FACTORS AFFECTING SEGREGATION IN THE CONTROLLED SOLIDIFICATION
OF ALUMINUM-COPPER AND ALUMINUM-ZINC ALLOYS

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ABSTRACT

An apparatus has been designed and constructed for the solidification
of alloys under conditions of constant temperature gradients,
constant linear rate of solidification, and constant liquid agitation.
It has been shown possible to suppress dendrite formation and maintain
plane front solidification in aluminum alloys of up to 2 per cent
copper and 10 per cent zinc. Solid temperature gradients were approxi-
mately 60 degrees centigrade per centimeter in all heats, and power
approximately one kilowatt. Liquid agitation was by low frequency in-
duction stirring.

Segregation was measured by chemical analysis in the aluminum-
copper and aluminum-zinc alloys. In alloys solidified with plane front,
nearly perfect segregation was observed at the lowest solidification
velocities studied (0.4 x 10^-3 centimeters per second). The segregation
ratio \( \frac{K}{K_{ij}} \) obtained at these velocities was 0.8 as compared to a
maximum value of \( \frac{K}{K_{ij}} = 1 \) at perfect segregation. Segregation
decreased with increasing interface velocities in both alloys, and segregation in both alloys at solidification velocities below about $1.5 \times 10^{-3}$ centimeters per second indicated a constant "effective boundary layer" of .03 centimeter. At higher velocities, the effective boundary layer thickness decreased.

Considerable macrosegregation was observed in heats where plane front solidification was not maintained, although entrapped second phase was observed. An interpretation of this phenomena and consideration of segregation in dendritically freezing alloys is included.
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I. INTRODUCTION

A. Purpose

Until recently, the study of the mechanism of alloy solidification has received relatively little quantitative consideration. The reason for this apparent neglect is the importance of a number of independent solidification variables, most of which are impossible to control during the freezing of an ordinary casting. During the solidification of an alloy, the following factors may vary over wide ranges:

1. Heat flow and temperature gradients.
2. Liquid metal composition.
3. Convection and other liquid metal flow.
4. Linear velocity of freezing.
5. The tendency and ability for nucleation.

The apparatus described here was designed and constructed to control the above factors during the solidification of a significant portion of an ingot, in order to be able to study independently the effect of variation of known quantities on alloy solidification. The experimental procedure described was designed to determine the effects of freezing rate and alloy composition on segregation in metals frozen under conditions of turbulent liquid agitation.

B. Factors Affecting Segregation of Solute Atoms on Solidification

Metals, generally possessing a different solubility of foreign atoms in the liquid and solid state, tend to undergo a redistribution of these atoms on solidification. This redistribution, or segregation,
results primarily from diffusion towards or away from a liquid-solid interface, although the position of the segregate may be altered by macroscopic movement of liquid or solid within the casting.

Inverse segregation, exudation, and certain types of macrosegregation result from movement of liquid or solid, as well as from liquid diffusion, while microsegregation, types of macrosegregation, banding in single crystals, coring, etc. result solely from diffusion toward or away from a liquid-solid interface.

This second type of segregation has been the subject of a number of analytical studies and is the type of segregation of concern here. The apparatus constructed permits metal solidification in the manner indicated in Figure 1. A liquid-solid interface is moved at constant velocity \( \mathcal{V} \), under constant temperature gradients into a stirred liquid of sufficiently large volume that the liquid concentration remains essentially constant.

If an alloy in which \( K = \frac{C_s}{C_0} < 1 \) (Figure 2) is solidified with a plane front in this system, the solid forming must be generally less rich in solute than the liquid, and have a minimum solute concentration of \( C_s \) as predicted by the phase diagram.

Conservation of mass then requires that there be a net movement of solute atoms away from the interface, and that if diffusion is a barrier, there be a liquid concentration gradient (Figure 3).

The actual concentration of the liquid adjacent the interface is then some value \( C_1 \), greater than \( C_s \). If the partition ratio is assumed constant, and the equilibrium value of the partition ratio
attained, the solid concentration is:

\[ C_s = \kappa C_i \]

Conservation of solute, however, requires that:

\[ C_s^{(\text{max})} = C_0 \]

The solid forming, then, must be some composition between \( C_s \) and \( C_0 \). Its exact value must depend on the partition ratio, and the build-up of solute atoms in front of the interface.

Systems studied were aluminum-rich, aluminum-copper, and aluminum-zinc alloys. The segregation coefficient \( \kappa \) is essentially constant in the composition ranges studied and is less than one. Because solid-state diffusion is orders of magnitude less than liquid diffusion, it is neglected.
II. LITERATURE SURVEY

A. Analyses of Segregation of Solute Atoms on Solidification

A number of mathematical analyses have considered the effect of solidification variables on segregation in idealized systems. These analyses will be considered according to the assumptions involved.

1. Analyses Involving the Assumption of Perfect Liquid Diffusion

Gulliver,\(^1\) Scheuer,\(^2\) Hayes and Chipman,\(^3\) and others, have investigated mathematically the segregation of solute atoms in normal freezing, assuming perfect liquid diffusion, constant \(\kappa\), and negligible solid-state diffusion. Pfann\(^4\) has extended this treatment to the unidirectional solidification of a molten charge, and derived the equation:

\[
\frac{C_s}{C'_0} = \kappa (1 - \delta)^{K-1}
\]  

(1)

where \(C_s\) = concentration of solute atoms in solid,

\(C'_0\) = initial concentration of solute atoms in the liquid,

\(\delta\) = fraction of charge solidified,

\(\kappa\) = segregation coefficient.

This equation is similar in form to those derived by the preceding authors and indicates, with these assumptions, no effect of rate of freezing (rate of liquid-solid interface movement) on segregation.

2. Analyses Involving Effect of Imperfect Liquid Diffusion

A number of recent analyses of solute segregation during
solidification have shown that the assumption of perfect liquid diffusion during solidification is not valid even under very slow freezing rates. The effect of imperfect liquid diffusion is the build-up of solute concentration in the liquid at the liquid-solid interface. If, then, the partition ratio between the solid and liquid at the interface is assumed to hold, the concentration of solute in the freezing solid must be higher than that value calculated assuming perfect liquid diffusion.

It is convenient to consider a long molten charge of constant cross-sectional area, with a plane-front solid interface moving at constant velocity along the length of the rod (Figure 1). With this model, Tiller, et. al.\textsuperscript{5} have shown that if no convection currents or stirring exist in the liquid, the composition of the freezing solid must rise to the composition of melt from which it is freezing. That is, with no stirring, no segregation can result from directional freezing (with the exception of the initial and final transitory regions). Tiller shows that when steady-state concentration distributions are reached, at constant freezing velocity $\omega$, the concentration distribution in the liquid is:

$$C_c = C_o \left(1 + \frac{1 - \kappa}{\kappa} \omega \mu \left(-\frac{\partial}{\partial x}\right)\right)$$

(2)

At point $x$ in the liquid, $x = \text{distance from liquid-solid interface}; \kappa = \text{partition ratio}, \omega = \text{diffusion constant of solute in liquid solvent},$ and $\omega = \text{velocity}$.
Implicit in equation (2) are the following assumptions:

a. Constant interface velocity.
b. Constant partition ratio.
c. Equilibrium of partition ratio attained.
d. Diffusion coefficient is not a function of concentration.
e. Constant cross-sectional area of freezing.
f. Solid diffusion is negligible.
g. The liquid bath is quiescent.

Wagner has treated the problem in a more general manner.

With similar assumptions to those listed above, but without the restriction of a quiescent bath, he shows that:

\[
\frac{C_s}{C_0} = \frac{\kappa}{1 - \frac{\delta_{H'f}}{\delta} (1 - \kappa)}
\]  

(3)

where \( \kappa \) = the partition ratio,

\( C_s \) = concentration of solute in solid,

\( C_0 \) = concentration of solid in bulk liquid,

\( \omega \) = velocity of freezing of plane-front interface,

\( D \) = diffusion coefficient

\( \delta_{H'f} \) = "effective thickness of the diffusion boundary layer".

\( \delta_{H'f} \) is determined by the interplay of liquid currents past the interface and by diffusion. The term \( \frac{C_s}{C_0} \) may be considered to be an "effective segregation coefficient". Thus, it is seen that the following factors will tend to decrease the "effective segregation coefficient" (increase segregation):
a. Small segregation coefficient.

b. High diffusion coefficient.

c. Low rates of solidification velocity.

d. Low value of "effective boundary layer", or high rates of liquid agitation.

