Modification in the Aluminum Silicon System

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Alloys in the range 0 to 24 wt pct Si have been examined by careful thermal analysis, macro- and microscopical study with modification by a mixed alkali fluoride flux, and by separate additions of sodium, potassium, lithium, and strontium. Sodium and strontium exert similar effects and potassium and lithium differing and minor effects; with a mixed alkali flux the influence of sodium is dominant. The normal and modified eutectic arrests in the presence of primary aluminum both show comparable supercoolings and recalescence behavior relative to the horizontal growth temperatures, but this is not observed in hypereutectic alloys containing primary silicon. Both normal and modified eutectics grow radially inward from crucible walls, but the details of the growth fronts are very different: there is no nucleation from the bulk liquid in modified alloys and it is uncertain if this occurs in normal alloys. It is concluded that the structural modification in furnace cooled ingots, as in directionally grown samples, is primarily caused by modified growth of silicon. The mechanism(s) for such modification are briefly discussed.

I. INTRODUCTION

THIS paper is concerned with the well-known modification of a faceted phase during solidification, specifically that of silicon in the Al-Si eutectic system (e.g., References 1 through 5). In this system, as in other faceted/nonfaceted combinations, there are microstructural changes with growth conditions (rate and temperature gradient) and, of particular interest, with minor additions of a third component. Probably the most effective modifying addition to this system is sodium, at concentration levels ≈ 0.01 wt pct, although other alkali and alkaline earth metals and elements of Group VB of the Periodic Table may also have various effects upon the structure. In the case of sodium the structural change, under certain growth conditions, is from one of interconnected silicon flakes in the metal matrix to an apparently finer distribution of irregular fibers[4,6,7] with attendant improvement in mechanical properties.

One can imagine that such a structural change might be caused by one, or a combination of four possible mechanisms:

(a) The effect of a soluble addition must involve some change in the equilibrium phase diagram. While it does not seem probable that this influence will be very important at concentrations as low as, e.g., 0.01 wt pct of sodium, it is conceivable that solute build-up at a growth front might involve some ternary phase reaction.

The Al-Na system has been determined with some care at low sodium levels[8,9] and involves a monotectic reaction at ≈ 0.014 wt pct Na and at about 1 K below the freezing point of the pure metal. The Al-K system is thought to be of similar form but has been less carefully studied. It is possible (e.g., Reference 4) that ternary additions of these metals to the binary Al-Si system also involve a monotectic type reaction at similar low concentrations.

A recent report by Kobayashi et al.[10] based on thermal analysis of normal and modified alloys claimed that one effect of sodium was to elevate the aluminum liquidus temperature by 1 to 2 K and so displace the apparent binary Al-Si eutectic to higher silicon concentrations. This was not confirmed in the present work.

The Al-Si-Li and Al-Si-Sr liquidus surfaces have recently been determined,[11,12] and each shows ternary eutectic reactions at 1.4 wt pct Li and 1.8 pct Sr, respectively, some 2 to 3 K below the binary Al-Si eutectic.

One may note that complete modification by sodium is effected at a level close to that of the binary Al-Na monotectic composition, while the morphologically similar modification by strontium[13,14] occurs at much lower concentrations than that of the ternary eutectic point in the Al-Si-Sr system. We do not know if these observations are relevant to the modification problem.

(b) The addition may influence the nucleation kinetics in such a way as either to promote more nucleation events, or, by interaction with some other impurity, eliminate some heterogeneous sites in the liquid and thereby possibly alter the relative rates of precipitation of the eutectic phases. This situation has been discussed by, e.g., Crossby and Mondolfo,[15] in the context of possible interactions between sodium and phosphorus additions. For a given rate of heat removal from a casting, if the distance between nucleation sites changes there will be a concomitant change in the growth rate, and it is therefore important in this connection to know something about the overall pattern of solidification.

Apart from interpretation of cooling curves — but see later — attempts to identify nucleation sites in the eutectic structure have been made by adding a soluble third component and by quenching partly solidified ingots. Thus, Day[16] examined ternary Al-Si alloys containing up to 10 wt pct Cu, using the ternary segregation pattern to identify eutectic colonies (cells, grains) such as sulfur and phosphorus delineate cells in a cast iron. In a comparison between normal and sodium modified castings it was concluded that there was little or no change in the nucleation density, but it must be stated that in the normal flake structure the distinction of individual colonies is still (i.e., with copper demarcation)

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ambiguous. More recently, Flood and Hunt[17] used a quenching technique to examine the solidification pattern and concluded that nucleation in bulk liquid was inhibited in sodium modified samples by comparison with the normal material where apparently isolated colonies were observed ahead of a general duplex growth front.

(c) At low undercoolings, faceted phases, almost by definition, grow anisotropically from the liquid by more rapid molecular attachment at certain preferred sites, with slow growth normal to certain crystallographic planes, usually those of close packing — e.g, {111} of silicon. At a duplex solid-liquid growth front a faceted phase can also reflect this tendency, and in normal Al-Si eutectic growth the silicon flake habit is {111} and the presence of numerous growth twins suggests that these facilitate more rapid growth in directions parallel to these planes.[18,19]

There then arises the possibility that selective absorption of a minor impurity may poison preferred sites and lead to a growth rate which is kinetically limited in many directions and therefore appears to grow more isotropically. Directional solidification studies of pure and modified eutectic alloys[4,6] and especially of eutectic growth on pure silicon substrates[20,21] do show, beyond reasonable doubt, that silicon crystal growth from the liquid is very clearly inhibited by sodium.

What exactly the consequences are of this poisoning effect upon the internal structure of the silicon is unclear: that is, the poisoning could either reduce the growth twin density[17,22] and thus inhibit easy growth at twin plane reentrant edges (T.P.R.E.),[18,19] or it might lead to an increased twin density and thus more rapid growth in many directions[4,6,23] — both consequences would result in a more isotropic morphology.

(d) There remains the problem of where the modifying agent is located in the solid product, whether uniformly within one or either phase or preferentially adsorbed at the solid-solid product interface. Studies of over modification bands[22] show that an excess of sodium, >0.01 wt pct, causes the growth of the eutectic front to be continually arrested, as if by a periodic build-up at the growth front, possibly a result of the formation of a layer of a sodium rich monotectic liquid.

If the sodium were adsorbed preferentially at the eutectic product interface with reduction in surface energy, it might also be expected that there could be an increase in surface area for a given undercooling and a finer spacing for a given structure. While the immediate impression of the modified fibrous structure is that it is very much finer than the normal flake arrangement, this is probably misleading. Measurement of the interflake and interfiber spacings as a function of growth rate[24] indicates an almost continuous transition, and careful analysis of the geometry of flake vs fiber morphology in the modified alloy[17] suggests that the diffusion distance at the duplex solid-liquid front is not so different as is generally assumed.

