which aluminum nucleates silicon. The continual need for renucleation of the silicon by aluminum causes the temperature to remain below the equilibrium eutectic temperature.

Davies and West[20] similarly conclude that sodium additions have two effects. Sodium poisons nucleants for silicon and also is absorbed on the fast-growing faces of silicon. This latter accounts for the change in morphology. Since less favorable directions of growth must be used, the silicon requires a higher driving force for any growth at all, and consequently there is a greater interfacial undercooling when Al-Si eutectic is treated with sodium.

Chadwick[21] found that Al-Si alloys which were grown at the same growth rate, with and without sodium, show the same microstructure. He holds the microstructure of the normal Al-Si eutectic to be discontinuous silicon in an aluminum matrix. The action of sodium is to allow the silicon to undercool to a temperature where, when silicon finally grows it does so rapidly, producing a fine microstructure. These results are inconsistent with all others and could be due to a loss of sodium before solidification.

Bell and Winegard[8] noted that although the freezing arrest temperature of an Al-Si alloy with sodium was depressed, the actual nucleation of silicon took place at a higher temperature. Thus, the action of sodium is not to produce undercooling of the silicon, but must be somehow affecting growth. This effect on growth must somehow cause the lowered freezing temperature.

Day and Hellawell[7] (by means of scanning electron microscopy) showed the structure of sodium-treated Al-Si to be fibrous and interconnected. The structure of a quenched alloy was similar. At various growth rates and temperature gradients unidirectionally solidified samples of Al-Si showed three distinct types of microstructures.[6] At low growth velocities and high gradients, the microstructure was that of large silicon particles in an aluminum matrix. At lower gradients the silicon assumed a $\langle 100 \rangle$ fiber texture. With higher growth velocities the silicon takes on the form of multiple $\{111\}$ twins. The addition of sodium did not alter the microstructure of alloys solidified in the region of $\langle 100 \rangle$ fiber texture. However, in the higher growth velocity region where there had previously been $\{111\}$ twins, the structure was that of a fine dispersion of fibers. This was taken to show that sodium affected the growth of silicon by poisoning the reentrant $\{111\}$ twin grooves. This leads to overgrowth of the silicon by aluminum and thus in turn to more frequent twinning, thus producing kinked and tangled fibers.

The identification of the silicon in sodium-treated alloys as fibers rather than globules rules out an explanation that an effect of sodium in reducing growth temperature is to allow the aluminum to pinch off the growth of silicon as suggested by Thall and Chalmers,[4] Ghosh and Kondic,[16] Plumb and Lewis,[5] Kim and

Heine,[18] and Crosley and Mondolfo.[19] The findings that silicon in a sodium-treated alloy nucleates above the temperature at which the alloy freezes, and that there is a definite difference in microstructure between alloys with and without sodium, grown with the same gradient and growth velocity, rule out sodium having an effect on undercooling as suggested by Chadwick and others.

The consistent facts are that there is an altering of the silicon microstructure in the presence of sodium, and that sodium lowers the eutectic arrest temperature, but that silicon has begun crystallizing above this temperature.

The proposal that there is a temperature dependence to the growth morphology of silicon[18] cannot be ruled out, since unidirectional growth data do not compare easily to solidification in bulk samples since no data are available for growth velocity of eutectic vs liquid composition and interfacial undercooling.

EXPERIMENTAL TECHNIQUE

Samples were prepared from aluminum and silicon of 99.999 pct purity. To protect alloys from oxidation, the samples were melted under a flux of LiCl-KCl. Comparison of alloys melted under this flux to those melted in a vacuum revealed no difference in microstructure, and it can be assumed that neither lithium nor potassium entered into the Al-Si alloys in any appreciable amount.

Samples were melted in the resistance wire furnace illustrated in Fig. 1. The temperature of the furnace was controlled by a 20 A autotransformer. The temperature of the furnace was monitored by a thermocouple extending into the furnace from the floor. Temperature of the sample was recorded on an X-T recorder from a thermocouple immersed in the melt.
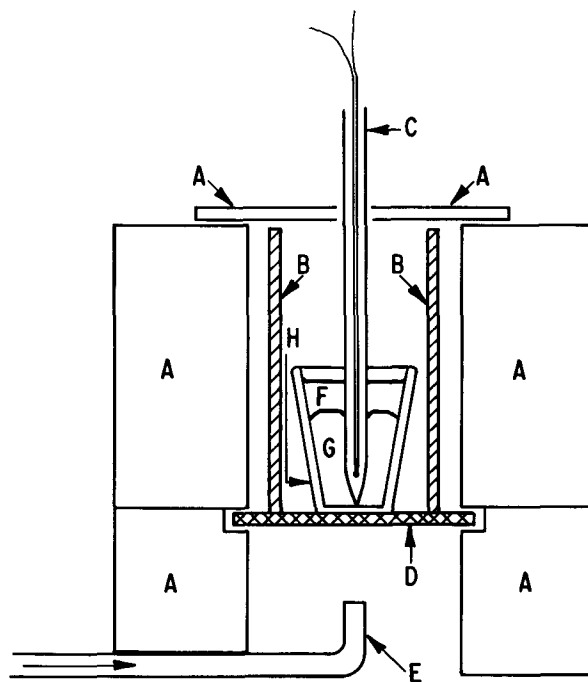

