THE INTERACTION OF DENDRITES AND FLOW
DURING SOLIDIFICATION

by

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S.B. Massachusetts Institute of Technology 1963
S.M. Columbia University 1966

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
1971

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Archives
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Submitted to the Department of Metallurgy and Materials Science on May 7, 1971, in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

ABSTRACT

The interaction of solidification structure and convective flow in the part solid region of a dendritically freezing aluminum-4.5 wt pct copper alloy has been determined using a slow freeze-transverse quench technique to observe liquid regions between dendritic structures.

Four types of liquid channels were observed:

(a) Liquid channels between groups of dendrites. These formed only in ingots which were freezing vertically.

(b) Liquid channels between similarly oriented dendrites. These formed in both vertically and horizontally freezing ingots.

(c) Tubular flow channels. These formed in the vertical direction in the bottom half of ingots which were freezing horizontally.

(d) Bottom flow channels. A flow channel of this type formed across the bottom surface of ingots freezing horizontally.

Measurements were made of the volume fractions and specific surfaces of liquid channels and interdendritic liquid. These were used to calculate the permeability of the part solid region to flow. The liquid channels do not increase the permeability which can therefore be calculated directly from the average dendrite arm spacing and the volume fraction of the unfrozen liquid.
The velocity of natural convective flow in a horizontally solidifying ingot was then calculated from the permeability. It has a maximum value within the part solid region.

Apparatus was developed to apply the slow freeze-transverse quench technique to both vertical and horizontal solidification of iron alloys.

Thesis Supervisor: John F. Elliott
Title: Professor of Metallurgy
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ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor John F. Elliott for his guidance, his patience, and his professional example during the course of this study;

The author also wishes to thank Professor Merton C. Flemings for his introduction to the study of solidification, and for the use of his laboratory for preparation of the aluminum-copper alloy;

Special thanks also are due to the following people for their assistance in completing the work:

Mr. Jeryl Wright, for constructing the rotating switch and for proofreading the manuscript;

Mr. Ted Bradbury, for help in constructing the iron-quenching apparatus;

Rabbi Michael Schachnow, for his help in completing the photographs and for managing the assembly of the manuscript;

Miss Frances M. Gedziun, for typing the body of the manuscript;

Mrs. D. Radcliffe, for typing the Appendices;

The author is particularly indebted to the following people who have contributed to his personal development:

His wife Barbara, for her continued encouragement and assistance. She helped with the literature survey, drew the diagrams, and helped print the photographs, all while caring for our two sons. Truly she is an eishes chayil - a valorous wife;
His parents, for guiding his growth and for teaching him to respect intellectual endeavor;
His wife's parents, for their understanding and encouragement;
Rabbi Herman Pollack, director of the B'nai Brith Hillel Foundation at M.I.T., for his enduring friendship;
His fellow graduate students, for many helpful discussions;
This work was accomplished, in part, through the use of the facilities at the M.I.T. Information Processing Services Center at Cambridge, Massachusetts;
Financial support for this project was provided by the American Iron and Steel Institute.
1. INTRODUCTION

This work is an indirect approach to the determination of convective flow in the part solid region of a solidifying ingot. The underlying assumption is that if the distribution of liquid in the part solid region can be modeled, and if the solute and temperature distributions are measured, the convective flow velocities can be calculated from equations which have been developed for flow in a packed column. Thus the idea is not to measure the flow directly, but to calculate it from the physical parameters which comprise the driving forces and the resistance to flow. This approach was used because there appeared to be no practical way to measure physically the flow rate within the part solid region.

The essence of the study is the development of a method for determining the location of the solid and liquid areas of a dendritically freezing alloy, and the application of the method to examine the interaction of natural convection and the solidification structure of an ingot which is freezing horizontally. The method is to begin slow unidirectional solidification and then, before solidification is complete, to rapidly quench the ingot. When the ingot is polished and etched, those regions which were unfrozen liquid before the quench are revealed as areas of very fine microstructure.

The method was first applied to both vertical and horizontal solidification of an aluminum-4.5 wt pct copper alloy. The macrostructures and microstructures of several
series of ingots are presented and compared. Since convective flow occurred only in horizontal solidification, differences in structure between the ingots which were frozen vertically and those which were frozen horizontally are ascribed to the effects of natural convection on the solidification structure.

Temperature measurements were made during solidification, and the concentration of copper in the unfrozen liquid was determined by electron probe analysis of the quenched ingots. These measurements are combined with a model of the distribution of liquid in the part solid region to calculate the convective flow of liquid during horizontal solidification.

The experience with the aluminum-copper alloy aided the modification of the experimental method for use with iron alloys. The solidification structures of an iron-copper alloy and an iron-carbon alloy are presented.

By nature, the observations are somewhat broad and often qualitative. The nature of the interaction between solidification structure and natural convection, however, is clearly drawn. In addition, this study shows the usefulness of the experimental technique for the study of the solidification structure of iron alloys.
2. THE PROBLEM

A number of words and phrases have acquired a specific usage and meaning in the field of solidification. These terms are presented here in the context of a brief discussion of the solidification of a binary alloy*. A specific statement of the problem follows this discussion.