The present paper describes a study of alloys from 0 to 24 wt pct Si, with and without modifying additions. Careful thermal analysis has been carried out with the object of separating the influences of modification on the phase equilibria, nucleation, and growth temperatures. These results have then been correlated with the macrostructure of par-

tially solidified samples, to identify the general patterns of solidification, and with the detailed microstructures.

II. EXPERIMENTAL

A. Materials

The aluminum used throughout contained $\approx$60 ppm of total impurities (Si, Fe, Mn, Zn, V, Zr) and was supplied by ALCOA Research Center. The silicon impurity content was <1 ppm and was in the form of polycrystalline ingot. Alloys were prepared by melting the components together in recrystallized alumina crucibles under argon and chill casting a series of master alloys. Samples of these alloys were then chemically analyzed and remelted as necessary.

Modifying additions were made in two ways. For most of the earlier thermal analysis over periods of one/two hours, to maintain a constant partial pressure of sodium, the alloys were melted under a salt flux of LiF + NaF + KF of approximately ternary eutectic composition, molar ratio 4.5:1:4.5. The eutectic temperature for this mixture is 454 °C, and the flux was therefore always molten in the temperature range of interest. It was found that (a) solid salts such as NaF (mp. 998 °C) were not effective, even if previously melted, and (b) chloride salts were ineffective whether molten or not and tended to volatilize, probably as $AlCl_3$. We attributed the modifying activity of the fluoride mixture to a relatively high partial pressure of alkali metals across the liquid flux metal interface because of stable anions such as AlF_6^{3-} (e.g., an equilibrium of the form $Al + 6NaF = Na_3AlF_6 + 3Na$).

In hypo-eutectic and eutectic alloys a weight ratio of salt to metal of 1:10 was sufficient to produce maximum modification as measured by undercooling. In hyper-eutectic alloys a larger ratio up to 1:4 was needed to modify the morphology of both primary and eutectic silicon. Subsequent analyses of the alloys were Na, 150 to 350 ppm; K, <100 ppm; Li, 400 to 700 ppm.

While the salt mixture ensured modification over extended periods and was therefore ideal for repeated thermal analysis cycles, it was clearly desirable to identify the effects of individual metals. To do this, the alkalis, Na and K, were added to the molten alloys at nominal, initial concentrations of $\sim$2 wt pct, wrapped in Al foil, under an argon atmosphere. Li and Sr were added as master alloys with Al which were also used in determination of the respective ternary liquidus surfaces as a separate exercise.[11,12]

B. Thermal Analysis

Approximately 6 ml samples were examined in recrystallized alumina crucibles within a sealed furnace tube under a small positive pressure of argon — the arrangement is shown in Figure 1. Direct and differential thermocouples were employed, the latter being necessary only to aid in detection of steep liquidus boundaries, low volume fractions of solid, notably of primary silicon in hyper-eutectic alloys. 0.2 mm diameter chromel-alumel thermocouples were used. The direct couple was enclosed in a 1.5 mm bore, thin walled alumina sheath, the differential being reentrant in the base of a graphite crucible containing alloy of approximately
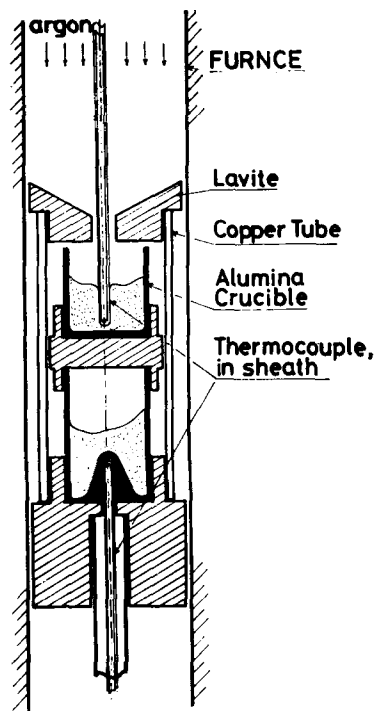
Fig. 1—Thermal analysis assembly.

eutectic composition. The combined assembly was surrounded by a copper cylinder to minimize vertical temperature gradients.

The assembly of Figure 1 was situated in a resistance furnace of relatively low thermal capacity which was controlled by a chromel-alumel thermocouple close to the winding, in conjunction with a ramped Eurotherm controller. Constant heating and cooling rates could be maintained from 0.1 K min.$^{-1}$ to 15 K min.$^{-1}$, but after a preliminary study of the effect of cooling rate all subsequent analyses were made at 4 K min.$^{-1}$.

The direct thermocouple emf was backed off against a standard source and both emf's were recorded on a Kipp and Zonen, two pen BD6 potentiometric recorder with extended ranges and full scale deflections as low as 20 μv ($\approx$2 K).

Typically, a series of three cooling and heating curves each for normal and modified samples was taken for each alloy composition. The normal eutectic heating arrest was taken as a substandard reference temperature of 578 °C for each sample, so that differences of depressions of the nucleation, growth, and melting temperatures were accurate and reproducible relative to that temperature in each alloy.

Examples of cooling and heating curves follow later, but in general it was considered that cooling arrests for the aluminum liquidus and eutectic were reproducible to within ±0.5 K while for the silicon liquidus the range was $\approx$±1.5 K. However, any individual cooling curve was sensitive to very small temperature fluctuations, <0.1 K, so that, for example, formation of overmodification bands could clearly be detected as small ripples on the horizontal part of the cooling arrest; see Figures 5, 6, and 7.