Fig. 1—Cutaway of furnace: A—firebrick, B—nichrome-wound zirconia tube, C—thermocouple, in sheath, D—ceramic floor with holes, E—pipe for argon, F—flux, G—melt, H—alumina crucible.

This latter thermocouple was in a fused silica sheath drawn to a fine point at the end. In the floor of the furnace was an alumina pipe through which the furnace could be flooded with argon to cool the sample at various rates.

The addition of sodium to certain of the samples was accomplished by putting a flux containing NaF on those samples.

Samples were cooled at various rates, and in all cases it was found that there was a distinct isothermal arrest at which eutectic solidification took place. This eutectic arrest temperature was an inverse function of cooling rate. At high rates of heat extraction the eutectic arrest temperature was depressed 10° to 15°C below the equilibrium eutectic temperature, at low rates of heat extraction the arrest temperature was close to equilibrium. Table I lists representative cooling rates and microstructures. The cooling rate referred to is the average cooling rate between 600° and 580°C. To solidify a sodium-treated alloy at 574°C required a very slow rate of heat extraction. The furnace temperature had to be about 570°C. This contrasts to the cases of growth without sodium, where the furnace would be turned off and flowing argon used to increase the rate of heat extraction.

Thus, there is the ability to compare microstructures of Al-Si alloys with and without sodium additions, the alloys grown at the same temperature, by varying the rate of heat extraction.

Seeding experiments were carried out in the manner used to determine the coupled zone in Sn-Bi alloys.[22] A sample of a certain composition would be cooled from about 700°C, and at the desired temperature a solid seed of Al-Si eutectic would be poked into the melt. The rate of heat extraction was adjusted to effect the desired growth temperature.

Samples were prepared for scanning electron microscopy. The samples were chosen to be typical of growth close to the equilibrium eutectic temperature and growth 10° to 15°C below equilibrium eutectic temperature. Preparation was by etching the aluminum away in a dilute HCl solution, taking care not to allow vigorous bubbling which would have caused the fragile silicon particles to break. Other samples were prepared for optical microscopy. Some were etched with a modified CP-4 reagent.[23]

RESULTS

Figs. 2 through 5 show optical and electron photomicrographs of Al-Si for different growth temperatures and for both the normal and sodium-treated case. The flat upper surface of the plates in the scanning electron micrographs is due to the samples having been polished before being used.

It is seen that sodium alters the structure of the eutectic silicon from plates to fibers at both growth temperatures. It is also seen that, even at the lower growth temperature, the alloys without sodium solidify with a eutectic structure of silicon plates in an alu-
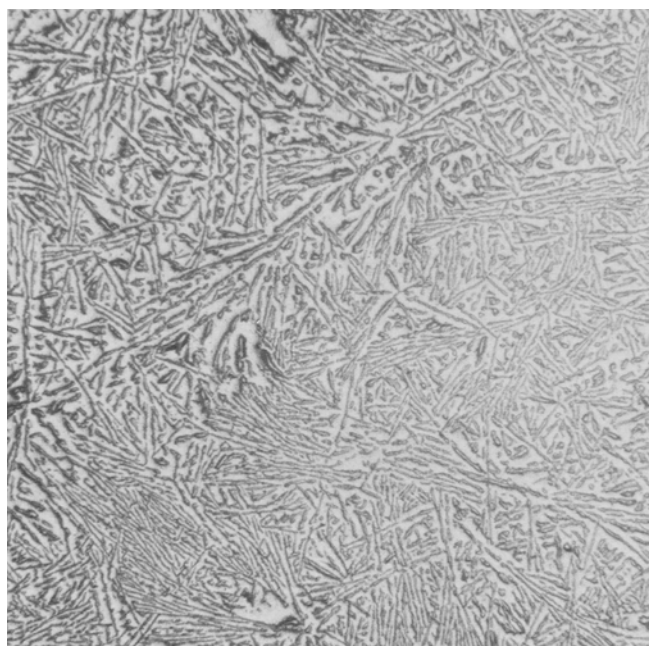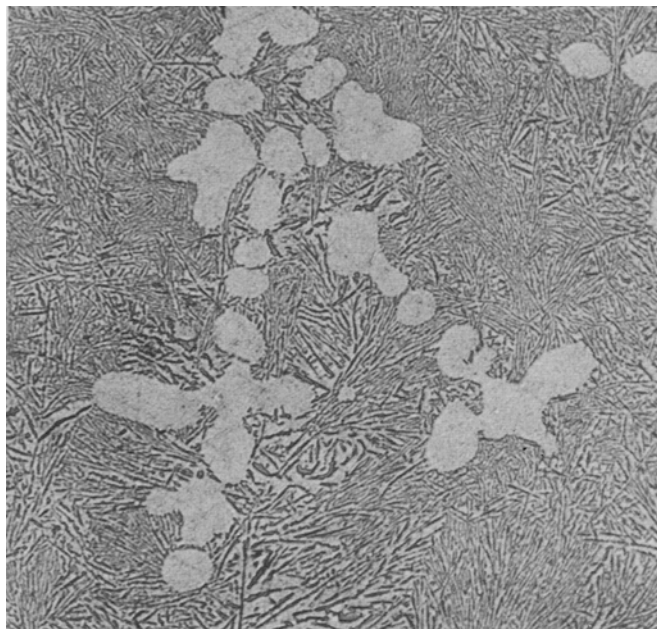