Figure 2.1 is a typical phase diagram of a binary alloy which undergoes a eutectic transformation on freezing. When liquid of composition $C_0$ cools to the liquidus temperature, $T_{l,0}$, relatively pure solid (2) begins to freeze. The ratio of the solid composition at the freezing interface, $C_s$, to the composition of the adjacent liquid, $C_1$, is called the partition ratio, $k$. If the temperature decreases rapidly, the solute is rejected by the solid at the freezing interface. Thus the concentration of solute follows the liquidus (1-3) and the concentration in the solid at the interface follows the solidus (2-4). At the eutectic temperature, $T_e$, the remaining liquid of composition $C_e$ (3) transforms to the two solid phases, $\alpha$ and $\beta$ (4 and 5). The sample is then completely solid. The temperature interval, $T_{l,0} - T_e$, over which freezing occurs is called the freezing range.

If freezing is rapid, growth is dendritic. That is, the solid freezes in a tree-like structure whose "branches" are all surrounded by interdendritic liquid, Figure 2.2. The dendrite

* They are also defined explicitly in a Glossary of Solidification Terms.
Fig. 2.1  Typical phase diagram of a binary alloy.
arms are denoted by their direction and connection with the rest of the structure. A main spine which grows in the direction which is approximately opposite to the direction of heat flow is called a primary dendrite arm. Secondary arms grow perpendicular to the direction of heat flow, from the primary arms, and tertiary arms grow from these. The spines of each arm, the straight lines on Figure 2.2, are the first part of the arms to freeze and thus have a low concentration of solute, which was rejected into the interdendritic liquid. At the surfaces shown, the solid has a higher concentration of solute than the solid in the spines of the dendrites. This gradient of solute across a dendrite arm is termed coring, and is one form of microsegregation.

Using these concepts, a brief description of the horizontal solidification of an ingot or a casting leads directly to the formulation of the problem which is investigated in this work. A liquid alloy, or melt, is heated to a temperature above the liquidus temperature. The metal is poured into a mold and heat is extracted directionally from one vertical face at the end of the mold, the chill. The heat content above the liquidus temperature, the superheat, is removed, and long primary dendrite arms grow from the chill, producing an oriented structure, called the columnar zone of the casting. The distribution of temperature at this time is shown in Figure 2.3(a). As seen from the phase diagram, Figure 2.1, all locations which have temperatures between $T_e$ and $T_{L_0}$ will contain solid dendrite arms surrounded by liquid whose
Fig. 2.2 Schematic diagram of a freezing dendrite.
Fig. 2.3 Temperature and solute distribution in the part solid region of a directionally solidifying ingot.
concentration of solute is higher than $C_0$. This region is
called the mushy zone. Assuming that the interdendritic liquid
is completely mixed on a local scale, the solute composition
at each location can be found from the temperature, Figure
2.3(a), and the equilibrium phase diagram, Figure 2.1, giving
Figure 2.3(b). Thus, going from the bulk liquid towards the
chill, the interdendritic liquid becomes colder and contains
more solute*.

The gradients of temperature and solute concentration in
the interdendritic liquid usually cause a gradient in the
liquid density as well. Given an alloy such as copper in
aluminum, for which the liquid becomes more dense as it cools
and as its solute concentration increases, there is an increase
in the density of the liquid towards the chill.

For horizontal solidification, this gradient of density
is perpendicular to the gravitational force, and convective
flow is possible. As shown schematically in Figure 2.4, the
denser interdendritic liquid might flow down through the part
solid region, across the bottom of the mold, and up into the
bulk liquid. Sufficient fluid motion of this type might
transport enough solute to change the average composition of
the ingot over large distances, called macrosegregation.

This type of flow has been characterized in the
literature as flow in a packed column.\(^{(4)}\) The difference of
density between the bulk liquid and the interdendritic liquid

* The presentation, to this point, has been extracted
from several basic references on the solidification of
metals,\(^{(1-3)}\) which may be consulted for further detail.
Fig. 2.4 Illustration of convective flow in a horizontally solidifying ingot.
provides the driving force for flow, while the solid dendrite arms are the resistance to this flow. Unlike the usual packed column, however, during solidification, a physical interaction between the structure and the flow is possible. That is, the motion of the interdendritic liquid may change the structure or growth of the dendrite arms.

Preliminary calculations of the velocity of this convective flow demonstrated that the driving force could be calculated by assuming complete local mixing of the interdendritic liquid, but the distribution of solid and liquid between primary dendrite arms, which has a large effect on the resistance to flow, could not be estimated.

Thus both the interaction of convective flow with the dendritic structure, and the distribution of liquid within the part solid region of a casting must be studied to develop an understanding of convective flow in the part solid region of a solidifying alloy. The statement of the problem follows directly from this analysis.

The Problem - This work is a study of the interaction of natural convective flow with the solidification structure of a binary metal alloy which freezes dendritically. In order to calculate the velocity of convective flow in the part solid region of an ingot which is solidifying horizontally, it will be necessary to determine three factors:

(1) The distribution (meaning the locations, the volume fraction, and the morphology) of solid and liquid in the part solid region
(2) The solute concentration of the interdendritic liquid

(3) The thermal gradients in the part solid region.
3. LITERATURE SURVEY

This chapter surveys the literature in two areas which relate to the thesis as a whole. First, various methods which have been used to investigate alloy solidification are presented, together with some of the results which have been obtained with these methods. This provides a certain background beyond that already given in Chapter 2, and will also allow a comparative evaluation of the experimental technique used in this study. Second, recent work which has been done on fluid motion in the part solid region of a solidifying alloy is treated here. The literature on other topics will be presented where appropriate during the discussion of the experimental results.