3. Analyses Involving Incomplete Establishment of the Partition Ratio

The preceding analyses have involved the assumption that the partition ratio between solute atoms in the solid and in the liquid at the interface is the segregation coefficient, \( \kappa \), as established from the phase diagram. Limited experimental evidence\(^7\) indicates that the ratio \( \frac{C_s}{C_i'} \) (Figure 1) may not be equal to \( \kappa \), and may depend on solidification rate and crystal orientation. A mechanism for this change of segregation factor with growth rate has been described by Wagner\(^8\) and Hall.\(^7\)

The mechanism postulates that a crystal, solidifying in a melt, has a monatomic surface layer of solute concentration \( C_s' \) in equilibrium with the melt. A value of the surface layer partition ratio may then be written \( \kappa' = \frac{C_s'}{C_o} \). A similar partition ratio for the atomic planes immediately beneath the surface may then be written as \( \kappa = \frac{C_s}{C_o} \), where \( \kappa \) is generally less than \( \kappa' \), and \( \kappa \) is the value of the equilibrium constant as obtained from the phase diagram.

After each surface layer is covered by a new one, the composition of the covered layer will tend to approach that value predicted by the standard partition ratio. If, however, new planes are added too
fast for diffusion to occur over even one atomic plane, then partition will not be that predicted by the segregation coefficient but will approach that determined by $k'$.

B. Experimental Investigations of the Segregation of Solute Atoms in Solidification of Metals

Several recent papers present experimental data on the segregation of solute atoms on solidification. Pfann and Olsen\(^9\) determined the segregation of antimony in germanium in zone melting. Solute concentration was the order of $10^{16}$ atoms of antimony per cubic centimeter of solute. A calculated, or effective, segregation coefficient was determined to be $k = .2$, as compared with the theoretical segregation coefficient of $k = .06$.

Dowd and Rouse\(^{10}\) directionally solidified a germanium crystal in a melt stirred with argon. Rate of growth was 2.5 centimeters per hour, and solute was indium. The calculated segregation coefficient was $k = 1.25 \pm 10^{-3}$, as compared with the phase diagram value of $1 \times 10^{-3}$, as determined by Pfann\(^{11}\).

Hall\(^7\) has showed the calculated effective segregation coefficient of antimony in germanium to vary with velocity of freezing. At higher velocities, he found, further, an effect of crystal orientation on the segregation factor. No effect of freezing velocity on the segregation of gallium in germanium was observed.

Segregation in dendritically freezing alloys is a vastly more complex case than that in plane-front solidification. It will be discussed
further in Part V, and several papers briefly mentioned here. It is common experience that considerable segregation results in a great number of dendritically freezing alloys. Some quantitative data have been published.\textsuperscript{2,12} Michael\textsuperscript{12} has found, in aluminum-copper alloys, a degree of segregation at certain rates of cooling that approach that calculated assuming perfect liquid diffusion.
III. APPARATUS

A. Basic Description

The apparatus used was designed to meet the basic criteria outlined in the discussion. Essentially, it was required that the apparatus have control over heat flow into and out of the melt, temperature gradients in the solid, rate of solidification, and stirring of the liquid metal.

Both stirring and power were produced by low frequency induction, mechanical stirring devices being found unfeasible due to materials limitations. Figures 5 and 6 show the overall design of the final apparatus and auxiliary measuring equipment. In Figure 7, the basic elements are shown schematically. Heat is supplied by an induction coil to a charge contained in an insulated crucible. The heat input is balanced by the heat abstracted by conduction through the solid ingot, which is cooled by a water spray. Both coil and spray may be moved at constant speed upwards, moving the liquid-solid interface upwards under constant heat flow and temperature gradients.

B. Electrical Design

1. General Considerations

In order to meet the desired condition of high liquid agitation without putting more than the required power into the melt, an unusual electrical design was necessary. Stated simply, induction stirring depends on the square of the coil current, and for maximum stirring, maximum coil current per unit power in the melt is desired.
The power in the melt is given by the expression:

$$P = \frac{1.77 \times 10^{-10} \omega a \sqrt{\mu} \mu Pa (N \lambda)^2}{\ell} \cdot \gamma_a.$$ \hspace{1cm} (1)

where

- $P$ = power in charge, kilowatts,
- $a$ = charge radius, cm.,
- $\mu$ = magnetic permeability,
- $\rho_a$ = charge resistivity, ohm-cm.,
- $N$ = number of turns in coil,
- $\lambda$ = coil current,
- $\ell$ = coil length,
- $F_a$ = correction factor,
- $\gamma_a$ = correction factor.

A generalization for the stirring force may be written:

$$\text{Stirring Force} = (\text{constant}) \frac{(N \lambda)^2}{\ell}.$$ \hspace{1cm} (2)

From equations (1) and (2), power, as well as stirring force, is proportional to $\frac{(N \lambda)^2}{\ell}$. Both $N$ and $\ell$ were fixed by the previously discussed conditions in Section 2. The other factors in equation (2) were, in general, chosen to minimize the power input per unit current. In this way, it was possible to take advantage of the square effect of current on stirring force while minimizing power development in the charge.

The frequency chosen was 960 cycles per second, because it was the lowest frequency readily available. The charge resistivity, $\rho_a$, 

being a property of the alloy system, could not be chosen. The remaining factors open to variation were coil radius and charge radius, which, in addition, determine $\gamma_\omega$ and $F_\omega$ when all other factors are fixed.

Thus far, only the stirring forces have been considered and not the motion caused by the forces. The stirring action is known to vary inversely as the density of the molten liquid\textsuperscript{13} and must also be related to hydromechanical properties of the liquid as well as to the size of the container. Unfortunately, no straightforward analysis can be made showing the quantitative relation of bath motion to stirring forces and other pertinent quantities. However, a qualitative analysis of the magnetic field and induced currents in the charge indicates that the stirring pattern is similar to that shown in Figure 7. No method was devised to measure the stirring velocity. The motion, however, was so vigorous that a pressure head of approximately 5 inches of molten alloy had to be maintained in order to keep the liquid from rising out of the crucible.

The same electromagnetic forces which cause stirring also cause the so-called "pinch effect". This effect tends to decrease the charge diameter, which in turn lowers the power input at a given current and therefore disrupts steady-state conditions. A sufficient pressure head of molten alloy combats this effect by forcing the liquid to assume the diameter of the crucible.

It is expected that the smaller the charge (or crucible) radius, the less will be the motion for a given stirring force. Several
different charge radii were tried, but no visual difference in bath motion was noted. Consequently, a convenient charge radius ($a = 1.65$ cm.) was chosen.

2. **Overall Circuit Design**

In addition to the electrical considerations governing coil design, coil dimensions were limited by apparatus considerations. Turns per unit length were limited by a minimum necessary cooling water flow rate, and total turns limited by a maximum desirable coil length. Too long a coil was undesirable since, during coil movement upwards, the top of the coil could not be permitted to pass the top of the liquid level. With the charge only partly in the coil, heating efficiency may be expected to drop, and steady-state heat flow disrupted. The design adopted was a coil 9.5 centimeters in diameter by 5.5 centimeters long, with a total of 13 turns.

A coil and charge assembly of the type adopted has too low an impedance to be directly connected to the commercial 960 cycle alternator used. In order to solve this problem, the circuit shown in Figure 8 was used. The movable stirring coil is connected in series with a large, empty induction furnace, the combination being connected in parallel with a capacitor bank for power factor correction. This circuit has two distinct advantages: (1) High currents (approximately 1000 amperes) can be passed through the stirring coil without drawing appreciable current from the alternator since the large coil has a power factor very much less than one. (2) The impedance of the large coil, which is very much greater than that of the small coil,
fixes the impedance of the coil branch at a value which is large enough to connect directly to a commercial alternator. The voltage required by such an impedance then falls in a range which is accurately controlled by the alternator control circuit. Precise control of power input is a primary consideration, since a delicate balance with power withdrawn must be maintained. Since resistivity in the solid state is approximately one half that in the liquid state, the liquid-solid interface must not move through the coil if constant power is to be maintained.

C. Furnace Design

1. Crucible and Plug

A photograph of the crucible and cooling plug in position for a heat is shown in Figure 5. The crucible consists of a zirconia tube, 1.30 inches (± 0.05 inch) inside diameter by 10 inches long. Surrounding the zirconia tube is a rammed refractory, held in place with a sixty-four millimeter (inside diameter) vycor tube. The cooling plug, shown beneath the crucible, is a wrought 2S aluminum rod, machined to 1.30 inch diameter.

The plug extends one inch into the crucible, the top inch being sanded before each heat to permit clearance for thermal expansion. Plug and crucible were fixed to the frame before each heat, and centered with respect to the water spray and heating coil. The thermocouple shown was embedded in a one-eighth inch hole immediately below the crucible and extending to the center of the ingot.
2. Heat Extraction and Solidification

The effects of thermal variables on solidification will be discussed in Part C, and only mechanical design of the essential parts described here.

Heat was removed by the water spray shown in Figure 5, which was maintained a fixed distance below the coil. Both coil and spray were mounted on a threaded shaft, rotation of which causes upward movement of the coil spray assemblies. The shaft was driven by a variable speed, direct-current motor through a gear reducer and set of bevel gears. Interchangeable bevel gears could be used for total reductions of 1800 to 1, 3600 to 1, or 5400 to 1.