(a)

(b)

Fig. 2—Normal Al-Si eutectic structure, 574°C growth temperature. (a) Optical photomicrograph. Magnification 52 times. (b) Scanning electron micrograph. Magnification 104 times.

Table I. Typical Cooling Rates and Eutectic Isothermal Arrest Temperatures for Al-Si Alloys

Alloy Composition	Total Weight	Cooling Rate	Eutectic Arrest	Time to Solidify	Microstructure
Al-8 pct Si	14.3 g	255°C/min	564°C	105 sec	Al dendrites + fine plate eutectic
Al-12 pct Si	10.51 g	60°C/min	574°C	175 sec	Al dendrites + coarse plate eutectic
Al-14 pct Si (Na-treated)	11.65 g	12°C/min	564°C	500 sec	Al dendrites + fine fibrous eutectic
Al-12.5 pct Si (Na-treated)	10.54 g	(see text)	574°C	6000 sec	Al dendrites + coarse fibrous eutectic

minum matrix. At both growth temperatures the sodium-treated Al-Si eutectic fibers are aligned for large distances. The fibers are not tangles, which disagrees with the observations of Day and Hellawell.[7]

The results of the coupled zone determination are presented in Fig. 6. Alloys richer in silicon could not be investigated due to the silicon nucleating independently of the seed. For the sodium-treated samples the coupled zone is highly skewed. In fact, the coupled zone appears to lie outside of the extended aluminum liquidus at temperatures above 570°C. The structure

of an alloy whose composition was just to the left of the coupled zone at 574°C showed what could be interpreted as a fluctuating growth front. This is illustrated in Fig. 7.