C. *Quenching Experiments — Metallography*

To examine the general pattern of solidification, a number of normal and modified eutectic samples were quenched
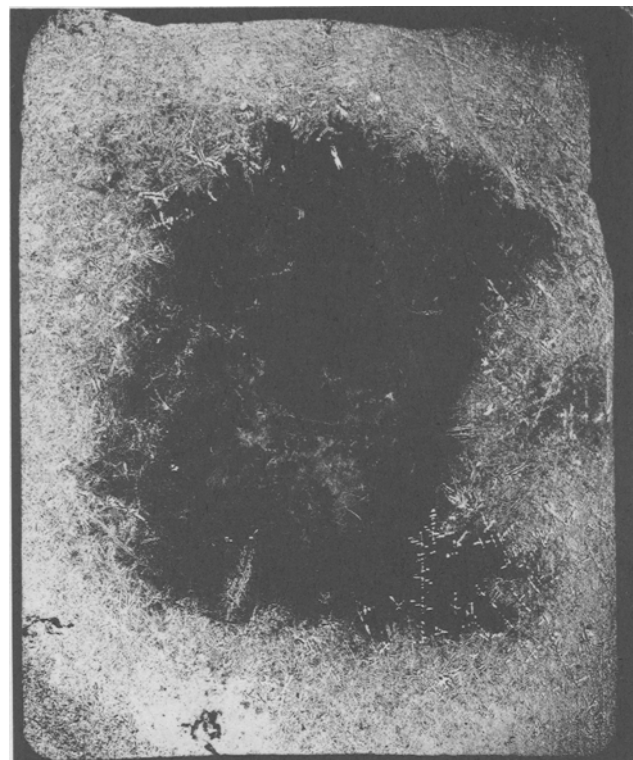
(a)

(b)

Fig. 2—Al-12.6 wt pct Si samples, water quenched when partly solidified, polished, unetched. (a) Normal, (b) modified. Magnification 3.6 times.

while partly solidified. Approximately 4 ml samples in graphite crucibles with a reentrant thermocouple were cooled at $\approx$14 K min.$^{-1}$, and the entire crucibles and contents were

plunged into a bucket of water when the cooling arrest had begun. Addition of sodium metal at a level of ~2 wt pct produced effective modification of the structure, and it did not seem to matter that graphite rather than alumina crucibles were used — contrary to previous reports.[25,26] In the case of thermal analysis samples the thermocouple sheath was withdrawn after the final heating cycle and the melt was then furnace cooled at the same rate as that employed for thermal analysis. Essentially standard methods of metallographic preparation were used for both quenched samples and thermal analysis ingots. In the former case, differences in reflectivity between regions of slow and fast cooling rates gave good contrast accentuated by high contrast film and paper (Figures 2(a) and (b)). No etchants were necessary for macro- or microstructures. Examination and photography was made with a Zeiss Axiomat microscope.

III. RESULTS

A. Macrostructure

Figures 2(a) and (b) were typical of quenched samples and are similar to those illustrated by previous workers.[15,17,27] In the normal alloy (Figure 2(a)), an irregular eutectic front has advanced radially inward toward the middle of the ingot. In the quenched region there are some fine aluminum dendrites and a number of apparently isolated eutectic colonies. However, these eutectic colonies do not necessarily originate as nucleation events in the bulk liquid as has been suggested by Flood and Hunt,[17] but are probably connected to the main growth front by outlying extensions of flake silicon, and this may be seen by polishing away successive layers (Figures 3(a) through (c)). The appearance of isolation on any given section frequently proves to be illusory.

In modified material (Figure 2(b)), the eutectic front is much more clearly defined, growing radially inward between primary aluminum dendrites which are present because the eutectic point is displaced to higher silicon concentrations[3,4,5] — see later. The quenched liquid also contains very fine aluminum dendrites for the same reason that the eutectic point is displaced at rapid growth rates.

In hypo- and hyper-eutectic alloys the pattern is essentially unchanged except that in the latter, coarse crystals of primary silicon occur at the crucible walls, and these are characteristically surrounded by a sheath of aluminum from which some secondary aluminum dendrites may grow before the eutectic structure develops (Figures 4(a) and (b)). In hypo-eutectic alloys ≲8 wt pct Si, quenched normal samples showed that the flake eutectic structure also grew uniformly between the increasingly large proportion of primary aluminum. All these events were detectable by a central thermocouple in a small sample, although, as already remarked, it is not easy, from the microstructures of fully solidified samples, to comment on the density of eutectic colonies as individual nucleation events.

B. Thermal Analysis

The principal comparison is between normal and modified alloys, but the details of eutectic cooling arrests also change with silicon content according to which primary phase is present. It is therefore necessary to describe, separately, the forms of thermal arrests for alloys of near eutectic compositions, hypo- and hyper-eutectic alloys. In any case we distinguish — for the eutectic cooling curves — a nucleation temperature which corresponds to the first departure from linear cooling, and the subsequent nearly horizontal part of an arrest, which corresponds to growth. All the following descriptions relate to modification by the molten salt flux, and the details are summarized in Table I and Figure 10.

1. Near eutectic compositions, 11 to 14 wt pct Si

Figure 5 shows cooling and heating curves for normal and modified alloy of eutectic composition, 12.6 wt pct Si.

The normal cooling curve shows no primary arrest but 1 to 1.5 K super cooling followed by recalescence to a growth temperature which lies at ~2 K below the corresponding heating arrest at this constant cooling/heating rate of 4 K min⁻¹. The modified cooling arrest shows a small initial arrest slightly below that for the normal eutectic, and this must correspond to pro-eutectic aluminum which can be seen in the modified microstructure (Figure 2(b)), resulting

Table I. Thermal Analysis Data for Normal and Modified Alloys at Cooling/Heating Rates of 4 K/Minute