3. Auxiliary Equipment

The motor, drive screw, and attached assemblies were housed in the frame shown in Figure 6. Also mounted on the frame were:

a. Water control valve.
b. Water flowmeter.
c. Motor speed resistor.
d. Electrical connections for power and motor.
e. Holding mount for liquid-solid interface measuring rod.
f. Coil indicator for reading the position of the coil.

An alternating current ammeter in conjunction with a current transformer was used to obtain reproducible coil currents.

D. Thermal Design

1. General
The heat flow characteristics of the apparatus can best be described with reference to Figure 9. The coil, water spray, and liquid-solid interface are shown schematically, and the temperature distribution throughout the length is plotted for steady-state heat flow.

Consider first the condition of water and coil stationary with respect to the ingot. If heat input exactly balances heat extraction, no solidification or melting can occur, although the temperature gradients shown must be present in the solid. The temperature gradients may be increased by decreasing the coil-spray distance, and adjusting power until at steady state the liquid-solid interface is again maintained at the original position. The increased heat flow must increase temperature gradients, but at steady state no melting or solidification will occur.

Consider now the coil and spray moving upwards at a constant rate, \( \nu \). If heat input, heat extraction, and the thermal resistance of the solidifying ingot remain constant, then the position of the liquid-solid interface must remain constant with respect to the coil, and solidification upwards is occurring at a rate \( \nu \). Note heat extraction must now be equal to heat input plus heat of fusion of the solidifying metal. Again, temperature gradients may be varied independently of freezing velocity by varying the coil-water spray distance and power input. Further, the temperature gradients in the solid must remain constant throughout solidification.

The thermal design of the apparatus was based on maintaining
constant temperature gradients in the solid, a constant linear freezing velocity $u$, and maintaining the interface a constant distance behind the stirring source (induction coil). Hence, the requirements were those mentioned above:

a. Constant heat input.

b. Constant heat extraction and constant thermal resistance of ingot.

c. Constant movement of water spray-coil assemblies.

These will be discussed below.

2. Maintenance of Constant Heat Input

Power to the coil may be considered constant. The power source used was a 960 cycle, 175 kilowatt motor generator set with an amphidyne control unit. Power into the charge, however, depends upon the charge geometry and resistivity as described previously. Two effects made precautions necessary to maintain heat input constant:

a. "Pinch" Effect

The strong electromagnetic field causing stirring also tended to cause "pinching" of the liquid aluminum. The field, in effect, tended to reduce the charge diameter within the coil, with a consequent reduction in power input. A total liquid head of approximately 5 inches was necessary to prevent this pinching.

b. Effect of Interface Position

Because of the different inductive characteristics of liquid and solid aluminum, it was found necessary to maintain the interface below the coil to maintain constant power input.
A second source of heat input may be considered to be heat of fusion. At the solidification rates used, however, the heat of fusion is completely negligible, with respect to the total power input.

3. Maintenance of Constant Heat Extraction and Constant Thermal Resistance of the Plug

a. Constant Heat Extraction

Heat removal from the liquid and solid ingot may be through three possible paths: the top of the liquid, radial heat losses from the plug, and at the water spray.

Heat losses from the top of the liquid (and radial heat losses through the crucible) may be considered to be constant because of constant temperature and constant surface area. It was necessary to abandon liquid temperature measurement during solidification, however, since solid metal tended to build up on the thermocouple, adding radiating surface, and affecting the heat balance.

Radial heat losses from the cooling plug, if appreciable, would result in gradual deceleration of interface velocity during solidification. At the temperature used, however, these heat losses were negligible, and heat flow may be considered to be essentially axial.

With the exception of heat losses from the top of the liquid, then, heat flow is entirely through the plug, cooled at the water spray. It may be presumed that a sufficiently high water flow rate will maintain the point of contact of water and ingot at essentially water temperature, and any further increase in water flow will have no effect on rate of
heat removal or temperature gradients. Experimentally, no difference in interface position during trial heats was observed when water flow rate was varied from .68 to 1.8 gallons per minute. The flow rate on all subsequent heats was approximately 1.8 gallons per minute.

Heat flow, then, is entirely axial, and the temperature in the solidifying ingot must vary from the melting point at the liquid-solid interface to water temperature at the water spray (Figure 9). The temperature variation along the ingot will then be linear if the thermal resistance of the plug remains constant and is not a function of temperature. (The thermal conductivity of aluminum varies very slightly with temperature.)

b. **Constant Thermal Resistance**

The sole barrier to heat flow through the solid plug has been shown to be the thermal resistance of the plug itself. Affecting this thermal resistance are contact resistance between ingot and plug, thermal conductivity of ingot and plug, cross-sectional area of ingot and plug.

1. **Contact Resistance Between Ingot and Plug**

Elimination of contact resistance between the melt and plug was found essential for two reasons. First, a variation of contact resistance during an individual run, due to solidification shrinkage, caused erratic interface movement. Second, variation of contact resistance from run to run prevented exact reproducibility of temperature gradients.

Before solidification of each heat was begun, and after
the charge was melted, the power and coil position was held constant until the top of the plug was melted, and the plug became an integral part of the heat.

A plot of temperature, at the base of the crucible, versus time, is given in Figure 10. Note the marked rise in temperature occurring when contact resistance is removed.

(2) **Effect of Plug Diameter and Thermal Conductivity**

Since heat flow was axial, freezing rate low, and plug conductivity the only barrier to heat flow, temperature gradients are expected to be constant throughout the plug and solidifying ingot if the plug and ingot have the same thermal conductivity and diameter.

Moreover, if the temperature gradients remain constant with time, the interface must move at exactly the same velocity as the coolant.

If the thermal conductivity, or cross-sectional area of the solidifying metal is constant, but different from that of the plug, interface velocity is expected to be constant but different from that of the water spray. Hence, in the more highly alloyed heats, where the thermal conductivity of the solidifying ingot was considerably less than that of the plug, interface velocity was found to be somewhat slower than water spray velocity.

On all heats of a given alloy system, the same 2S plug, 1.30 inches in diameter, was used as cooling plug. Crucible sizes varied within .05 inch, and the thermal conductivities of the alloys varied slightly. It was possible, however, in all alloys studied, to
achieve a linear freezing rate, and in all but the highly alloyed heats, to maintain the interface a nearly constant distance behind the coil.

4. **Summary and Presentation of Typical Thermal Data**

Heat flow, with the exception of constant heat losses at the top of the liquid, has been shown to be entirely axial through the plug to the water spray. Heat of fusion of solidifying metal has been shown to be constant. Rate of interface movement is then independent of total power and dependent only on rate of movement of water spray, and any change in thermal resistance of the plug that may occur during solidification. At steady-state heat flow, rate of drop of temperature at any point in the plug must be constant with time if temperature gradients are linear, and the rate of travel of the water spray with time is constant.

Figure 11 plots position of the coil-spray assembly versus time for a 1.5 per cent copper heat. Note the time lag before constant interface velocity is attained. Also plotted in Figure 11 is temperature at the base of the crucible versus time. When the interface travel becomes linear after approximately twelve minutes, the rate of temperature drop with time is constant.

Figure 12 plots similar data for an aluminum 5 per cent zinc heat run at a velocity approximately six times that of the heat of Figure 13. Note the essential characteristics are the same. It was found that in the rather low alloy content ranges used for most of the work, the effect of the alloy content on the thermal conductivity was
not sufficient to appreciably affect rate of interface travel.

Figure 13 shows the temperature distribution in the plug of a 1.5 per cent copper heat at several times. Note the lines are parallel for times above 12 minutes.
IV. PROCEDURE

A. General

The overall procedure used was determined by the following factors:

1. Required purity of alloys.

2. Maintenance of constant interface movement, temperature gradients, and stirring pattern over a period long enough to obtain an ingot of size suitable for examination.


B. Preparation of Melt and Contamination

1. Charge

Metals used were high-purity aluminum (99.99 per cent), electrolytic copper (99.92 per cent), and chemical purity zinc (99.97 per cent). Alloying was performed directly in the apparatus for each individual heat. Pure aluminum was melted in the crucible and the alloy added, homogenization being obtained by the induction stirring. The copper was added as master alloy, 50 per cent copper-50 per cent aluminum.

2. Contamination from Cooling Plug

Before solidification, a portion of the cooling plug was melted to remove contact resistance. That portion of the plug (one-quarter to one-half inch) therefore became an integral part of the melt. For reasons discussed previously, a wrought 2S plug was used. Contamination of the melt from the 2S plug was prevented by running several pure aluminum "wash heats". In each "wash heat", the plug was melted to a
depth of three-quarters of an inch and purified by dilution with the high-purity aluminum melt. Subsequent segregation on controlled freezing further purified the top portion of the plug. The same plug was used throughout the study of a given alloy system.