3.1 Methods of Investigating the Solidification Process

A great variety of methods have been used to determine the nature of the solidification process in dendritically freezing alloys. A number of these methods, together with some of the results which have been obtained are presented here.

These experimental procedures are divided into three groups. First are methods which allow solidification to proceed to completion. While some variables may be observed, recorded, or changed during the course of solidification, the end of the procedure always involves examination of a completely solid ingot. The second group of methods allows observation of the
solidification structure at some one time between the beginning and end of solidification. This produces one "frame" as it were, in the movie which might have been produced were it possible to observe the solidification process continuously. The last group of methods allows actual observation, under certain limiting conditions, of the process of freezing as it is occurring.

3.1.1 Methods Which Involve Complete Solidification

Most investigations of the nature of dendritic solidification have been done by studying the end results of the freezing process. Once solidification is complete, however, the original solidification surface no longer exists, and the process by which solidification took place can only be inferred from the final structure. Therefore, although much of what is known about solidification was discovered in this way, considerable ingenuity and effort was expended in the process. Some of the methods which have been used and the results of these methods are described here.

**Observation of Surface Shrinkage** - The dendritic nature of alloy solidification may be observed directly on the surface of many castings, since the last liquid to freeze often shrinks back from the surface. The spines of the dendrites are then clearly visible. (5)

**Examination of a Polished Section** - When an ingot is sectioned, ground, and etched, a number of gross internal features, such as "bubbles" and segregate streaks are plainly visible. (6) If a small area is cut out, polished, and etched,
microscopic details of the structure and composition may be examined. For example, Kattamis and Flemings\(^7\) analyzed the composition of dendrite arms, using an electron beam microprobe. They found that dendrite arms in steel castings contain less of certain solute elements in their centers than at the surface adjacent to the interdendritic material, which indicates that diffusion in the solid arms was not rapid enough to erase the results of solute rejection during solidification.

The spacing of the dendrites which are readily visible on a polished and etched section of a cast alloy increases as the time during which solidification occurred increases. The work of a number of investigators, as summarized by Bower, Brody, and Flemings\(^8\) demonstrates that the average distance between secondary dendrite arms in an aluminum-copper alloy increases approximately as the square root of the local solidification time, the time between the start and the completion of freezing at a specific location within an ingot.

As mentioned in Chapter 2, a solid ingot usually contains several areas with distinctly different solidification structures. In a region near the chill, the primary dendrite arms are long and grow nearly perpendicularly to the chill surface, forming a "columnar zone". In the central part of the ingot, the dendrites are small, and contain several primary arms of approximately equal length. This area is called the "equiaxed zone." The transition from columnar to equiaxed growth has been studied extensively, mostly by examining ingots which have been solidified completely. The methods and results of some of these studies are presented here.
Changing the Conditions of Solidification - To find the causes of the formation of the equiaxed zone, a number of investigators have altered drastically the external and internal conditions of the melt. Uhlman, Seward, and Chalmers\(^9\) have placed the mold in a magnetic field to slow the convection of fluid ahead of the solidifying interface. They found that the formation of the equiaxed zone was thereby suppressed. Cole and Bolling\(^{10}\) have found that a larger equiaxed zone was formed when an electric current was passed through a solidifying ingot, which had been placed in a magnetic field. They assume that the increased convection in the melt which was caused by the interaction of the electric and magnetic fields caused the formation of the equiaxed zone. Southin\(^{11}\) found that vibration of the mold also increased the size of the equiaxed zone.

Measuring the Temperature Distribution During Freezing - Thermocouples placed in an ingot mold can yield significant information about conditions in the melt and show the progress of solidification, even though freezing is allowed to go to completion. In many studies (e.g., that of Bower, Brody, and Flemings\(^8\)), the motion of the solidification front was determined from the time at which each of a series of thermocouples began to indicate temperatures below the equilibrium liquidus temperature of the alloy. Cole and Winegard\(^{12,13}\) have used thermocouples to determine the existence of turbulent convection in the liquid ahead of the solidification front. They have demonstrated that very small thermocouples in good
contact with the liquid produced an oscillatory potential whose amplitude increased with increasing turbulent convection.

**Placing of Obstructions in the Mold** - Several investigators have inserted mesh screens into ingot molds to demonstrate the course of solidification. Cole and Bolling\(^{(14)}\) inserted a number of such screens to limit convection ahead of the solid-liquid interface and increase the length of the columnar zone, while Southin\(^{(15)}\) used a horizontal screen to "catch" dendrites falling from the surface of the ingot.

**Summary** - A large number of methods have been used to investigate the solidification process without interfering with the completion of solidification and without observing the freezing structure until the entire ingot is solid. These include simple visual observations of the exterior surfaces and polished and etched sections of castings; changing the conditions of solidification by application of magnetic fields, electric currents, and vibration; making thermocouple measurements during solidification, and placing physical obstructions in the mold. Evidently, because the freezing process can only be inferred, but not actually seen with these methods, there is a need for more direct ways of investigating the process of solidification.