The moving of the coupled zone can be interpreted as the velocity of silicon being slowed relative to that of aluminum in the presence of sodium. The position of the coupled zone is probably a strong function of sodium content, and it is also possible that the fibrous silicon structure could be caused by other sodium contents, which would have lesser or greater effects on
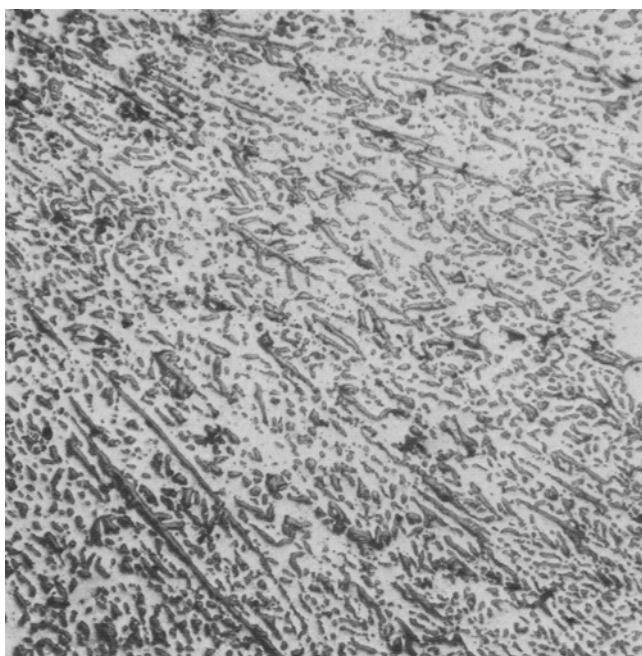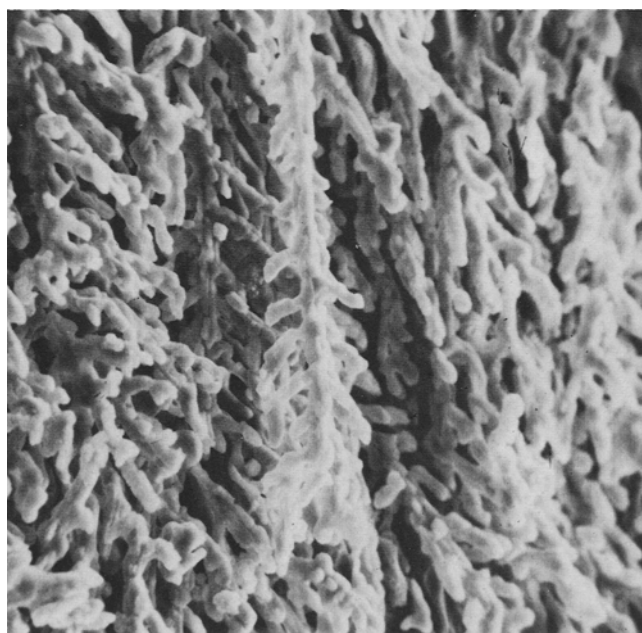

(a)
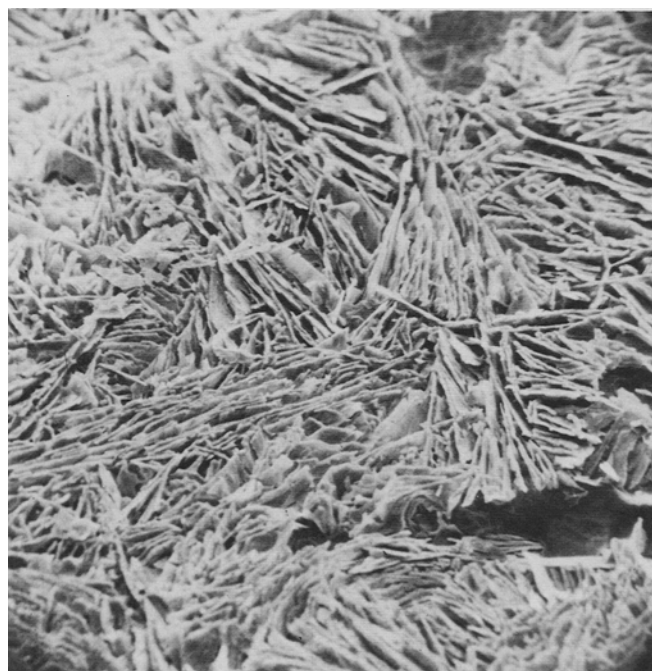
(b)

Fig. 3—Normal Al-Si eutectic structure, 565°C growth temperature. (a) Optical photomicrograph. Magnification 104 times. (b) Scanning electron micrograph. Magnification 208 times.
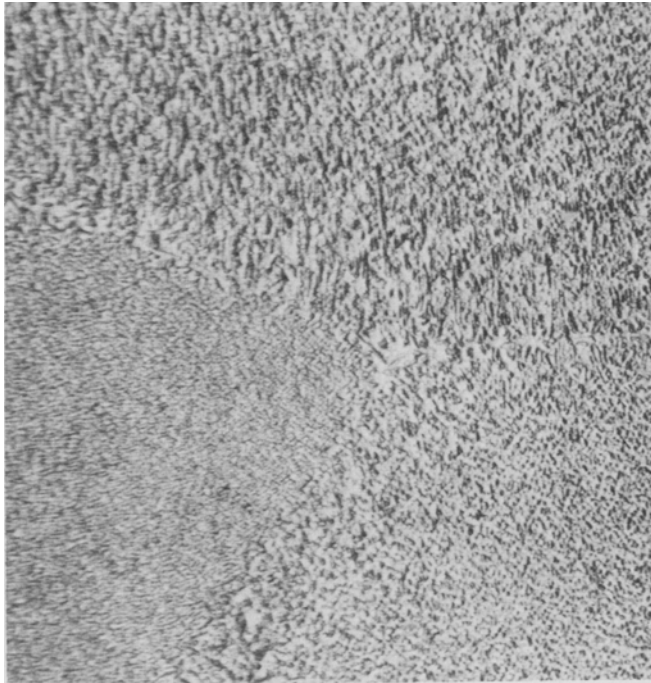