3. **Contamination from Other Sources**

With the exception of the zirconia crucible, the remaining possible source of contamination was the steel measuring rod. From thermal and mechanical considerations, one-sixteenth inch steel rod was found the most satisfactory interface measuring rod. Contamination was minimized in two ways: A heavy alumina wash was applied to the rods, and the measuring rod was used as sparingly as possible, generally not more than four or five times during the course of a heat.

C. **Effect of Starting Conditions on Interface Movement**

The equilibrium interface velocity and position with respect to the coil is expected to be independent of the thermal conditions existing at the start of solidification. Experimentally, this was found to be true. A standard procedure was adopted, however, which enabled the condition of constant interface velocity to be reached in a reasonable length of time.

Solidification was started in the following manner: Coil position was one inch above crucible bottom (measured from coil bottom). The liquid-solid interface was melted to a position corresponding to approximately the coil bottom. Power was reduced to running power, and the drive motor started. Figure 11 presents a typical plot of
interface and coil position versus time. Note that constant interface velocity was attained after approximately 12 minutes.

D. **Maintenance of Interface Close to Stirring Source**

The interface position with respect to the coil was fixed with a view to two opposing factors. It was desirable to have the interface as close to the coil (stirring source) as possible, but it was found extremely difficult to maintain constant interface velocity when the interface was too close to the coil field.

With constant plug size, crucible size, composition, and with constant coil-water spray distance, interface position with respect to the coil was controlled by:

1. Power.
2. Thermal conductivity of solidifying ingot.
3. Melting point of solidifying ingot.

With the exception of the more highly alloyed heats, the power level was maintained the same for all heats, to maintain stirring force constant, and in all heats it was possible to maintain the interface at a position of between one-half and one inch below the coil, over a sufficiently long period of time to obtain the desired ingot length.

E. **Measurements During Solidification**

During meltdown, interface position was estimated from the temperature reading of a thermocouple embedded in the cooling plug at the bottom of the crucible. For each heat, the solid plug extended one
inch up into the crucible. The time at which melting of the top of
the plug occurred (removal of contact resistance) was determined from
a nearly discontinuous rise of the thermocouple reading (Figure 10).

Coil and water spray position were fixed initially with respect
to each other and also with respect to the thermocouple at the cruci-
ble bottom. They were measured at intervals throughout the heat by
readings from the coil indicator scale.

Motor drive was started when the interface was close to the bottom
of the coil as estimated from temperature and checked by the interface
measuring rod. Interface position was measured several times at the
start and completion of each heat, and temperature measured at fre-
quent intervals throughout the heat.

As expected from axial heat flow conditions, when the interface
was moving with constant velocity, the rate of change of temperature
at the crucible base was observed to be constant (Figure 11).

Power and water flow rate were measured and held constant through-
out the bulk of the experimental work.

F. Physical and Chemical Tests

After each heat, the ingot and plug were removed from the cruci-
ble. The ingot was cut from the plug a distance of one inch above
the thermocouple, and the plug re-used. The ingot was sectioned and
one-half polished for macro- and micro-graphic examination. An
eighth inch thick section, three-quarters of an inch below the top of
the directionally frozen portion of the ingot, was used for chemical
analysis. The as-cast surface of this section was removed by sanding before analysis.

A liquid sample was taken of each heat, shortly before constant velocity of interface movement was achieved. By sampling the liquid at this time, it was possible to avoid disturbing steady-state conditions later in the heat.

Note from Figure 11, however, that the liquid analysis was taken at time (A) and the solid at time (B). A calculation used subsequently is:

\[ \frac{C_{L}}{C_{S}} = \frac{C_{S}}{C_{o}} \]

where \( C_{o} \) is equal to the liquid composition and \( C_{S} \) the solid composition. This calculation is strictly true only if \( C_{o} \) and \( C_{S} \) are the compositions of the liquid and solid at the same time. It is considered, however, that \( C_{o} \) is essentially constant throughout the heat, since only a small portion of the ingot is solidified.

Tables II through V present, in the second column, the calculated enrichment in \( C_{o} \) during solidification between time (A) and (B) (Figure 12). It is seen to be quite small. Calculations of this correction were made by means of the modified Pfann's Equation discussed in Part D of Section V.
V. RESULTS AND DISCUSSION

A. General

Segregation was investigated in a series of experimental aluminum-base aluminum-copper alloys and aluminum-zinc alloys. Alloy content was varied up to 10 per cent in the case of copper, and up to 50 per cent in the case of zinc. Temperature gradients and heat flow were maintained essentially constant throughout solidification in all heats. Interface velocity was varied in the range of from $0.4 \times 10^{-3}$ centimeters per second to $3.0 \times 10^{-3}$ centimeters per second. Ingot length frozen was between one, and one and one-half inches.

The effect of solidification variables on ingot structure has been discussed generally by Wagner and Tiller, et. al., and with particular reference to the system used here, by Hucke. Ingots with sufficiently low interface velocities and alloy content solidified to produce a macrostructure similar to that seen in columnar cast structures (Figures 14 and 15). In none of the "columnar" grains, however, could entrapped second phase be discerned metallographically. Figure 16 presents a typical microstructure of the slowly frozen, coarse-grained castings. Figure 17 shows, for comparison, the region at the top of the directionally frozen portion of the casting, where the power was turned off and the remaining metal quickly frozen. Note the second phase in the microstructure of Figure 17, and the lack of it in the microstructure of Figure 16.

From the lack of entrapped second phase, it was assumed that
dendrite formation was effectively suppressed. Hucke has analyzed
the thermal stability of the solidification front and shown that this
front in the coarse grain heats must be essentially smooth, or "plane".

In the subsequent section, the following assumptions will be made
for mathematical analysis:

1. Liquid concentration ($C_o$) constant.
2. Equilibrium of partition ratio attained.
3. Partition ratio independent of concentration.
4. Diffusion constant D independent of concentration when con-
   centration is expressed in weight per cent.
5. Solidification contraction negligible.

B. **Segregation with Plane Front Interface Movement**

Segregation data obtained from heat frozen with plane front are
presented in Tables II through V. Analysis requires some discussion
of the important variables affecting the data.

With plane front freezing, and after an initial transition period,
Tiller, et. al. have shown that no segregation can result in a system
without liquid agitation. Wagner has demonstrated that liquid agita-
tion can lead to significant segregation at low freezing rates and
analyzes mathematically several special cases. He points out that if
the fluid velocity distribution at a liquid-solid interface is known,
the concentration distribution may for certain cases be calculated, as
can the effective segregation.

A quantitative picture of the velocity distribution at the interface
in the system used was not attempted, and appears difficult to obtain due to the complex nature of the stirring. Fluid-flow theory, however, shows that if a turbulently flowing liquid wets a solid in contact, then there is a laminar region adjacent to the liquid-solid interface. In this laminar region, the velocity is zero directly at the liquid-solid interface, and increases rapidly with distance away. In the laminar region, near the interface, diffusion of solute is only by molecular diffusion, and the concentration gradient at the interface \( x = 0 \) must be:

\[
\left( \frac{\partial c}{\partial x} \right)_{x=0} = -\frac{1}{D} \frac{dm}{d\tau} \quad (1)
\]

The mass transfer is given by the amount of solute swept out of a thin layer per unit time and is:

\[
\frac{dm}{d\tau} = + A \omega c_i (1-K) \quad (2)
\]

The concentration gradient is then rigorously determined as:

\[
\left( \frac{\partial c}{\partial x} \right)_{x=0} = -\frac{A \omega c_i (1-K)}{D} \quad (3)
\]

A small distance away from the interface, however, the eddy diffusivity of solute becomes of rapidly greater importance and the solute concentration distribution is no longer readily calculable. In a system of violent stirring, there is some point a distance away from the interface where the eddy diffusivity may be considered to be essentially infinite. That is, there is some point where the violent
stirring may be considered to have essentially reduced the concentration distribution in the boundary layer to zero. This is shown schematically in Figure 18, with the extremity of the boundary layer indicated by the letter $l$.

Although the concentration distribution between the interface and the fully turbulent region is not known, the gradient at the interface is known and Wagner's concept of an "effective boundary layer" may be introduced. Wagner has shown that the segregation may be described by the equation:

$$\frac{C_S}{C_0} = \frac{K}{1 - \delta_{eff} \frac{\nu}{D} (1 - \kappa)}$$  \hspace{1cm} (4)

Wagner's equation may be written in the form:

$$\frac{K}{K_{eff}} = 1 - \delta_{eff} \frac{\nu}{D} (1 - \kappa)$$  \hspace{1cm} (5)

where

$$K_{eff} = \frac{C_S}{C_0}$$

$K_{eff}$ may be considered an "effective segregation factor", and its significance is the following: In idealized, perfect liquid diffusion solidification, the segregation coefficient is a measure of the degree of segregation obtainable. For systems in which no segregation results, $K = 1$, and for systems exhibiting complete segregation (no solid solubility), $K = 0$. Similarly, when a liquid diffusion barrier increases the solid composition above that predicted by the phase diagram, an "effective segregation factor" may be used to describe the
$\kappa_{\text{eff}}$ showed a general increase with increasing velocity in the lower ranges. The heat at a velocity above about 1.4 centimeters per second showed little further increase in $\kappa_{\text{eff}}$, as did the copper heats. Data are shown in Table III and Figure 20. The zinc data were somewhat more scattered, and scatter in both alloys is discussed subsequently.