3.1.2 Methods Which Involve Partial Solidification

In order to observe better the progress of solidification, a number of methods of partial, or interrupted solidification have been devised. These methods move the observation of the
freezing process back from the end of freezing to some one point in time during the solidification process.

**Dumping the Unfrozen Liquid** - In a number of steel-plant studies, including those of Marburg (16), Nelson (17), Spretnak (18), and Chipman and Fon Dersmith (19), the rate of solidification of steel ingots was determined by inverting the ingot at some time after freezing has begun and pouring out, or "dumping", the unfrozen liquid. Measurement of the thickness of the frozen shell which remained after a series of such experiments gave the thickness solidified as a function of the freezing time. Solidification generally followed the Chipman-Fon Dersmith equation, in which the solid thickness is the sum of a negative constant and a multiple of the square root of the freezing time. (16)

**Replacement of the Unfrozen Liquid** - A sophisticated version of ingot dumping has been employed by Bower, Brody, and Flemings (8). After the start of slow equiaxed freezing of an aluminum-copper alloy, liquid lead was poured into the mold to displace the lighter unfrozen liquid of the alloy. After removal of the resulting ingot, the lead was remelted and drained, leaving only the solid dendrites of the aluminum-copper alloy. They found that regular arrays of pointed dendrites protruded out of the solidification front.

**Quenching the Ingot During Slow Freezing** - Utilizing the fact, cited above, that the microstructure becomes finer as the local freezing rate is increased, several investigators
have drastically increased the rate of heat extraction from the chill at some time after freezing has begun. Kohn and Philibert\(^{20,21}\) show a series of aluminum-copper ingots in which coarse dendrites at the top surface of the ingots and coarse dendrites falling into the melt are clearly distinguished from the closely-spaced dendritic structure which surrounds them. Bower, Brody and Flemings\(^{8}\) delineated the interface of a vertically solidifying aluminum-copper alloy and Backerud and Chalmers\(^{22}\) have shown the interface of a horizontally freezing aluminum-copper alloy by the same method. In both studies, dendritic tips extending into the melt are visible.

**Addition of a Radioactive Tracer to the Melt** - Kohn\(^{23}\) and Andrews and Gomer\(^{24}\) have added radioactive tracers to the melt of steel ingots in the middle of solidification, to obtain the outline of the solid zone and to follow the motion of liquid in the ingot. Although solidification was allowed to proceed to completion, the result was similar to interrupting the freezing at about the time the addition was made.

**Summary** - A number of methods have been developed which can give views of the solidification process at specific times. They all involve some singular activity such as dumping, quenching, or adding a radioactive tracer, which separates the time preceeding the action from the time following the action. Repeating the process for differing amounts of solidification allows construction of a more or less continuous picture of the solidification process.
3.1.3 Methods Which Allow Direct Observation of the Solidification Process

Were liquid metals transparent, the entire freezing process could be viewed directly, so that the structures which develop on freezing could be characterized unambiguously. Effort might then be devoted directly to investigating the causes for the formation of these structures. A certain very limited success has recently been achieved in this direction.

**Modeling Solidification with Transparent Media** - Jackson and Hunt\(^{25}\) and Jackson, et al\(^{26}\) have demonstrated that certain transparent organic materials which have a low dimensionless entropy of fusion freeze dendritically. From a study of the solidification of these materials, they concluded that dendrite arms can melt off from the main dendrite structure and fall off into the melt. The use of these transparent materials to simulate the solidification of metals has become quite popular and helpful (Section 3.2).

**Observation of the Top Surface of the Melt** - The same solidification shrinkage which often causes dendrites to be visible at the surface of a solidified ingot, makes it possible to observe their formation at the top surface of a freezing melt. Glicksman and Schaefer\(^{27-29}\) have used a transparent flux to keep the top surface of bismuth and tin melts clean during horizontal solidification and have observed dendritic structures protruding into the melt as solidification proceeds.
Freezing in an Electron Microscope - An even more novel approach is the solidification of a thin film of metal in an electron microscope. Glicksman and Vold\(^{30}\) have been able to cause bismuth to melt and refreeze by varying the energy transferred from the electron beam to the metal. This method allows continuous observation of the freezing process on a submicroscopic scale.

Summary - Under certain limited conditions, continuous observation of the advancing solid-liquid interface has been possible. In addition a number of transparent materials appear to freeze in a manner similar to metal alloys.

3.1.4 Discussion

A wide variety of methods have been developed for investigation of the process of solidification in metal alloys. Some of the methods are simple and involve almost no intervention in the freezing process, while some are marvelously ingenious in the way they "get inside" the metal to delineate the solid-liquid interface. It is clear that each method has particular suitability in certain studies. In Chapter 4, a modification and extension of the sudden quench method is devised for use in this study. The effectiveness of this method will be discussed in Chapter 11 in relation to some of the other methods which have been presented here.
3.2 Liquid Motion in the Part-Solid Region of a Dendritically Freezing Alloy

The main direction of this study is the examination of the physical factors which cause convective flow of the interdendritic liquid through the solid dendrite structure. The existing evidence for the flow of interdendritic liquid during solidification is quite varied. Exudation of the interdendritic liquid onto the surface of an ingot, and inverse segregation, have been shown to result from liquid flow. Recently, studies done with transparent media have produced liquid flow channels which are very much like segregate streaks found in solidified metal alloys. Also, interdendritic flow has been modeled mathematically to account for the vertical macrosegregation caused by horizontal solidification. These studies are presented briefly here.