(a)

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Fig. 4—Sodium-treated Al-Si eutectic structure, 574°C growth temperature. (a) Optical photomicrograph. Magnification 52 times. (b) Scanning electron micrograph. Magnification 520 times.
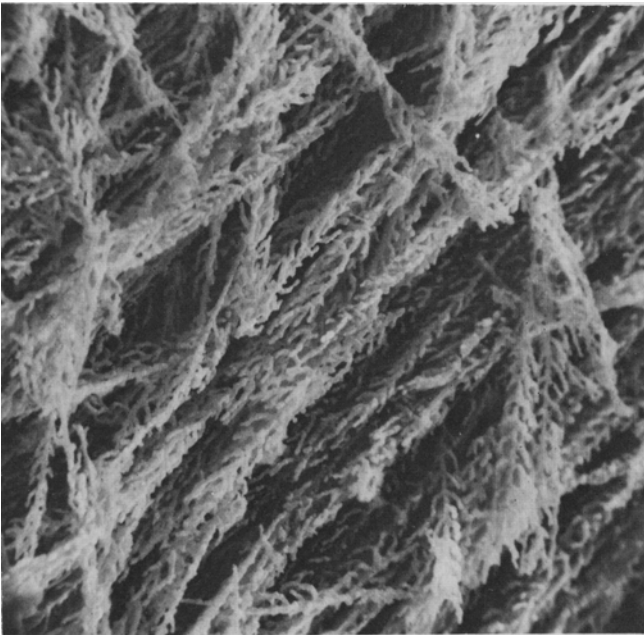
the coupled zone position in the Al-Si system, however always skewing it.

The seeded ingots were composed of many eutectic colonies. This does not interfere with determining the coupled zone, since that which is being determined is the temperature-composition region in which cooperative growth of aluminum and silicon is faster than the growth of either phase alone.

The ingots would undercool to a lower temperature than that at which they were seeded thus, the original nucleation event is that of aluminum and silicon by the seed. The generation of many eutectic grains after this event, by whatever mechanism, occurs in the presence of aluminum and silicon, and if the composition and temperature of growth lie in the coupled zone, a eutectic-like structure is obtained.

In normal Al-Si alloys "dendritic" silicon is found at high silicon contents. This structure is a coupled growth form, as it is unlikely that silicon would grow alone in this manner—with such fine plates. This struc-

(a)

(b)

Fig. 5—Sodium-treated Al-Si eutectic structure, 565°C growth temperature. (a) Optical photomicrograph. Magnification 208 times. (b) Scanning electron micrograph. Magnification 520 times.
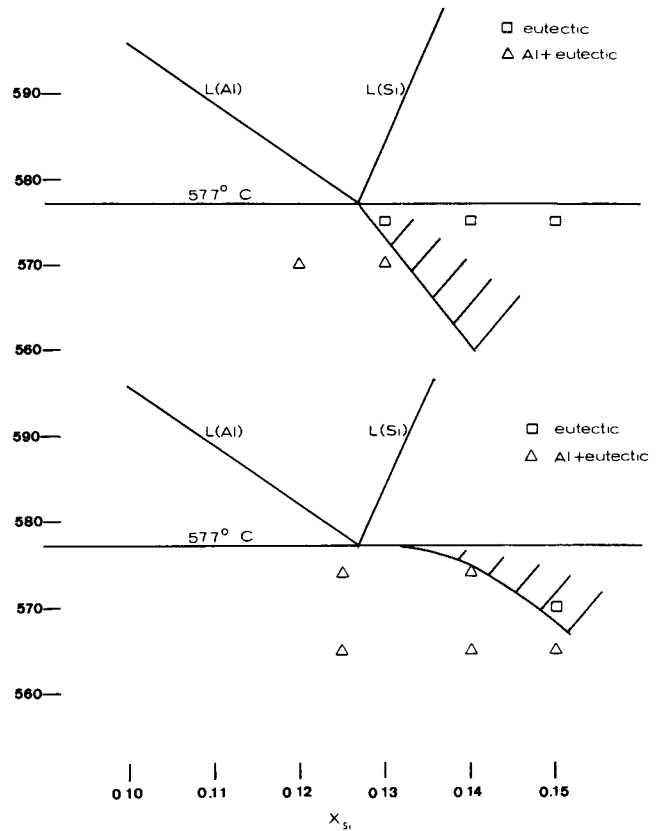