A physical picture which may be built of a boundary layer of length $l$ (Figure 18) extending from the interface to a point where overall liquid diffusion is essentially infinite has been described. This picture suggests a constant boundary layer, independent of velocity of interface movement at constant stirring.

The concept of an "effective boundary layer", however, is a mathematical convenience and there is no reason to expect it to be completely independent of velocity. However, in several specialized cases of velocity distribution past a liquid-solid freezing interface, Wagner has indicated that $\delta_{\text{eff}}$ is essentially constant at low rates of freezing and decreases at higher rates of freezing.

The effect of velocity on the "effective boundary layer" may be shown further by considering an idealized boundary layer of length $l'$, fixed by stirring. At a distance $l'$, the concentration distribution of the liquid is considered to be reduced to zero, and mass transfer within the boundary layer is considered to be only by molecular diffusion. This model is equivalent to an assumption of a laminar zone of length $l$, in which eddy diffusivity is negligible, and outside of this a fully turbulent region in which eddy diffusivity is
essentially infinite. A model of this is shown in Figure 18, if the laminar region is assumed to extend to the length \( l \), and the liquid is in fully turbulent flow at all points beyond \( l \).

With this model, an equation may be derived for the effective segregation factor (Appendix A). This equation may be written in a form similar to that of Wagner's:

\[
\frac{K}{K_{\text{eff}}} = 1 - \left(1 - e^{-\frac{\omega}{D'}} \right) (1 - K) \tag{6}
\]

where \( l \) is the boundary layer thickness, dependent only on stirring.

Comparison of equation (6) with equation (5) indicates that if a physical boundary layer \( l' \) be considered constant, then at high rates of stirring (low \( l' \)), low velocities, and high rates of molecular diffusion, equation (6) reduces to the form of equation (5), and \( \delta_{\text{eff}} \) may be considered equal to \( l' \).

Further, substitution of equation (6) in equation (5) provides the relation:

\[
\delta_{\text{eff}} = \frac{\omega}{D'} \left(1 - e^{-\frac{\omega}{D'}} \right) \tag{7}
\]

and it is seen that if the term \( \frac{\omega}{D'} \) is large, then \( \delta_{\text{eff}} \) must decrease with increasing interface velocity.

Data from both the zinc and copper alloy coarse grain heats are plotted in Figure 20. The abscissa is \( \delta_{\text{eff}} \frac{\omega}{D} (1 - K) \), and the ordinate \( \frac{K}{K_{\text{eff}}} \). Note that a straight line drawn from \( \frac{K}{K_{\text{eff}}} = 1 \), and \( \delta_{\text{eff}} \frac{\omega}{D} (1 - K) = 0 \), has the slope \( -\delta_{\text{eff}} \). If \( \delta_{\text{eff}} \) is truly
constant, experimental data, regardless of alloy or solidification velocity, should fall on the line.

In Figure 20, the best straight line has been drawn through the experimental points for both copper and zinc. The line has a slope of approximately minus .03 centimeter; that is, the "effective boundary layer" for these heats may be considered to be .03 centimeter.

Note the straight line must stop when \( \frac{K}{K_{c_0}} = \left( \frac{K}{K_{c_0}} \right)_{H_0} \); that is, when no segregation is occurring. The minimum value of \( \frac{K}{K_{c_0}} \) is .445 for zinc and .171 for copper. For heats run at higher values, \( \frac{K}{K_{c_0}} \) versus \( \frac{u}{\theta} (1 - \kappa) \) must be a horizontal line.

Note the points at these higher values of \( \frac{u}{\theta} (1 - \kappa) \). All three were run at approximately the same velocity \((3 \times 10^{-3} \text{ centimeters per second})\). All three points, when substituted in equation (5), yield an effective boundary layer of .02 centimeter as compared with the average value of .03 centimeter for heats solidified at lower velocities.

The apparent conclusion then is that for a given base metal and stirring conditions, \( \frac{u}{\delta} \) may be considered a constant in the apparatus used at low rates of freezing. Segregation may then be predicted from the Wagner analysis. At higher rates of freezing, however, the effective boundary becomes smaller, and segregation is higher than that predicted by the Wagner analysis.

Possible contributing factors to the scatter in data of both the aluminum-copper and aluminum-zinc heats are the following:
1. Distance of interface from stirring source.

The interface distance from the stirring source was kept constant from heat to heat to within approximately ± 1/4 inch. No apparent correlation between this distance and $K_{ij}$ was observed.

2. Striations.

In a number of macroetched specimens, striations were present, indicating possible slight variations in cooling rate or power input, and hence in $K_{ij}$. In no case, however, was second phase observed metallographically.

3. Lack of perfectly plane interface.

Rutter, in plane front solidification, has observed the appearance of small "knobs" on the interface at certain growth rates. As discussed by Huke, these knobs, in the apparatus used, are expected to be small, if they exist at all. They may, however, sufficiently increase the surface area or disturb the flow pattern to affect $K_{ij}$.

4. Variation of liquid diffusion constants with concentration.

5. Variation of segregation coefficient $K$ with crystal orientation and freezing rate.

6. Chemical analysis.

C. **Segregation in Fine Grained Ingots**

Macrosegregation was measured in a number of heats frozen under conditions promoting fine grain formation. It was found that at sufficiently high values of interface velocity and solute concentration, a stable plane front interface was no longer maintained and the resulting
structure was comprised of fine grains. Conditions affecting the
critical values of velocity and concentration where stability break-
down occurs have been discussed by Hucke.\textsuperscript{14} Several typical macro-
structures of fine grain heats are shown in Figures 21 and 22.

A typical microstructure of a fine grain heat is shown in Figure
23. Deep etching did not reveal a fully developed dendritic struct-
ure. However, entrapped second phase was apparent in the aluminum-
copper alloys, generally at the grain boundaries, extending into the
grains.

As with plane front solidification, an effective segregation factor
\[ K_{eff} = \frac{C_s}{C_o} \]
will be used to describe the macrosegregation. It is
pertinent to note that with fine grain heats, since the solid is not
homogeneous, the effective segregation factor might better be written:
\[ K_{eff} = \frac{C_s \text{ average}}{C_o} \]

\( K_{eff} \), however, remains a valid index of the amount of segregation
from a given volume, and hence a valid index of the macrosegregation.

For comparison with segregation data of heats solidified with a
plane front (Figure 20), the segregation ratio (\( \frac{K}{K_{eff}} \)) is plotted
versus the same function of velocity in Figure 24. Comparison of
Figures 20 and 24 indicate that macrosegregation of fine grained heats
was of the same order of magnitude as macrosegregation in coarse
grained heats, in the ranges studied. Because of the entrappment of
solute-rich liquid in the fine grain heats, this result is somewhat
surprising. Explanation, however, may be in the following factors:
1. Increase in surface area.

The surface area of the solidification front in the fine grain ingots is expected, at some times at least, to be larger than the surface area of a plane front.

2. Transient concentration distributions in liquid at interface.

A plane front can conceivably be maintained for short periods of time in fine grained heats. As described by Hucke,\(^\text{14}\) the mechanism is as follows: At the beginning of solidification, the boundary layer has not had a chance to build up, and the solid freezing is essentially that predicted by the phase diagram. During this transitory state, the interface continues to grow, rejecting solute. The solute concentration in the liquid at the interface gradually rises, and with it the solid solute concentration. When the boundary layer reaches a certain \(C_i (\text{max})\), thermal conditions permit breakdown of the plane front and eventual formation of fine grains. During this transient plane front solidification, it is notable that the solid composition has been lower than that would be obtained in steady state, plane front solidification.

A conclusion of interest, then, is that if macrosegregation of rather large concentrations of solute is desired, conditions may be such that the most efficient separation may be obtained in this type of apparatus under conditions other than plane front. Table VI compares segregation data from two 1-1/2 per cent copper heats, one solidified at a velocity permitting plane front solidification, and the other at a higher velocity. Note the efficiency of segregation as indicated by the relative grams of solute segregated per unit time is higher in the
fine grain heat than in the coarse grain heat.