| Composition Wt Pct Si | Liquidus °C | | Eutectic °C | | | |
| | Normal | Modified | Normal | | Modified | |
	(Cooling Only)		Cooling	Heating	Cooling	Heating
1.94	647.5	647.5	574.2	577.3	568.0	576.3
3.95	632.0	632.0	573.8	577.8	566.4	576.3
6.35	618.5	617.0	574.7	578.0	569.0	578.0
8.08	605.0	605.0	575.2	577.0	568.8	576.0
10.91	588.5	588.0	577.0	579.6	571.4	578.0
12.0	579.0	580.0	576.6	579.0	568.5	577.8
12.60	—	575.5	574.4	578.5	571.0	577.1
13.78	588.0	580.0	576.2	578.4	573.0	577.0
14.56	599.0	585.0	577.3	579.8	572.0	577.1
16.22	623.0	613.0	576.5	578.3	570.0	577.5
18.00	646.0	636.0	575.5	—	569.4	578.0
19.24	664.0	659.0	575.5	578.0	569.0	578.0
21.0	692.0	682.0	574.3	—	568.0	—
23.0	715.0	709.0	574.0	578.0	569.1	577.0
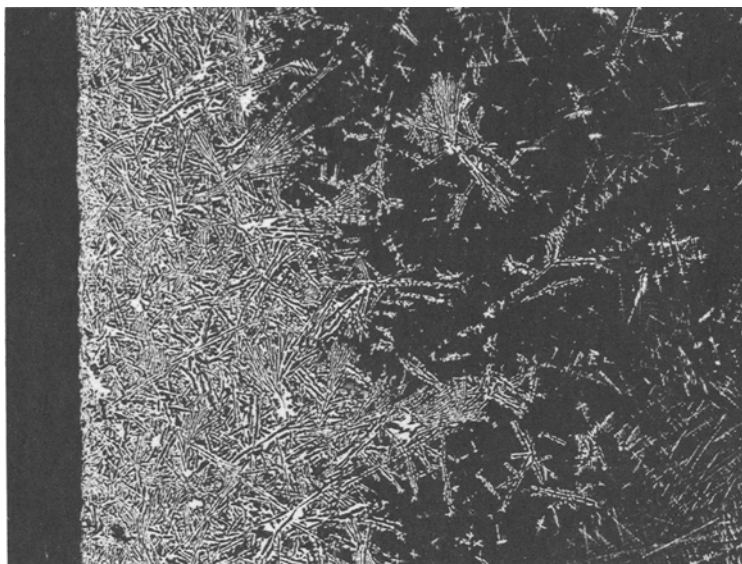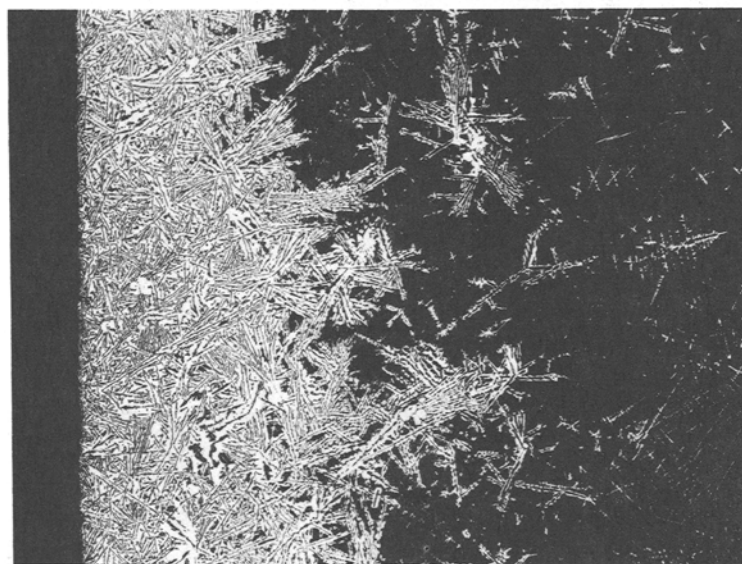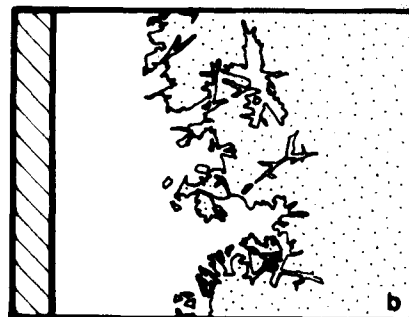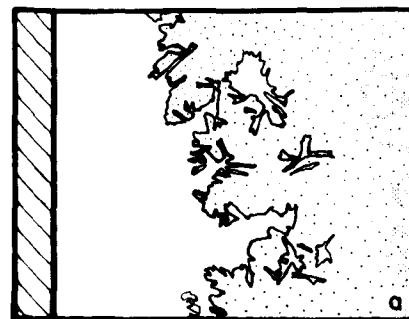
Fig. 3—Successive sections through sample shown in Fig. 2(a). (a)-(c) and traced outlines to emphasize continuity of eutectic colonies. Magnification 21 times.
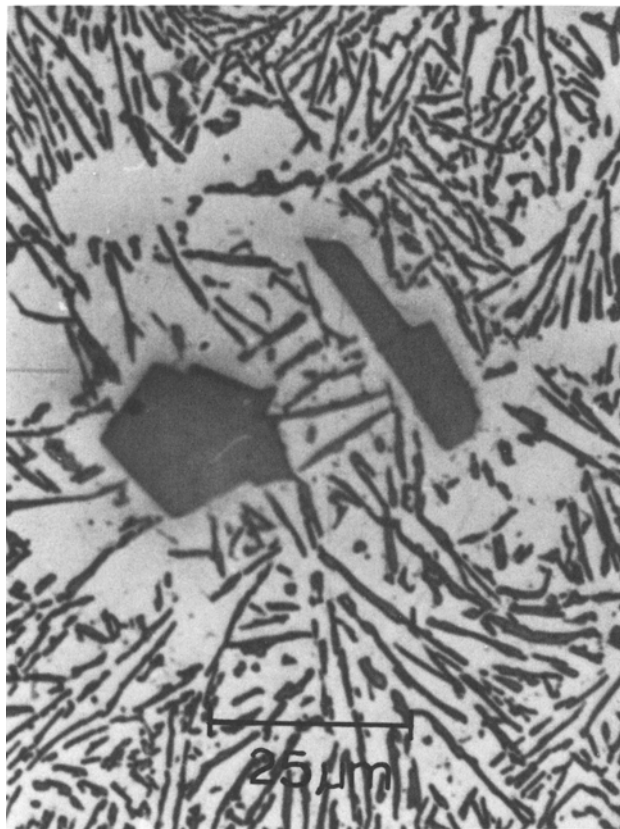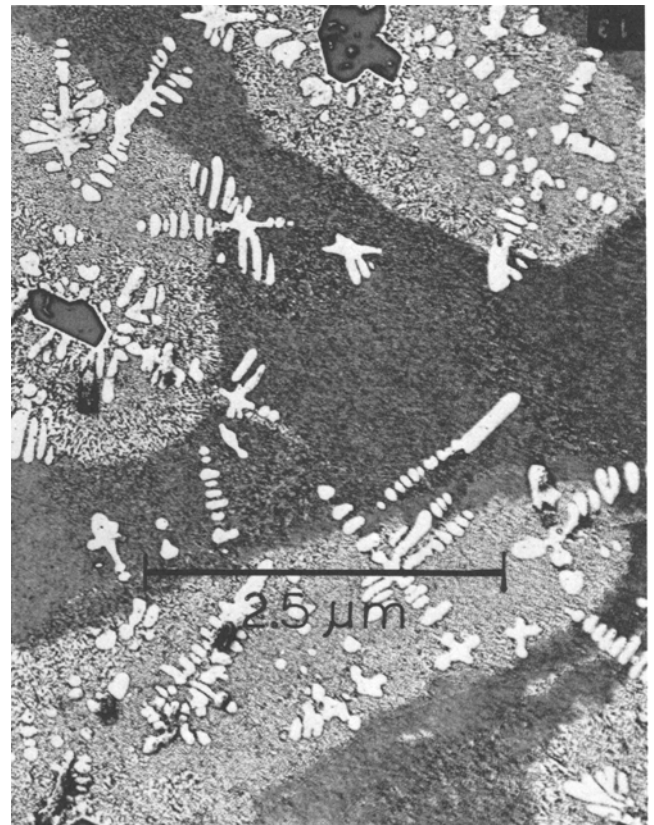
(a)   (b)