**Exudation of Interdendritic Liquid** - A visible manifestation of liquid motion occurs in casting processes when the mold wall and part solid region separate at the chill face during solidification. This allows interdendritic liquid to flow onto the ingot surface in small "drops". \(^{(31)}\)

**Inverse Segregation** - Inverse segregation is the presence of a higher than average concentration of solute near the chill surface of a cast ingot. \(^{(32)}\) It has been explained qualitatively by Scheil, \(^{(33)}\) and quantitatively by Kirkaldy and Youdelis, \(^{(34)}\) as the result of interdendritic liquid moving toward the chill between the solid dendrite arms. This motion is caused by the decrease in volume which occurs when liquid is
frozen. This creates a negative pressure which causes fluid flow. This concept of fluid motion to feed solidification shrinkage has been further developed by Flemings, Nereo, and Mehrabian, (35-38) into a description of other types of ingot segregation, such as centerline segregation, and under-riser segregation.

**Flow Channels in Transparent Models** - Using a solution of ammonium chloride in water to model the freezing of a steel ingot, McDonald and Hunt (39, 40) have found upward flow of the interdendritic liquid. In their case, the rejected solute made the interdendritic liquid less dense than the bulk fluid. In addition, the fluid motion formed clearly visible cylindrical channels through which the liquid rose rapidly through the part-solid zone. They assume that the flow channels produced in the model system are the same phenomenon as the type of segregate in cast steel ingots, called "A segregates", which has been described often in the literature (e.g., by Marburg (16)). Standish (41) however, questioned the validity of using aqueous ammonium-chloride as an analog for the solidification of steel.

In a corresponding study, Copley, et al (42) have used a water-ammonium chloride system to model the vertical, unidirectional solidification of nickel alloys. Giami and Kear (43), in a companion paper, present observations on vertical arrays of equiaxed dendritic material which occur in vertically solidified nickel alloys. They characterize the structures, called "freckles," as regions of high porosity,
and high solute content, indicating that they were the last part of the casting to freeze. The number of freckles was proportional to the ingot cross-section. The results in the model system indicate that freckling was caused by solute rejection into the interdendritic liquid which decreased the density of the liquid and created a density inversion. This inversion is unstable, as it is opposed by the gravity field. The condition is relieved by upward flow of liquid through narrow vertical channels. The flow dissolved and carried the dendritic structure away, creating an array of vertical liquid jets, or "freckles." The authors construct a "freckling potential" which is the difference in the potential energy per unit area of the system with and without the density inversion. From this they show that freckle formation is favored by a low thermal gradient, a large density inversion, a high thermal diffusivity, a low solute diffusivity, and a low viscosity.

It is obvious that the vertical flow phenomena observed by McDonald and Hunt and by Copley et al are identical. It is also likely that "A segregates" and "freckles" are similar, if not identical phenomena.

Mathematical Model of Flow – Mehrabian, Keane, and Flemings (44) have combined earlier work on the freezing of solidification shrinkage (35-38) with consideration of the influence of gravity on the flow of interdendritic liquid and the mechanics of flow through porous media. They have constructed a mathematical model in which the value of the permeability of an aluminum-copper alloy is chosen empirically
to obtain the best fit between the results of their calculations and the experimentally determined macrosegregation of a horizontally solidified aluminum-copper ingot. Additionally, they relate the formation of "channel type segregates" to the flow of interdendritic fluid away from the chill at a velocity sufficient to cause solution of the dendritic structure by the solute rich liquid. The critical parameter involves the velocity of the flow vector, the thermal gradient, and the rate of temperature decrease. An ingot frozen by them under conditions favorable to channel formation (slow growth, high solute content) does in fact show segregate formation. (45)

Thus there are a number of studies in the current literature which indicate that the flow of interdendritic fluid through the part solid region of an ingot can have significant effects on the macrosegregation and structure of castings. The object of this study is to obtain a better understanding of the nature of the interaction between convective flow and the solidification structure.
4. THE METHOD

Natural convection in the part solid region was investigated in two ways. First, as described below and in Chapters 5, 6, 9 and 10, a method was developed which makes visible the solid-liquid interface at specific times during the freezing of an ingot. Using this method, the solidifying structures of ingots which are freezing vertically are compared to the solidifying structures of ingots which are freezing horizontally. Since no natural convection normally occurs in an ingot which is freezing vertically, marked differences in the solidifying structures are to be attributed to natural convection in the part solid region. (An exception to this rule is the case in which rejected solute in the part solid region causes a density inversion in the interdendritic liquid. (39,40,42,43) For the aluminum-copper alloy which is discussed in Chapters 5-8, however, vertical solidification produces a density gradient which is stable.)