D. **Segregation With Other Procedures**

In the course of preliminary investigation, a number of mechanical and procedural variations were investigated. The technique and apparatus design found most satisfactory have been described previously, and other modifications were abandoned because of lack of sufficient control of one or more solidification variables. Several heats cast under slightly different conditions, however, are of interest to the problem investigated, and will be mentioned briefly.

1. Effect of Varying $C_o$ During Solidification, Effect of Higher Stirring Rates

Figure 25 shows a photograph of an aluminum 1.0 per cent copper heat, directionally frozen over the greater portion of its length. The liquid-solid interface was maintained close to the center of the coil, and both coil and water spray moved during solidification. Note the surface defects caused by "pinch" of the electromagnetic field.

Figure 26 plots interface velocity versus length of ingot frozen. The velocity was essentially constant during the first and last periods of the heat, but showed a marked rise and fall in the center portion of the heat.

Chemical analyses were taken at three-quarter inch intervals up the length of the ingot, and the data may be related by an equation similar to that of Pfann.\textsuperscript{4} Pfann's equation, assuming perfect liquid diffusion, is:
\[
\frac{C_s}{C_0} = \kappa \left(1 - \frac{q}{\rho}\right)^{\kappa-1}
\]  

(9)

It has been shown that liquid diffusion is not perfect, and that Pfann's equation is not valid. Appendix B shows, however, that at constant interface velocity and constant rate of stirring, a modified Pfann equation may be written:

\[
\frac{C_s}{C_0} = \kappa \left(1 - \frac{q}{\rho}\right)^{\kappa \left(\kappa \frac{\rho}{\rho}\right)^{-1}}
\]  

(10)

In Figure 27, \( \frac{C_s}{C_0} \) is plotted versus fraction of ingot solidified for several values of \( \kappa \frac{\rho}{\rho} \). Chemical analyses of sections taken from the ingot are superimposed, and it is seen that the three points taken from the portions of the ingot frozen at relatively constant velocity fall close to the curve for \( \kappa \frac{\rho}{\rho} = .25 \). The analysis of the portion solidified at higher velocity, however, indicates a \( \kappa \frac{\rho}{\rho} \) of approximately .35.

The effective segregation coefficients determined are somewhat smaller in this heat than in those heats solidified at the same speed with the interface below the coil, indicating a stronger stirring force near the center of the coil.

2. Enrichment of Liquid to Eutectic Composition

It is of interest to note that while stability limitations prevent maintenance of plane front interface movement when the liquid becomes too highly concentrated in solute, sufficient stirring has been found to be able to raise the liquid composition to nearly the eutectic composition.
Figure 28 shows a photograph of a 4.5 per cent aluminum-copper heat directionally solidified through the greater portion of its length. A coil of height comparable to that of the ingot was used as power source. The coil was maintained in constant position and the liquid-solid interface frozen into it. Constant interface velocity was not maintained as shown in Figure 29. Figure 28, however, shows a very high percentage of eutectic in the last portion of the ingot to solidify.

E. **Consideration of Segregation in Dendritically Freezing Alloys**

Results discussed in Part V have shown that very low freezing velocities and high rates of liquid agitation were necessary to obtain appreciable segregation with plane front solidification. Theoretical reasoning has been cited, indicating that without appreciable stirring or convection little or no segregation is expected. It is common experience, however, that considerable microsegregation may result in dendritically freezing alloys and in certain cases, this microsegregation may be nearly the amount expected if perfect liquid diffusion occurs.

The explanation of this apparent anomaly must lie in the fact that a number of characteristics of dendritic freezing make it a vastly more complex case than the idealized picture of plane front interface freezing. Among these are the rate of movement of the liquid-solid interface.

The "linear freezing rate" of a sand cast alloy must be very low-
because of the large surface area present. The linear freezing rate is further expected to decrease with time, because the rate of heat extraction generally decreases, and because the dendrite surface area increases. Finally, the freezing velocity cannot be considered even approximately equal at various portions of dendrites, the tips being expected to grow faster than the average. Other differences expected to be of importance include the complicated diffusion path in the liquid due to the dendrite geometry, and the tendency of these alloys for random nucleation.

A number of equations governing segregation in plane front solidification have been discussed in Part A of Section V. Direct application of similar equations to dendritic freezing appears extremely difficult because of the unknown variables in dendrite freezing rate and geometry. Inferences can be obtained from the discussion in Part V, however, which are of at least qualitative value in the consideration of dendritic solidification. In this discussion, several assumptions will be made:

1. Equilibrium of partition ratio is attained.

2. No thermodynamic barrier to growth exists. That is, liquid at a liquid-solid interface will solidify at a temperature $dT$ below its liquidus. This solidification will proceed at a speed sufficiently large that it is not a barrier to growth.

3. No solid-state diffusion exists.

4. No temperature gradients exist in the liquid in a sand casting.

5. Further, initial supercooling due to nucleation barrier is not
considered, the supercooling of interest being that which occurs during growth. Thus, "supercooling" here refers to the constitutional supercooling of Tiller, et al.\(^5\)

With these assumptions, consider first a specialized case which may be closely approximated in practice:

1. A Dendritically Freezing Alloy Which Exhibits "Perfect"

   **Microsegregation**

   "Perfect" segregation has been defined as the theoretical amount that would be obtained assuming perfect liquid diffusion and no solid diffusion. In a system with a eutectic, "perfect" segregation requires that a second phase be precipitated, and the amount of second phase may be calculated by means of an equation similar to that of Pfann, where:

   \[ \frac{C_0}{C_\ell} = (1 - q)^{\kappa - 1} \]  

   \(q\) is now the weight fraction solidified, whatever its geometry.

   Let \(C_\ell = C_0\) where \(C_\ell\) = eutectic composition. Further, let \(\ell\) equal the weight fraction of liquid remaining when this liquid is of eutectic composition. It is therefore equal to \((1 - q)\), where \((1 - q)\) is the weight per cent of eutectic existing at the end of solidification. Pfann's equation may now be written:

   \[ \ell = \left( \frac{C_\ell}{C_0} \right)^{\kappa - 1} \]  

   and \(\ell\) is the weight per cent eutectic calculated by assuming perfect liquid diffusion.
It will be shown that equation (12) may be derived, and "perfect" segregation predicted without the assumption of perfect liquid diffusion.

Consider the growth of a dendrite nucleus, with reference to Figures 1 through 3. In order to grow, it must reject solute, and the solute concentration in the liquid must rise to some value \( c_i \). In order for solidification to proceed, the temperature at the interface must decrease to the liquidus temperature of \( c_i \). This temperature is equal to \( T_m + m c_i \), where \( m \) is the slope of the liquidus (Figure 2). If there is no temperature gradient in the liquid, the true liquid temperature must now be \( T_{\text{actual}} = T_m + m c_i \) (Figure 30). Since liquid diffusion is not complete, the bulk liquid composition is termed \( c_o \), and its solidification (liquidus) temperature is \( T_L = T_m + m c_o \). From Figure 30, it is seen that:

\[
T_L = T_m + m c_o, \quad T_{\text{actual}} = T_m + m c_i
\]

or

\[
T_L - T_{\text{actual}} = m (c_o - c_i)
\]

and for solidification to proceed, supercooling in the bulk liquid must exist.

Consider now that nucleation, and the geometry of dendrite growth, can effectively suppress this supercooling to a negligible amount. That is, that when a portion of liquid becomes very slightly supercooled, nucleation will occur, or a dendrite arm will "reach out" into it. This restriction is that, in the limiting case,

\[
T_L - T_{\text{actual}} = 0
\]
and, hence,
\[ m (c_0 - c_i) = 0 \]
or
\[ c_0 - c_i = 0 \]  \hspace{1cm} (14)

It is then seen that the liquid composition at the interface is always essentially \( c_0 \), and the effective segregation factor (\( K_{ij} \)) equal to the partition ratio (\( \kappa \)). Under these conditions, the weight fraction of eutectic from calculation similar to Appendix B is:
\[ C = \left( \frac{C_C}{C_o} \right) \frac{1}{K_{ij} - 1} \]  \hspace{1cm} (15)

where \( K_{ij} = \kappa \), and
\[ C = \left( \frac{C_C}{C_o} \right) \frac{1}{\kappa - 1} \]  \hspace{1cm} (16)

which corresponds to equation (12) derived with the assumption of perfect liquid diffusion.

Consider now the case of a sand casting exhibiting less than "perfect" segregation.

2. A Dendritically Freezing Alloy Which Exhibits Less Than "Perfect" Segregation

If a casting exhibits less than the amount of second phase as calculated above, the conservation of mass requires that the primary solidification phase be higher in solute than calculated according to the assumption of perfect liquid diffusion. This requires that,
during solidification, the liquid concentration at the interface be built up to some value \( C_i \) greater than \( C_o \), and, consequently, by the reasoning discussed above, that there be supercooling in the bulk liquid.