Fig. 4—Al-16 wt pct Si (a) normal, (b) modified—showing nucleation of secondary aluminum and eutectic upon primary silicon. Refer to cooling curves in Fig. 8.
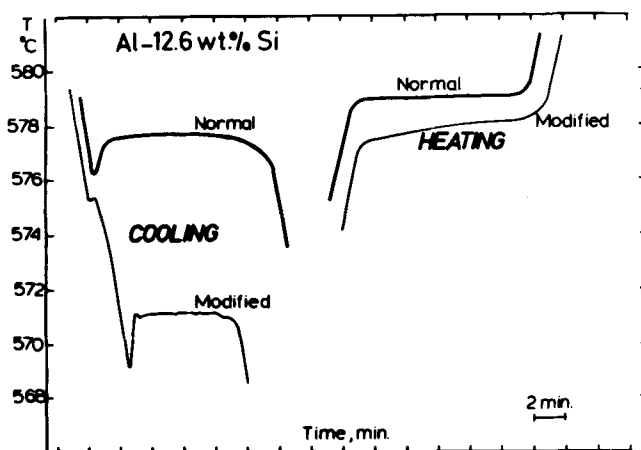

Fig. 5—Cooling and heating curves for alloy of nominal eutectic composition.

from the shift in eutectic composition to higher silicon contents. Subsequently the modified eutectic arrest occurs, with similar relative supercooling and recalescence to that of the normal, but at ≈ 6 K lower temperature. The heating arrest for the modified alloy then shows a single arrest at ~ 1 K below that of normal. Finally, the portion of the modified arrest corresponding to eutectic growth shows a characteristic ripple which is attributed to the interrupted growth[21] associated with overmodification bands, which are to be seen in such specimens (Figure 6).
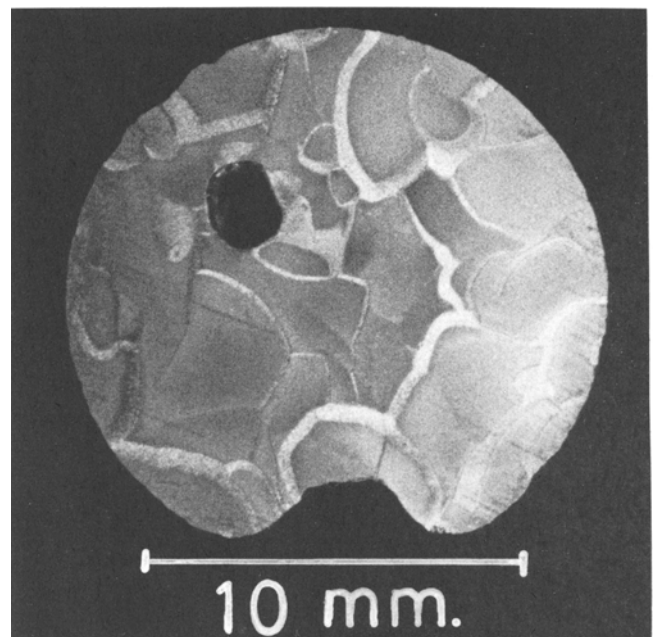

Fig. 6—Over modification bands in Al-14 wt pct Si.

2. *Hypo-eutectic alloys, 2 to 8 wt pct Si*

Figure 7 shows eutectic thermal arrests for an alloy approximately midway between the aluminum solid solubility limit and that of eutectic composition.
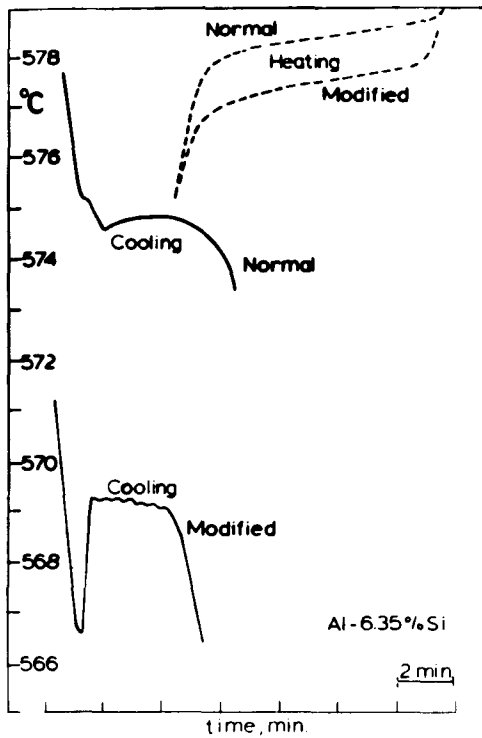
Fig. 7—Cooling and heating curves for Al-6 wt pct Si in eutectic temperature range.

Fig. 8—Cooling and heating curves for Al-23 wt pct Si in eutectic temperature range.

It is apparent that the modified arrests do not differ in form but only in extent from those of the eutectic alloy; the same depression of nucleation and growth temperatures are observed. The growth temperature of the normal eutectic is still ~2 K below the melting temperature, but there is no supercooling and recalescence and, instead, the major horizontal is preceded by a nucleation arrest at the same temperature or even slightly above that. This change of shape became apparent in an alloy containing 8 wt pct Si and was more pronounced in 4 wt pct and 2 wt pct alloys.

In all these alloys the eutectic cooling arrests followed well-defined liquidus arrests for the pro-eutectic aluminum phase, and these arrests were reproducible within <1 K in normal and modified alloys. The aluminum liquidus temperature is not affected by modification to within 0.5 K.

3. Hyper-eutectic alloys, 14 to 24 wt pct Si

The eutectic arrests are shown in Figure 8 for an alloy containing 23 wt pct Si. It is seen that the heating arrests have not changed by comparison with eutectic and hypo-eutectic compositions, but the forms of the cooling arrests are quite different, especially for modified alloy. Similar curves were also observed on alloys containing 16 wt pct, 18 wt pct, and 20 wt pct Si.