Besides this comparative analysis, the three factors which determine natural convection in the part solid region were found directly for a series of horizontally solidifying aluminum-4.5 wt pct copper ingots. The distribution of liquid within the part solid region was found from measurements on ingots which, as described below, were partly solidified and then quenched. The concentration of solute in the interdendritic liquid was found by electron microprobe analysis. The thermal gradients in the solidifying ingots were determined
by thermocouple measurements. Based on these three factors a model for flow and macrosegregation is presented in Chapter 8.

Experimental Method - The experimental method used to distinguish the solid-liquid interface as it exists during freezing is a modification of the "sudden quench" method described in the Section 3.1.2. That method uses the fact that the more rapidly an ingot or a portion of an ingot is solidified, the more finely divided is the resultant microstructure. An ingot is partly solidified at a relatively slow rate of freezing, Figure 4.1(a). The freezing rate is then rapidly increased, surrounding the coarse dendrite arms of the slowly frozen portion of the ingot with very fine dendrite arms, (b).

A primary disadvantage of this method is that unfrozen liquid at a point far from the chill undergoes a less drastic quench than unfrozen liquid closer to the chill. Thus the ability of this method to delineate a solid-liquid interface depends in part on the distance of that interface from the chill.

This disadvantage is eliminated, at the expense of certain experimental complications, by the method used in this study. As shown in Figure 4.1(c), the rapid quench was applied, not at the chill, but all along the freezing ingot, in a direction transverse to the direction of slow freezing. For this reason, this method is referred to as the "slow freeze-transverse quench technique."
Fig. 4.1  Schematic illustration of quenching techniques.  (a) Slow freezing of an ingot.  (b) Quench applied at the chill.  (c) Transverse quench used in this investigation.
Two distinct arrangements for application of the method will be described. The first, for an aluminum-4.5 wt pct copper alloy is presented in Chapter 5. The second, for iron alloys is described in Chapter 9.

A discussion of the effectiveness and relative usefulness of the slow freeze-transverse quench technique is given in Chapter 11.
5. INVESTIGATION OF THE VERTICAL SOLIDIFICATION OF ALUMINUM-4.5 WT PCT COPPER

The slow freeze-transverse quench method described in Chapter 4 was applied to an aluminum-4.5 wt pct copper alloy which was solidified vertically under various conditions. Vertical solidification was investigated to provide a standard, or control in which no convection can occur. Changes in solidification structure which are caused by convection in horizontally solidifying ingots can then be noted by comparison with the structure of these vertically solidifying ingots.

The aluminum-4.5 wt pct copper alloy was chosen to aid the development of the experimental method. It has a moderate melting temperature, 648°C, a large freezing range, 100°C, and considerable work has been done on the solidification of this alloy. (8,35,46)

5.1 Outline

Apparatus is described for the application of the slow freeze-transverse quench method to vertical solidification of the aluminum-4.5 wt pct copper alloy.

Temperature measurements in the vertically solidified ingots are presented. They indicate that the solidification front advanced at a nearly constant rate.

Photographs of the quenched ingots show the presence of vertical liquid channels between groups of primary dendrite arms during vertical solidification. Ingots frozen under
various conditions indicate the effects of superheat and freezing rate on the solidification structure.

Measurements relating the volume fraction of channels to the volume fraction of liquid show that most of the unfrozen liquid in the part solid region is distributed between the secondary and tertiary dendrite arms.

Electron microprobe analysis shows positive segregation of solute into the liquid channels.

The initial vertical macrosegregation which was present at the start of each experiment was determined by chemical analysis of ingots which were quenched directly from the liquid state. No macrosegregation from the surface to the vertical center plane of the ingot was found either by chemical or by electron microprobe analysis.

Discussion of the experimental results for both vertical and horizontal solidification is presented in Chapter 7.

Discussion of the value of the slow freeze-transverse quench technique, which is illustrated in part by the results of this chapter, is deferred to Chapter 11.

5.2 Apparatus and Materials

The mold which was designed for applying the slow freeze-transverse quench method to solidification of the aluminum-4.5 wt pct copper alloy is illustrated in Figure 5.1. It was essentially a multilayered sandwich held together by stainless steel bolts. The mold cavity (4) was 7.7 cm long, 12 cm high and 1 cm thick, and was formed by wrapping 0.03 cm
Fig. 5.1  Ingot mold for applying the slow freeze-transverse quench technique to the aluminum-4.5 wt pct copper alloy.
thick graphite paper (3) around two interlocked grade AUC graphite blocks (5), and sealing the seams with a graphite cement. A wire screen (2), was placed over the graphite paper and held in place by stainless steel plates (1). Openings had been cut in the plates to correspond to the location of the mold cavity. The narrow mold and the very thin mold wall made of graphite paper were designed to allow rapid transverse heat transfer during the quench.

After assembly, the mold unit was placed in an oven at 100°C for at least four hours to cure the graphite cement. A graphite rod was fastened vertically in the mold cavity to preserve a space for the thermocouples. Then an aluminum-4.5 wt pct copper alloy made from 99.99 wt pct aluminum, and OFHC copper, was cast into the mold with a superheat of 70°C to 90°C. Details of the preparation are given in Appendix A. The aluminum-copper phase diagram is shown in Figure 5.2.