Fig. 6—Zones of coupled growth in Al-Si alloys. Upper: Normal alloy. Lower: Sodium-treated alloy.
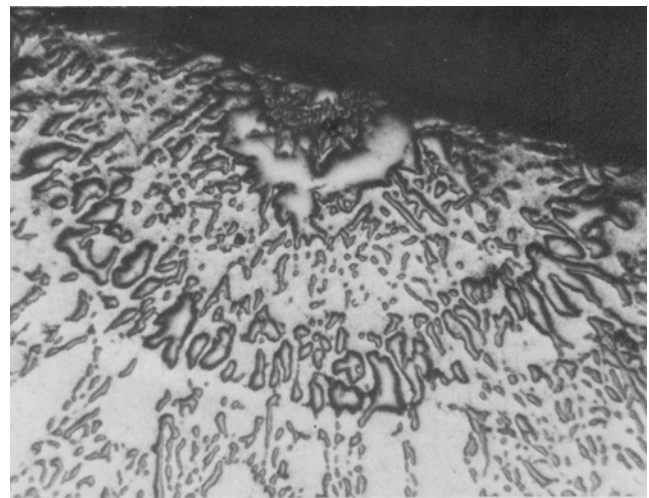

Fig. 7—Sodium-treated Al-14 pct Si, 574°C growth temperature. Fluctuating growth front from independently nucleated silicon crystal. Magnification 56 times.

ture, seen in Fig. 8, is perhaps the way excess silicon is accommodated in the eutectic structure. At Al-15 pct Si, growth at 574°C the dendritic silicon appeared about to form a distinct primary phase as in Fig. 9. This composition was somewhat arbitrarily chosen as the silicon-rich limit of the coupled zone.

Figs. 10 and 11 show sodium-treated alloys etched with CP-4. Fig. 10 shows a coarse fiber area. There is a twin trace running down the trunk of a fiber. Fig. 11 shows fine fibers and running down the fibers is a twin trace. Fig. 12 is a close-up of the fibers shown in Fig. 4. There is a groove running down the fiber which may also be a twin.

DISCUSSION

It is apparent from Figs. 2 to 5 that the growth morphology of silicon is not growth temperature-dependent. That is, the action of sodium is not to allow the silicon to undercool to a temperature where its growth morphologies were different as suggested by Kim and Heine.[18] If this were true, structures at a given growth temperature would be identical, which they are not.

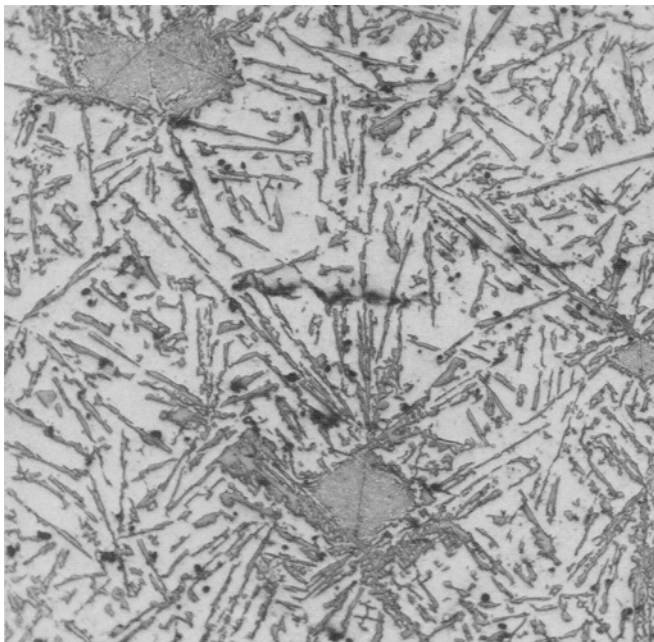The results of the coupled zone determination indicate that sodium slows the growth of silicon with re-