A general statement may then be made as follows: If "perfect" microsegregation results in sand castings, the solidification mechanism was such as to prevent appreciable constitutional supercooling; if "imperfect" segregation results at a finite cooling rate, supercooling must have existed during solidification.

Supercooling, during the mushy solidification of an alloy, then, is seen to be an index of the amount of segregation to be expected in the alloy. It is therefore of interest to consider the effect of solidification variables on this supercooling.

The effect of solute concentration on the amount of supercooling to be expected is not known. The effect of cooling rate on supercooling must depend on the following factors: (1) Number of nuclei present, (2) tendency for dendrite arms to effectively suppress supercooling, and (3) diffusion time. Stated differently, the essential problem is the removal of solute from the liquid-solid interface, and this must depend on the time allowed, and the diffusion path over which it must travel. The diffusion path depends on the liquid-solid area, and the fineness of the dendrite structure, both of which are known to increase with increasing cooling rate.

Constitutional supercooling then is seen to depend on cooling rate in two opposing ways: Increasing cooling rates decrease diffusion
time allowed, but also decrease diffusion path necessary. It is conceivable then, that in certain cases, a decrease in diffusion path could more than counterbalance an increase in diffusion time. In these cases, increasing cooling rates would, contrary to intuition, lead to greater, rather than less microsegregation.

3. Summary of Consideration of Segregation in Dendritically Freezing Alloys

The problem of segregation in dendritically freezing alloys is complicated as compared to segregation in plane front solidification. Segregation is necessarily tied up with structure, and so closely it appears difficult in some cases to isolate cause from effect. The geometry of dendritic growth indicates that a mathematical model such as that derived for plane front solidification is extremely difficult to achieve. The necessary relationship between solidification temperature and segregation, however, makes it appear a fruitful avenue of research.

A fuller understanding of dendritic growth and segregation is of immense practical, as well as theoretical, interest. Mechanical properties, annealing times, and hot tearing are but a few of the items of practical interest dependent on structure and segregation in sand castings.
VI. CONCLUSIONS

1. An apparatus has been designed and constructed for solidification of alloys into a stirred liquid bath. The apparatus independently controls (1) temperature gradients in the solid, and (2) rate of solidification.

2. Unidirectional, plane front interface freezing, heretofore achieved only with very low solute concentrations, has been maintained with aluminum alloys of up to 2 per cent copper and 10 per cent zinc.

3. In directionally frozen, plane front ingots, macrosegregation is shown to be favored by:
   a. Slow freezing velocities.
   b. High degree of stirring.
   c. High liquid diffusion.
   d. Low partition ratio.

4. Because of the complex nature of liquid stirring used, no analysis of the liquid velocity distribution at the interface was possible. At low interface velocities, however, results showed general agreement with the Wagner Analysis, assuming a constant "effective boundary layer" thickness of .03 centimeter.

5. At higher interface velocities, better segregation was obtained than would be expected assuming a constant "effective boundary layer" thickness.

6. Under the stirring conditions imposed, the alloys studied exhibited nearly perfect segregation (\( \frac{\alpha}{\alpha_{ref}} = .8 \)) at interface velocities
the order of $0.5 \times 10^{-3}$ centimeters per second. The segregation ratio
of $\frac{K / K_c}{\phi}$ decreased with increasing interface velocities to a mini-
mum value at about $1.5 \times 10^{-3}$ centimeters per second. Higher inter-
face velocities showed little further decrease in the segregation
ratio.

7. In ingots frozen under conditions not favoring plane front
interface, fine, equiaxed grains were formed with entrapped second
phase. Appreciable macrosegregation was obtained, however.

8. In separation processes involving apparatus similar to that
used here, greater amounts of segregation may in some cases be ob-
tained per unit time in unstable front solidification than in stable
plane front solidification.

9. With constant stirring conditions and interface velocity, a
modified Pfann's equation is shown applicable to solidification when
the solute concentration is not constant.
VII. SUGGESTIONS FOR FUTURE WORK

Heretofore, experimental work on segregation in plane front solidification has been conducted with metals of extremely low alloy content, and low rates of liquid agitation. Further work along the same general lines of that conducted here appears of considerable theoretical interest. A limitation of the apparatus used is the inability to calculate the velocity distribution of liquid flow at the interface. It appears possible, however, on the basis of data presented here, to design an apparatus in which fluid flow, as well as heat transfer variables, can be determined. With complete control of these experimental variables, a fully qualitative insight into segregation in plane front solidification of metals should be possible.

A study of segregation in dendritically freezing alloys in the light of the concepts of imperfect liquid diffusion appears of theoretical, and practical, interest. The necessary relation between supercooling and segregation has been discussed. An experimental determination of this relationship would be of great interest.
<table>
<thead>
<tr>
<th></th>
<th>Definition of Terms and Numerical Value of Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$C_L$ = weight per cent solute in liquid at liquid-solid interface.</td>
</tr>
<tr>
<td>2</td>
<td>$C_C$ = weight per cent solute at composition of second phase.</td>
</tr>
<tr>
<td>3</td>
<td>$C_L$ = weight per cent solute in liquid at any point.</td>
</tr>
<tr>
<td>4</td>
<td>$C_0$ = weight per cent solute in bulk liquid.</td>
</tr>
<tr>
<td>5</td>
<td>$C_0'$ = weight per cent solute in bulk liquid at start of solidification.</td>
</tr>
<tr>
<td>6</td>
<td>$C_s$ = weight per cent solute in solid.</td>
</tr>
</tbody>
</table>
| 7 | $D$ = diffusion coefficient of solute in liquid (cm$^2$ per second). $16$
|   | $\bar{D}_{\omega} = 7 \times 10^{-5}$ (cm$^2$/sec.) |
|   | $\bar{D}_{\xi\nu} = 6.2 \times 10^{-5}$ (cm$^2$/sec.) |
| 8 | $\xi$ = weight per cent second phase in solidifying alloy. |
| 9 | $\xi$ = weight fraction of ingot solidified. |
| 10 | $\kappa$ = segregation coefficient (partition ratio). |
|   | $\kappa_{\omega} = .171$ |
|   | $\kappa_{\xi\nu} = .445$ |
| 11 | $\kappa_{H}$ = effective segregation coefficient, equal to $C_s/C_0$ in solidifying alloy. |
| 12 | $l$ = diffusion boundary layer (centimeters). |
| 13 | $l'$ = idealized diffusion boundary layer (centimeters). |
| 14 | $m$ = slope of liquidus of alloy system (degrees centigrade per per cent). |
| 15 | $T_{l\xi\nu}$ = actual temperature in the liquid at any point. |
16) $\tau_L$ = liquidus temperature of an alloy of a given solute concentration.

17) $\tau_m$ = melting point of pure solvent.

18) $\omega$ = linear freezing velocity of plane front interface (centimeters per second).

19) $\lambda$ = distance from liquid-solid interface into liquid (centimeters).

20) $\frac{dm}{dt}$ = rate of solute transfer (grams per second).

21) $\delta_{ef}$ = "effective" diffusion boundary layer:

$$\delta_{ef} = \frac{C_L - C_0}{-(\frac{\partial C}{\partial x})_{x=0}}$$
TABLE II.

Chemical Analyses and Segregation Data For Aluminum Copper Heats

Plane Front Solidification

<table>
<thead>
<tr>
<th>t</th>
<th>Per Cent Copper, Liquid</th>
<th>Per Cent Copper, Liquid at Time of Solid Sample (C₀)</th>
<th>Solid Composition (Cₛ)</th>
<th>Kₛ/Kₛ</th>
<th>Kₛ/Kₛ</th>
<th>Interface Velocity (cm/sec x 10^3)</th>
<th>( \frac{u}{D(1-k)} )</th>
<th>cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.02</td>
<td>1.09</td>
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<td>.81</td>
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<td>.405</td>
<td>1.59</td>
<td>11.9</td>
<td>53</td>
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</tbody>
</table>

* Sample taken at end of heat
### TABLE III.

Chemical Analyses and Segregation Data For Aluminum Zinc Heats

**Plane Front Solidification**

<table>
<thead>
<tr>
<th>Zn, Liquid (C₀)</th>
<th>Zinc, Solid (Cₜ)</th>
<th>Solid Composition (Cₛ)</th>
<th>κₑ/₁₀</th>
<th>κ₋/κₑ</th>
<th>Interface Velocity (cm/sec x 10²)</th>
<th>( \frac{L}{b} (1-\lambda) ) cm⁻¹</th>
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</thead>
<tbody>
<tr>
<td>1.91</td>
<td>1.98</td>
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<td>9.35</td>
<td>7.84</td>
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</table>
### TABLE IV.