Figure 5.3 illustrates how the ingot mold was surrounded with insulation so that unidirectional solidification could be carried out. The mold is tied to the steel frame (a) and surrounded by insulating bricks which were fitted together and packed with insulating fiber to prevent air infiltration (b). The bricks which covered the openings in the steel plates could be raised quickly (c) exposing the graphite paper mold walls. Thermocouples were made from 0.033 cm chromel and alumel wires, all taken from the same lots of wire. Two hole alumina insulation tubes were used, and the measuring junction was protected with a coating of Sauereisen cement.
Fig. 5.2  Aluminum rich portion of aluminum-copper phase diagram. (47)
Fig. 5.3 Assembly of apparatus for the aluminum-4.5 wt pct copper alloy. (a) Attachment of ingot mold to the steel frame. (b) Top view showing thermocouple leads. (c) Side view showing sliding insulating bricks. (d) Resistance heater. (e) Insulated mold unit. (f) Nitrogen gas cooling tube.
Fig. 5.3, continued.
The thermocouples were inserted from the top of the mold, and a kanthal wire resistance heater (d) was placed at the top of the mold. The assembled unit is shown in e. A sliding brick at the bottom of the unit could be removed to allow placement of the nitrogen gas cooling tube (f) beneath the mold. Holes of 0.16 cm diameter drilled in this copper pipe on 0.64 cm centers directed nitrogen gas up onto the graphite block which formed the bottom surface of the mold, causing vertical solidification.

The transverse quench was done with a water spray of 0.34 liter/min on each side of the ingot and caused a cooling rate of 500°C/min at the center of the ingot.

The voltage produced by a thermocouple in the melt was recorded on a chart recorder with a 10 mv span. A voltage suppression box, Appendix B.1, was used to reduce the output voltage of the chromel-alumel thermocouple to the 0-10 mv scale of the recorder without reducing the amplitude of the variations of voltage. A rotating switch, built by J. Wright, Appendix B.1, was used when it was necessary to record sequentially on one recorder the output of two different thermocouples in the melt. This switch eliminated the errors of comparison which would have been caused by using two separate recorders.

5.3 Procedure

The preliminary preparations for the experiment were the construction of the ingot mold, pouring of the ingot, and
placing of the ingot in the insulation unit, as described above. The complete insulation unit, containing the ingot, was then placed in a resistance furnace, through which nitrogen gas was passed at 1.4 liter/min to prevent oxidation of the graphite paper.

The remelting cycle is illustrated by the temperature of the ingot as it is heated, Figure 5.4. The power in the furnace was turned on at A. When the eutectic temperature was reached, B, there was a noticeable thermal arrest which occurred within one degree of 548°C. This measurement provided a temperature calibration for each experiment.

Temperature measurements showed that the heating was not uniform, the bottom of the ingot being some five degrees hotter than the top. As the temperature reached the liquidus, 647°C, the rate of increase of temperature decreased until all of the solid was melted, C. The temperature then increased more rapidly until the power was turned off, D. The maximum temperature was reached slowly, E.

When this occurred, the insulation unit containing the molten ingot was removed from the furnace and clamped between the two water spray nozzles. The small resistance heater within the insulation unit was then turned on. It produced 15 cal/sec, but only one-third of this heat was directed to the top of the ingot. The power of this heater was calculated to prevent solidification from occurring at the top surface of the ingot without affecting the temperature below the surface.
Fig. 5.4 Temperature of aluminum-4.5 wt pct copper ingot as it is reheated in the resistance furnace.
The entire unit cooled slowly in the air to the desired starting temperature. Depending on the experiment, this was generally between 700°C and 720°C. The insulating brick below the ingot was then removed, and the nitrogen cooling gas tube was inserted. The gas flow was turned on to cause vertical solidification. The temperatures in the ingot during this time are given in detail in Section 5.3.1.

When the solidification front had progressed upwards into the ingot, the sliding insulating bricks facing the broad sides of the mold were raised, and the water sprays were turned on. Figure 5.5 shows the orientations of the ingot mold, cooling gas probe, and spray nozzles.

After removal from the mold, the ingot was ground, polished, and etched to reveal the solidification structure, Appendix C. Due to sagging of the wire screen which supported the graphite paper, the ingot usually bulged out slightly near its bottom.

To review, the experimental procedure was begun by constructing the mold, pouring the ingot, and mounting the mold within the insulation unit. The entire unit was reheated to remelt the ingot and then clamped between the water spray nozzles. Vertical freezing was caused by nitrogen gas which cooled the bottom surface of the mold. After some solidification, the ingot was quenched by sprays of water which impinged directly on the graphite paper walls of the mold.
Fig. 5.5 Orientation of the ingot mold, cooling gas tube, and water spray nozzles for the vertical solidification and transverse quench of the aluminum-4.5 wt pct copper alloy.
5.4 Results

For clarity, presentation of the experimental results is divided into several sections. Separate sections are devoted to the temperature measurements, macrostructures, distribution of the liquid within the part solid region of the ingot, microstructures and microprobe analysis, and macrosegregation. The relations between the various results are discussed in Chapter 7.

5.4.1 Temperature Measurements

The temperatures within the ingot during slow vertical freezing are presented here in detail. Figure 5.6 shows the relative positions of two thermocouples within the ingot. Thermocouple 1 is near the top of the ingot and is thus at a higher temperature during solidification than thermocouple 2 which is near the chill at the bottom of the ingot.