In both the normal and modified alloy the growth horizontals lie at essentially the same temperatures as before, but no supercooling below these temperatures occurs. In the normal alloy the initial bump can be attributed to nucleation and growth of a small quantity of secondary aluminum on primary silicon which is then followed by the usual flake eutectic growth. In the modified alloy this effect is more pronounced, and before the fine fibrous eutectic develops there is some earlier growth of partly modified and coarser eutectic, causing the larger earlier part of the arrest.
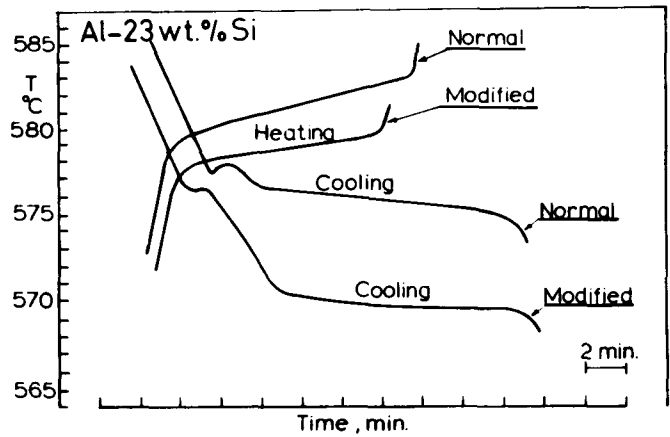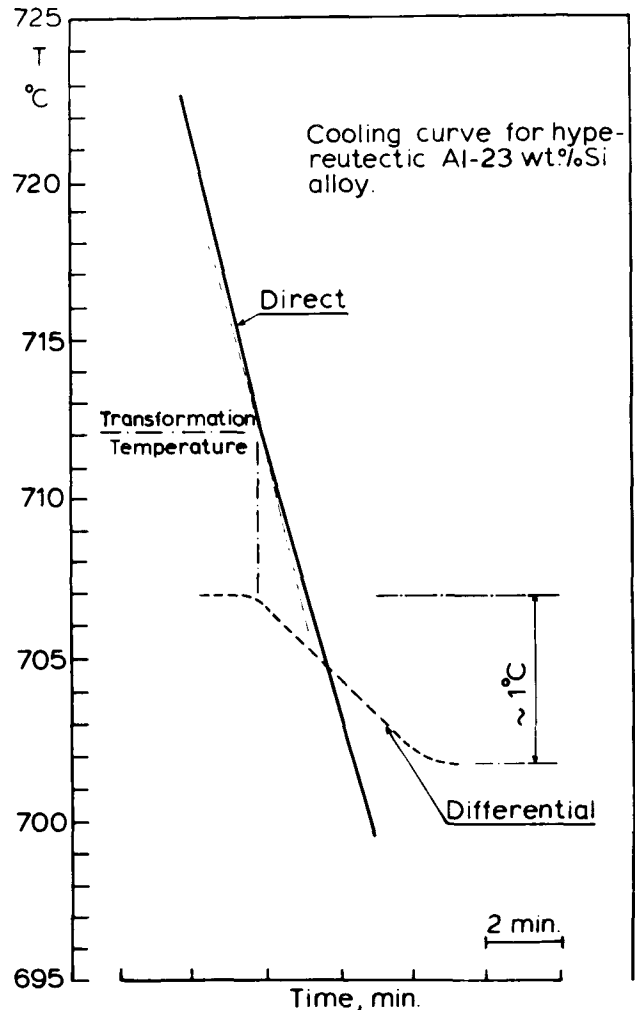

Fig. 9—Direct and differential cooling curves for silicon liquidus in Al-23 wt pct Si normal alloy.

These events are to be found around the edge of samples close to the crucible walls, and no primary silicon is to be found elsewhere.

At higher temperatures the silicon liquidus arrest could be detected with the aid of the differential thermocouple arrangement—Figure 9 shows an example from the same alloy. The quantity of pro-eutectic silicon is so small that
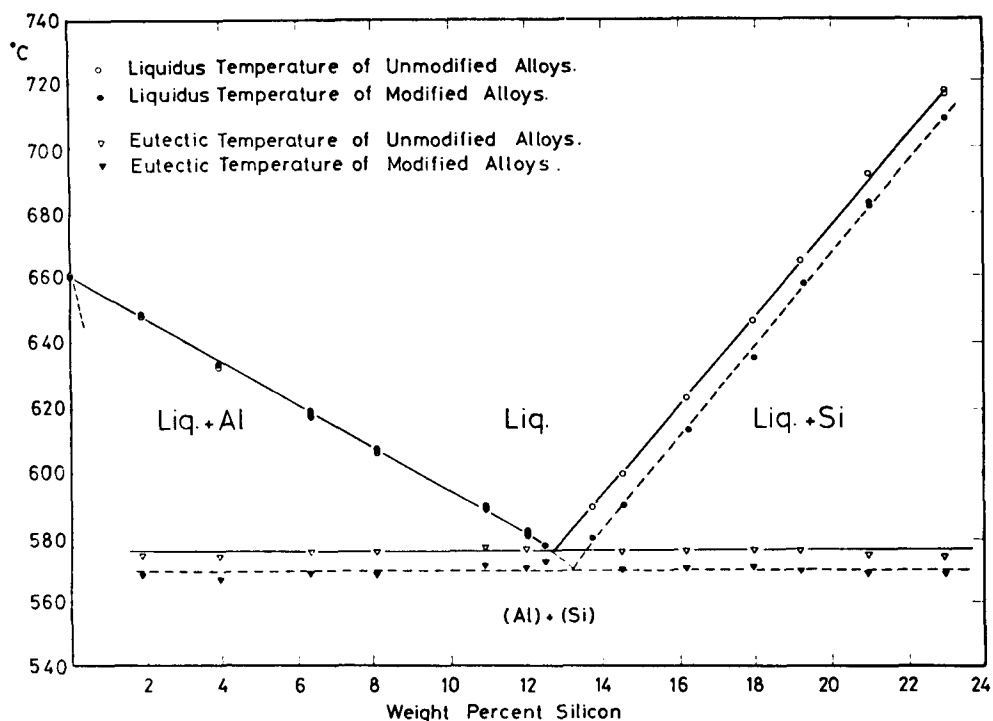
Fig. 10—Liquidus and eutectic temperatures based on cooling curve data for normal and modified alloys.

only a minor slope change can be seen on the direct cooling curve, but with repeated runs it was possible to place the liquidus reproducibly within $\sim\pm1.5$ K. The modified silicon liquidus arrests lay 4 to 8 K below those of the normal alloy, and with so little subsequent growth over a wide temperature range, these depressions must be attributed principally to the nucleation process, although it follows that growth was also occurring at lower temperatures.

From the above types of cooling curve we can construct the phase diagram(s) of Figure 10, which is based on the liquidus arrests for the pro-eutectic phases and the growth temperatures from the horizontal portions of eutectic arrests — as in Figures 5, 7, and 9.