Fig. 8—Normal Al-14 pct Si, 574°C growth temperature. Dendritic silicon. Magnification 104 times.
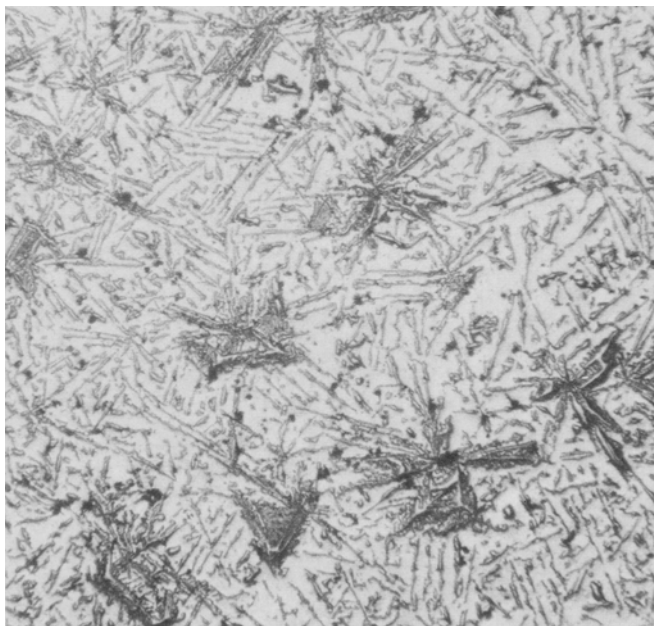
Fig. 9—Normal Al-15 pct Si, 574°C growth temperature. Dendritic silicon. Magnification 52 times.
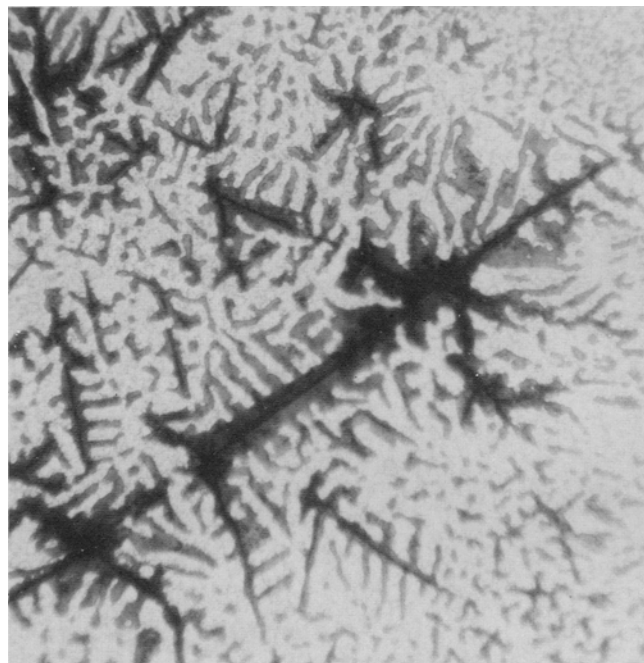

Fig. 10—Sodium-treated Al-15 pct Si, coarse fiber area. Etched in CP-4. Black lines are twin trace. Magnification 205 times.
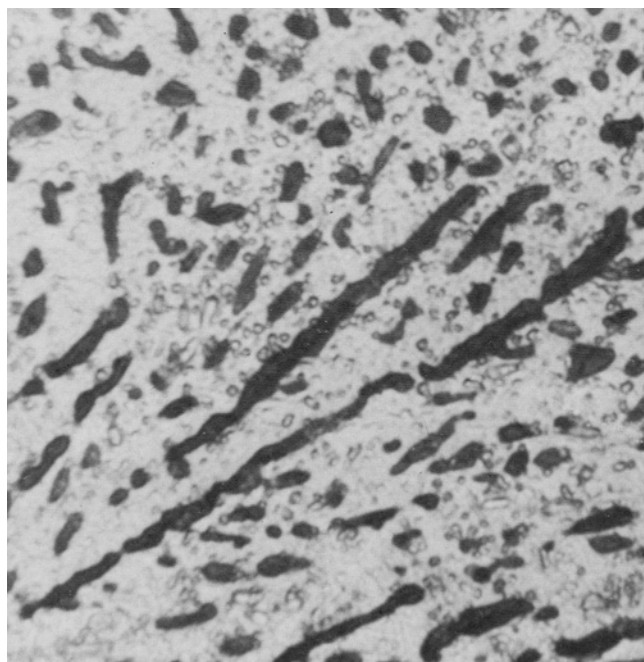

Fig. 11—Sodium-treated Al-15 pct Si, fine fiber area. Etched in CP-4. Black lines are twin trace. Magnification 2340 times.
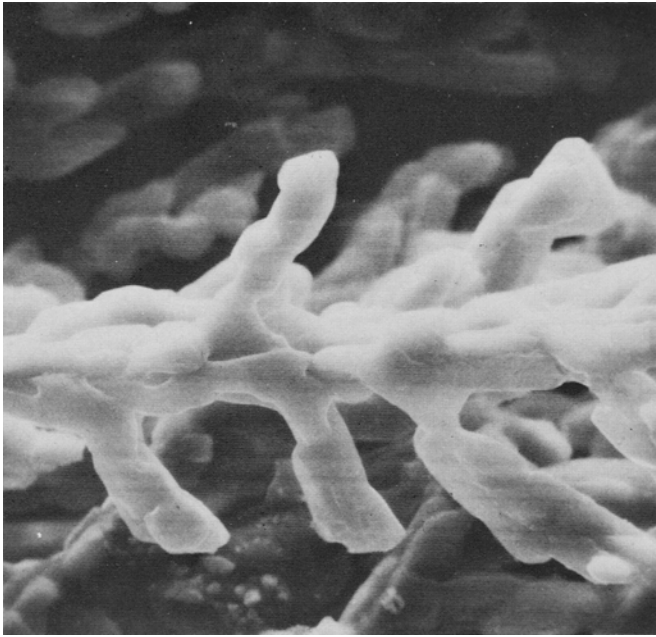
Fig. 12—Sodium-treated Al-Si eutectic structure, 574°C growth temperature. Scanning electron micrograph. Groove running down axis of fiber. Magnification 2080 times.