Chemical Analyses and Segregation Data For Aluminum Copper Heats

Fine Grain Samples

<table>
<thead>
<tr>
<th>Test</th>
<th>Per Cent Copper, Liquid</th>
<th>Per Cent Copper, Solid Analysis (C₀) (%)</th>
<th>Solid Composition (Cₛ) (%)</th>
<th>$\kappa_{eff}$</th>
<th>$\frac{\kappa}{\kappa_{eff}}$</th>
<th>Interface Velocity (cm/sec x 10^3)</th>
<th>$\frac{\kappa}{D(1-k)}$</th>
<th>$\frac{L}{cm}$</th>
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<tbody>
<tr>
<td>0</td>
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TABLE V.

Chemical Analyses and Segregation Data For Aluminum Zinc Heats

Fine Grain Samples

<table>
<thead>
<tr>
<th>Zinc, Liquid</th>
<th>Per Cent Zinc, Liquid at Time of Solid Analysis (C₀)</th>
<th>Solid Composition (Cₕ) (%)</th>
<th>Kₑff</th>
<th>K_eff/Kₑff</th>
<th>Interface Velocity (cm/sec x 10³)</th>
<th>( \frac{\nu}{D} (1-\kappa) ) cm⁻¹</th>
</tr>
</thead>
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<tr>
<td>20.25</td>
<td>20.7</td>
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TABLE VI.

Comparison of "Efficiency of Segregation" in a Coarse and Fine Grain Heat
Efficiency is Measured in Relative Grams of Solute Segregated Per Unit Time

<table>
<thead>
<tr>
<th>Heat</th>
<th>Structure</th>
<th>(C_o) (% Cu)</th>
<th>(C_s) (% Cu)</th>
<th>(\omega) cm/sec x 10^3</th>
<th>Relative Grams of Solute Segregated Per Unit Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>C</td>
<td>1.52</td>
<td>.82</td>
<td>1.66</td>
<td>1</td>
</tr>
<tr>
<td>23</td>
<td>F</td>
<td>1.47</td>
<td>1.00</td>
<td>3.18</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Figure 1. Schematic Diagram of Plane Front Solidification

Figure 2. Schematic Phase Diagram (For Segregation Coefficient Less Than One)

Figure 3. Schematic Diagram of Concentration Distribution in Liquid at Liquid-Solid Interface

Figure 4. Schematic Diagram of Temperature Distribution and Liquidus Temperature Distribution at Liquid-Solid Interface
Figure 5. Photograph of Furnace
Figure 6. Photograph of Furnace and Equipment
Figure 6. Photograph of Furnace and Equipment
Figure 7. Schematic Diagram of Furnace
Figure 8. Circuit Diagram of Power Source
Figure 9. Schematic Diagram of Temperature Distribution in Liquid and Solid Ingot
Figure 10. Typical Plot of Temperature versus Time at Crucible Bottom During Meltdown
Figure 11. Typical Plot of Temperature, Coil, and Interface Measurements Taken During Solidification. Aluminum 1.5 Per Cent Copper Nominal Composition.
Figure 12. Typical Plot of Temperature, Coil, and Interface Measurements Taken During Solidification. Aluminum 5 Per Cent Zinc Nominal Composition
HEAT 23
ALUMINUM - 1.5 % COPPER

Figure 13. Plot of Temperature Distribution in Solidifying Aluminum 1.5 Per Cent Copper Ingot
Figure 14. Typical Macrostructure of Ingot Solidified with Plane Front. Aluminum One Per Cent Copper. Heat 7. (Approx. 1X)
Figure 15. Typical Macrostructure of Ingot Solidified with Plane Front. Aluminum 5 Per Cent Zinc. Heat 12. (Approx. 1X)
Figure 16. Typical Microstructure of Ingot Frozen with Plane Front. Aluminum 3 Per Cent Copper. (Approx. 75X)

Figure 17. Photomicrograph of Top of Portion of Directionally Frozen Ingot. Aluminum 3 Per Cent Copper. (Approx. 75X)
Figure 18. Schematic Concentration Distribution in a Stirred System
Figure 20. Plot of Segregation Ratio versus Function of Velocity for Aluminum-Copper and Aluminum-Zinc Heats (Heats Solidified with Plane Front)
Figure 21. Typical Macrostructure of Fine Grain Ingot.
Aluminum 3 Per Cent Copper. Heat 22.
(Approx. 1X)
Figure 22. Typical Macrostructure of Fine Grain Ingot. Aluminum 4.5 Per Cent Copper. Heat 19. (Approx. 1X)
Figure 23. Typical Microstructure of Fine Grain Ingot. Aluminum 3 Per Cent Copper. (Approx. 75X)
Figure 24. Plot of Segregation Ratio versus Function of Velocity for Fine Grain Heats (Aluminum-Copper and Aluminum-Zinc)
Figure 25. Macrostructure of Ingot Directionally Frozen for Major Portion of Its Length. Aluminum One Per Cent Copper. Heat 7-28. (Approx. 1X)
Figure 26. Interface Velocity versus Fraction of Ingot Frozen for Heat 7-28

Figure 27. Comparison of Segregation Data of Heat 7-28 with Modified Pfann Equation
Figure 26. Macrostructure of Aluminum 4.5 Per Cent Copper Alloy, Solidified into Stationary Coil. Heat 7-22A. (Approx. 1X)
Figure 29. Plot of Temperature, Coil, and Interface Measurements During Solidification of Heat 7-22A
Figure 30. Schematic Diagram of Actual and Liquidus Temperature Distributions in Alloy Sand Casting
APPENDIX A.

Derivation of Segregation Ratio as a Function of Velocity

Assuming Idealized Boundary Layer

Let $\delta' = \text{boundary layer of constant thickness.}$

A differential equation governing the diffusion of solute from a plane front interface may be written:

$$D \frac{dc}{d\delta'} + u \frac{dc}{d\delta} = 0$$  \hspace{1cm} (1)

where $u = \text{interface velocity}$

Equation (1), solved for $\frac{dc}{d\delta}$:

$$\frac{dc}{d\delta} = \frac{c'}{c} - \frac{u}{D}$$  \hspace{1cm} (2)

where

$$c' = \left(\frac{dc}{d\delta'}\right)_{x=0} = -\frac{uc_i(1-k)}{D}$$  \hspace{1cm} (3)

at $x = 0$, $c = c_i$

$x = \delta'$, $c = c_0$

and substitution of (2) and (3) yields:

$$\int_{c_0}^{c_i} dc = -\frac{uc_i(1-k)}{D} \int_{\delta'}^{0} e^{-\frac{u\delta'}{D}} d\delta'$$  \hspace{1cm} (4)

then:

$$c_i - c_0 = c_i (1-k) \left( 1 - e^{-\frac{u\delta'}{D}} \right)$$  \hspace{1cm} (5)

but:

$$\frac{c_0}{c_i} = \frac{K}{K_{eff}}$$  \hspace{1cm} (6)

and substitution of (5) and (6):

$$\frac{K}{K_{eff}} = 1 - \left(1 - e^{-\frac{u\delta'}{D}}\right)(1-k)$$  \hspace{1cm} (7)
APPENDIX B.

Derivation of Modified Pfann Equation for Plane Front Interface

Movement in Case of Imperfect Liquid Diffusion

Consider a long molten charge solidifying with a plane front from one end (Figure 1).

A materials balance yields:

\[(1 - \varphi) C_0 + \int_0^t C_5 dq = C'_0 \quad (1)\]

Assume a thin boundary layer of small thickness \(d\) held constant by stirring. The remainder of the liquid is of homogeneous composition \(C_0\), which is a function only of \(\varphi\), the fraction solidified.

Differentiation of equation (1) yields:

\[(1 - \varphi) dC_0 - C_0 d\varphi + C_5 d\varphi = 0 \quad (2)\]

or

\[(1 - \varphi) dC_0 = (C_5 - C_0) d\varphi \quad (3)\]

If the boundary layer is of sufficiently small capacity and thin with respect to the remaining bulk liquid, the relationship

\[\kappa_{2\varphi \varphi} = \frac{C_5}{C_0} \quad (4)\]

must hold throughout solidification.

Substitution of (4) and (3) yields:

\[(1 - \varphi) dC_0 = C_0 (1 - \kappa_{2\varphi \varphi}) d\varphi \quad (5)\]
Integration of Equation (5):

$$
\int_{c_0}^{c_0'} \frac{dC_0}{C_0} = (1 - \kappa_{\text{eff}}) \int_{0}^{g} \frac{dg}{1 - g}
$$

(6)

$$
c_0 = c_0' \text{ at } g = 0
$$

$$
c_0 = c_0 \text{ at } g = g
$$

$$
\frac{c_0}{c_0'} = (1 - g)^{\kappa_{\text{eff}} - 1}
$$

(7)

and:

$$
\kappa_{\text{eff}} = \frac{c_s}{c_0}
$$

(8)

Substitution of (7) and (8):

$$
\frac{c_s}{c_0'} = \kappa_{\text{eff}} (1 - g)^{\kappa_{\text{eff}} - 1}
$$

(9)
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BIOGRAPHICAL NOTE

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