The diagram(s) is essentially that concluded by some previous workers (e.g., Reference 27) but, we would like to think, more precise and definite. It should be noted, that contrary to an earlier report by Kobayashi et al.[10] we could not detect any significant change in the aluminum liquidus and certainly no rise with modification. The silicon liquidus and eutectic horizontal are depressed with modification by ~6 K under our experimental conditions. The result of this is the consequential shift in the composition of the modified eutectic point to 13.5 wt pct Si. At more rapid cooling rates or possibly with a higher partial pressure of sodium (or other), the modified silicon liquidus and the eutectic temperature fall at yet lower temperatures, and the composition shift increases toward higher silicon concentrations.

C. Separate Additions

Inasmuch as sodium was a minor component of the mixed fluoride flux, it was desirable to ascertain that the principal modifying effect could, in fact, be attributed to that metal rather than lithium or potassium. The thermal analyses and structural examinations were therefore repeated with individual metallic additions of up to 2 wt pct of sodium and

potassium and by addition of lithium as a binary Al-Li master alloy.[11] The analyzed compositions were 0.011 wt pct Na and 0.01 wt pct K with up to 0.1 wt pct Li in various ternary alloys.

The results showed that the modifying effects of Li and K were minor by comparison with Na, both as detected by thermal analysis and from the microstructures. The metallic addition of sodium modified the thermal analysis curves in almost exactly the same way as did the mixed fluoride flux except that at the same cooling rate the eutectic arrest was depressed by 1 to 2 K more — i.e., by up to 8 K. It was therefore concluded that the major influence by the salt flux could be attributed to sodium.

IV. DISCUSSION

A. Macro- and Micro-Solidification Patterns

It was shown in Figures 2 and 3 that the macroscopic growth patterns for both normal and modified eutectic growth were essentially the same, namely, radially inward from the crucible walls.

Although the details of the growth fronts are very different, it was our impression that in neither the normal nor modified alloys did there occur independent nucleation of eutectic colonies ahead of the mean position of the growth front. In a similar study, Flood and Hunt[17] observed the same structures and considered that in the normal alloys (Figures 2(a) and 3(a) through (c)), apparently isolated eutectic colonies arose from nucleation events ahead of the general growth front in the bulk liquid. Our study cannot be said to be exhaustive, but after repeated repolishing we found that colonies which grew larger on successive sections, eventually connected with the main radial growth front. It follows that, on average, approximately half of

the apparently isolated colonies became smaller and disappeared on repeated sections which we took to imply that they could have been joined to the main growth front in a plane above the original section. Clearly, there is some scope here for a very laborious three-dimensional study on multiple and inclined sections, which we have not attempted, but for the above reasons we are doubtful about any argument based on repeated nucleation rather than continuous growth.

Growth rates and temperature gradients

The heat flow characteristics for a furnace cooled specimen are somewhat different from those in a casting. In the former, cooling at a constant rate of, e.g., 4 K min^{-1}, with a horizontal arrest of 7 to 8 minutes, early growth begins slowly as the furnace temperature is only a little below that of the sample, but accelerates as the ambient temperature continues to fall — in those experiments, to about 30 K below that of the sample at the end of an arrest. In a casting where the mold is a relatively poor conductor, the situation is essentially reversed as the walls heat up to a temperature closer to that of the alloy, i.e., the initial growth is the more rapid.

An analysis of the growth conditions is given in Appendix I, but a mean radial growth rate can easily be derived for such cases from the duration of the arrests and the radial distance of growth (7.5 mm), being ≈ 16 μm s^{-1} in the experiments described here. The question then arises as to whether the strictly radial estimate of the growth rate is comparable for the very different growth fronts in normal and modified eutectic alloys (Figures 2(a), (b) and 3(a) through (c)). Flood and Hunt argued that because the normal interface presents a much larger solid-liquid surface area than that of the modified front, unit local advance of that front creates a correspondingly larger volume of solid — or, for the same rate of heat abstraction, the local growth rate for the normal irregular front will be slower, the phase spacing coarser, and the undercooling less — as thermal analysis does indeed show. This argument, coupled with relative estimates of the diffusion distances in the flake and fibrous morphologies, is used to suggest that growth rate, V, and undercooling ΔT, are related by a similar proportionality constant, A, as in an expression $V = A \, \Delta T^2$, for both normal and modified alloy.

For an interface advancing at a constant rate at all points this argument is irrefutable and might be extended to directionally frozen samples in which there is an increase of normal flake spacing with decreasing temperature gradient,[24,28] i.e., as the gradient decreases the growth front becomes more irregular and so presents a greater solid-liquid area. It is suggested here, however, that the argument begs the question of why the profile of the growth front is gradient dependent in the first place. The difference between directional grown experiments and growth in furnace cooled or cast ingots is that in the former it is very difficult to reduce and control the mean temperature gradient below ≈ 0.5 to 1.0 K mm^{-1}, whereas in the latter the gradients can be an order of magnitude lower. An estimate for the conditions prevailing in the present experiments, see Appendix I, suggest that the temperature gradients will not exceed ≈ 0.1 K mm^{-1}, i.e., they are in order of magnitude less

than can be controlled in a typical directional solidification arrangement.

In these circumstances the eutectic flakes of silicon grow irregularly in bursts, only very loosely aligned along the heat flow direction and the aluminum matrix, and further silicon gradually fill the intervening spaces. In fact, if one were to trace the path of a continuous silicon flake from the crucible wall to the center line of an ingot, the path length would far exceed the crucible radius, and in that sense the mean growth rate — of silicon — would have to be accounted faster in the normal than in the modified case where growth is more strictly radial.

We would conclude, from the above, that the modification is primarily a result of change in growth mechanism and that it concerns a transition from one in which the minor phase "leads" almost independently at the front (albeit wetted by the major aluminum phase which produces most of the latent heat) to one at which the minor phase has become nonfaceted and no longer projects ahead of the matrix phase; the diffusion process then approximates to a short range, quasi-steady-state, eutectic reaction. We return to the question of how this might happen — section IV-C.

B. Nucleation

The cooling curves of Figures 5, 7, and 8 show a clear difference between eutectic and hypo-eutectic alloys vs hyper-eutectic compositions. In alloys of near eutectic and slightly hypo-eutectic (~ 11 to 14 wt pct Si) both the normal and modified eutectic arrest horizontals (growth) are preceded by 1 to 2 K of supercooling, and the nucleation processes are apparently affected by modification to the same relative extent (undercooling) as the growth processes. Were it possible to have identified nucleation events in the eutectic structures one would therefore have expected little change, as was actually reported.[16] It is presumed that the nucleation events in question were those of silicon on primary aluminum or elsewhere, close to the crucible walls. In hyper-eutectic alloys containing primary silicon, nucleation of the eutectic is preceded by that of aluminum on silicon (Figures 4 and 8), and this requires little supercooling and is not significantly depressed by modification. Therefore, there is no recalescence before eutectic growth and instead, following nucleation, the temperature falls to the eutectic growth temperature. Primary silicon nucleation is also depressed by modification; that of the aluminum is not. Therefore, we conclude that the modified nucleation concerns only the silicon phase — as it does the growth process — but we do find it somewhat remarkable that both nucleation and growth are almost equally affected.