spect to aluminum.[24-27] This is also consistent with the observed fact that for a given rate of heat-extraction the sodium-treated alloys freeze at a lower temperature than the normal alloys. If the freezing arrest temperature is determined by a balance between heat released by growth and heat extracted from the sample, the lower growth temperature for a given cooling rate of the sodium-treated alloys imply that the sodium-treated alloys grow slower for a given driving force.

A restricted growth mechanism has been proposed by Day and Hellawell[6,7] for the action of sodium in Al-Si alloys. They propose that sodium is selectively absorbed in the twin plane reentrant edge sites on the surface of the growing silicon. This should lead to frequent overgrowth of the silicon and multiple twinning of the silicon. They identify eutectic silicon on addition of sodium as random irregular fibers, the same as produced on quenching. Figs. 2 to 5 and Figs. 10 to 12 contradict this. The fibers are aligned, not random, and the fibers appear to have twin planes along their axes, implying that growth is still by the twin-plane-reentrant-edge mechanism. The twin trace down the axis of the silicon fibers also rules out $\langle 100 \rangle$ as a growth direction of the fiber, so the fibers are fundamentally different from those Bell and Winegard[3,8] and Day and Hellawell[6,7] found in unidirectional growth of pure Al-Si alloys.

Obinata and Komatsu[15] reported that sodium produces [100] facets on primary silicon in Al-Si alloys. According to theories of crystal growth based on the periodic bond chain (PBC) concept, the [100] face is a K face, and the $\langle 100 \rangle$ direction should be a direction of fastest growth.[28-34] The presence of a [100] face on the silicon crystals from sodium-treated Al-Si alloys indicates that [100] has become one of the slowest growing faces. This can be explained in terms of sodium forming a two-dimensional compound on the [100] faces. This compound may also involve aluminum.

As Figs. 10 to 12 show, the fibers have a twin plane running down their axis. The change from plates to fibers is geometrically easy—the fiber is merely the plate which is allowed to grow in only a few selected directions. This can be accomplished by adsorption of sodium, or a sodium complex, on the fast growing faces of the twinned crystal.

The data and conclusions of Davies and West[20] support the view of a selective adsorption on certain faces. They found that sodium restricted the growth of certain silicon planes.

Hunt and Hurle[35] described various possible eutectic morphologies for faceted-nonfaceted eutectic systems. Eutectic microstructures could be irregular, complex-regular, or pseudoregular. Irregular microstructures occur for small amounts of the faceted component, complex-regular for intermediate amounts of the faceted component, and pseudoregular for large amounts of the faceted component.

The fact that the coupled zone in Al-Si alloys becomes skewed to high silicon content on addition of sodium is consistent with the eutectic microstructures being altered from irregular to pseudoregular on addition of sodium.

CONCLUSIONS

The change in position of the coupled zone in Al-Si alloys on addition of sodium indicates that an action of sodium is to slow the growth of silicon with respect to that of aluminum.

We have shown that this effect is independent of temperature. The morphology of the eutectic silicon is not temperature dependent in the temperature region studied, but solely depends on the presence or absence of sodium.

The morphology of the eutectic silicon changes from interconnected plates to bundles of aligned fibers on addition of sodium. The presence of twin planes indicates that growth is by the twin-plane-reentrant-edge mechanism even when sodium is present.

All of the observations are explained by the hypothesis that sodium adsorbs on the fast-growing faces of silicon. This epitactic compound may also contain aluminum.

This adsorption would change the crystal habit of silicon, as has been observed.[15] This adsorption would alter the position of the coupled zone, skewing it further toward silicon-rich compositions. The adsorption would lower the growth rate of the eutectic for a given undercooling, causing the freezing arrest to be lower. These effects are independent of temperature, and do not depend on suppressing the nucleation of silicon.

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