It is noted (Figure 7) that in hypo-eutectic alloys in the range 2 to 8 wt pct Si, there was no supercooling and recalescence of the normal eutectic arrests. We attributed this change in pattern to enhanced microsegregation and locally high silicon concentrations which did not develop when the fraction of primary aluminum was small, i.e., closer to eutectic compositions. Whatever is providing more efficient sites for silicon nucleation is markedly influenced by modification when the usual ~ 2 K of supercooling returns.

Notwithstanding these variations in nucleation behavior and events preceding the subsequent growth, we have to

conclude that it is primarily the latter stage on which modification operates.

C. *Modified Silicon Growth*

There remains the recurring question as to what the sodium (and possibly also strontium) actually do to the growth front to cause the dramatic change in morphology of silicon from markedly anisotropic to isotropic shapes. From the foregoing we conclude that the activity is at the silicon-liquid interface and therefore involves inhibition of preferred growth in certain crystallographic directions. As already noted in section I(c), it is known that[4,6] the primary flake and eutectic flake silicon are intricately twinned and the presence of sufficient reentrant twin plane reentrant edges, TPRE[4,6,18,19] is thought to be important in aiding rapid growth parallel to the {111} habit planes of the flakes. If such preferred sites for molecular attachment are somehow poisoned by sodium (and strontium which produces a similar change in eutectic, if not in primary morphology) we might expect either no twins in the modified fibrous material, or a higher twin density caused by higher interfacial undercooling and consequently more isotropic growth in many directions. The former possibility would seem to be more probable, but resolution of this question must await the results of some detailed TEM study of the fibrous silicon — even then, the exact mechanism will remain somewhat obscure, and why it should be sodium (or strontium?) in particular is a further enigma.

In terms of kinetic undercooling, the effect of inhibiting the more rapidly growing sites for molecular attachment must be to increase that undercooling until growth can occur at the same rate on less advantageous planes, e.g., normal to the closely packed {111} planes. In this sense the influence of sodium would not be to lower the threshold undercooling for isotropic growth as Flood and Hunt suggest,[17] but rather to increase it to a level where all crystallographic directions are equivalent. In the normal alloy the presence of the solid aluminum phase during growth is almost incidental, except inasmuch as it largely covers the sides of silicon flakes, but in the modified alloy the silicon is constrained to grow at a front which is much more nearly isothermal and is no longer the "leading" phase.

V. SUMMARY

1. In Al-Si alloys modified by a mixed, molten alkali-flux the dominant effect is considered to be caused by sodium. Modification by lithium and potassium is minor and essentially different in result.
2. In small furnace cooled ingots of near eutectic and hypereutectic alloys, both the normal and modified eutectic fronts advance radially inward. Nucleation of eutectic colonies from the bulk liquid does not occur in modified alloys, and limited evidence suggests that it is also absent in the normal material.
3. With the prevailing low temperature gradients the normal eutectic growth is very loosely coupled and coarse silicon flakes grow almost independently of the major aluminum phase — the effect of sodium (and probably strontium) additions is to change this growth form to a near planar front at which quasi-steady-state, coupled growth occurs.

4. The modification depresses nucleation of silicon, on whatever substrate, to about the same extent as it does that of primary silicon and eutectic growth. The aluminum nucleation and growth temperatures are not significantly affected by modification.
5. Modified growth rather than nucleation is thought to be the primary cause of the effect and involves a mechanism which causes silicon to grow more nearly isotropically; the actual mechanism remains speculative.

APPENDIX I
Estimation of growth rate and temperature gradient during furnace cooling

We consider a cylindrical specimen, radius r_0, at temperature, T_H, losing heat to an environment at T_c by radiation only. The presence of a refractory container is neglected.

(a) Prior to a thermal arrest (at 850 K) only specific heat is lost. Equate rate of heat loss with cooling rate, R.

$$e\sigma(T_H^4 - T_c^4)2\pi r_0 \cdot \Delta h = C_p \cdot R \cdot \pi r_0^2 \cdot \Delta h$$

where:

h = height of crucible
e = emissivity   = 0.5
σ = Stefan's radiation constant − 6.10^{-8} Jm^{-2} K^{-4} s^{-1}
r_0 = 7.5 10^{-3} m
R = 4 K min^{-1} = 6.7 10^{-3} K s^{-1}
C_p = 3.10^6 Jm^{-3} K^{-1}

yields $T_H - T_c = \Delta T \approx 10$ K, *i.e.*, at start of thermal arrest at 850 K, the environmental temperature is 840 K, and after the arrest begins: $T_c = T_{Eu} - \Delta T - Rt$, where T_{Eu} is the eutectic temperature and t = time.

(b) Below T_{Eu} it is necessary to equate the rate of heat loss by radiation with the latent heat of fusion, ΔH, released:

$$e\sigma(T_H^4) - T_c^4)2\pi r_0 \Delta h = \Delta H 2\pi r\, dr/dt \cdot \Delta h$$

and $\quad r\, dr/\mathrm{dt} - \dfrac{r_0 \cdot e \cdot \sigma}{\Delta H}(T_H^4 - T_c^4) = 0$

in which the parameters are as above with $\Delta H = 1.45$ 10^9 Jm^{-3} and the boundary condition is that $r = r_0$ for $t = 0$.

Solution to the above expressions yields a radial growth rate from $V = 0$ at $t = 0$ increasing toward $V = \infty$ at $r = 0$. This also yields a time for total solidification of 435 s = 7.25 minutes, which is very close to that observed.

(c) Heat flow within the sample by conduction must also balance the rate of evolution of latent heat:

$$kG = \Delta H \cdot V$$

where

k = thermal conductivity $\approx 10^2$ Jm^{-1} k^{-1} s^{-1}
G = radial temperature gradient:
yields $G = 1.45\ 10^7\ V$ Km^{-1}.

Combining the above for V and G shows that, *e.g.*, when the growth front has advanced halfway toward the center of the ingot, $r = 3.75$ mm, the growth rate is $\approx 3\ \mu$m s^{-1} and the temperature gradient ≈ 0.05 K mm^{-1}.

ACKNOWLEDGMENTS

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