Figure 5.7 shows the temperatures within ingot A-48 as it froze vertically. For this experiment, thermocouple 1 was 8.7 cm from the chill and thermocouple 2 was only 0.2 cm from the chill. At point A, the insulation unit holding the molten ingot had been removed from the resistance furnace and clamped between the spray nozzles. The small resistance heater at the top of the ingot was turned on when the temperature in the ingot dropped to the starting temperature, B. A vertical temperature gradient of approximately one degree per centimeter developed within the ingot during this cooling.
Fig. 5.6  Location of thermocouples for vertical solidification of the aluminum-4.5 wt pct copper alloy.
Fig. 5.7 Temperatures measured in an aluminum-4.5 wt pct copper ingot as it froze vertically. T.C.1 was 8.7 cm from the bottom surface and T.C.2 was 0.2 cm from the bottom. The dashed lines are interpolated for imaginary thermocouples located 3.0 cm and 5.9 cm from the chill (see Appendix F).
This was probably caused by a slight infiltration of air between the insulating bricks and the ingot mold.

When the starting temperature was reached, corresponding to a superheat of 50 - 70 degrees, the bottom insulating brick was removed, the nitrogen cooling gas tube was placed below the bottom surface of the mold, and the flow of nitrogen gas was begun. For the experiment represented by Figure 5.7, the gas flow rate was 12 liters per minute.

As shown by the temperature curve, the cooling rate of the ingot was more than doubled by the cooling gas. The rate of cooling increased immediately at the bottom of the ingot, and after a delay of about one minute it increased at the top of the ingot. The average vertical thermal gradient within the ingot increased to about three degrees per centimeter.

After solidification began at the chill, C, the rate of temperature decrease in the liquid slowed. This occurred because the advancing dendrite tips remained at the liquidus temperature and thus as the superheat was removed from the melt, the vertical temperature gradient became smaller. This change in the cooling rate occurred first at the chill, and later at the top of the ingot, D. As solidification proceeded, the vertical thermal gradient in the liquid dropped to zero. It took thirteen minutes for the dendrite tips to reach the top of the ingot.

The rate of cooling in the part solid region was approximately constant as long as some superheat remained in the liquid. Once all of the liquid was at the liquidus
temperature, however, the rate of cooling increased, F. After the dendrite tips reached the top of the ingot, the rate of cooling in the ingot again increased, G.

Most ingots were quenched before the dendrites tips at the top of the columnar zone reached the top of the ingot, between points C and G on Figure 5.7. The cooling rate due to the water quench was about 500 degrees per minute.

**Rate of Solidification** - As the macrostructures in the next section show, the location of the dendrite tips in an ingot which was quenched before solidification had reached the top of the ingot can be measured directly on the etched ingot. This distance can be plotted against the time between the start of nitrogen gas cooling and the water quench, Figure 5.8. Similarly, the location of a thermocouple can be plotted against the time between the start of gas cooling and the time at which the temperature of the thermocouple drops below the liquidus temperature. Thus points H and I from Figure 5.7 are also shown in Figure 5.8. Since the superheat was different for each experiment, the data in Figure 5.8 have been corrected to correspond to a starting temperature of 710°C. The correction is made using the rate of cooling during the time when the superheat was being extracted from the melt, between points B and D in Figure 5.7. This was taken as ten degrees per minute. Details of this correction are given in Appendix B.2. Similar data from some earlier experiments are shown in Figure 5.9. Freezing began about a minute earlier, because the insulation unit was not as well constructed as for the later experiments.
Fig. 5.8  Position of the solidification front for vertical solidification as a function of the time after the start of nitrogen gas cooling at 12 liter/min. Open symbols represent measurements made on etched ingots. Solid symbols are from thermocouple data. All of the data has been corrected to an apparent starting temperature of 710°C.
Fig. 5.9  Position of the solidification front for vertical solidification as a function of the time after the start of nitrogen gas cooling at 12 liter/min. These data are from the earlier ingot. All of the data has been corrected to an apparent starting temperature of 710°C.
Thus Figures 5.8 and 5.9 show the position of the solidification front at any time after the start of the cooling gas flow. The points measured on the etched ingots agree with those obtained from thermocouple measurements. The motion of the solidification front is assumed to be constant, 0.9 cm/min.

For ingots frozen by cooling gas flow rates of 48 liter/min., the initiation of solidification at the chill occurred about one half minute sooner. The rate of advance of the dendrite tips, however, appeared to be the same as with the lower gas flow.

**Thermal Gradients** - Using the value 0.9 cm/min for the dendrite tip velocity, and interpolating between the temperature curves in Figure 5.7, as described in Appendix B.2, it is possible to obtain the vertical thermal gradients which existed in ingot A-48 at successive times after the start of the gas cooling, Figure 5.10.

**Selected Thermal Gradient** - As shown by Figure 5.10, the thermal gradient in the part solid region of the ingot proceeded forward during solidification without changing its form very much. Since the subsequent sections deal mainly with the part solid region, a simplifying assumption was made about the form of the temperature distribution. It was assumed that the thermal gradient progressed through the ingot without changing its form. The particular form of the thermal gradient which was chosen is the curve shown at eight minutes in Figure 5.10. A tabular function was constructed to represent this curve in
Fig. 5.10 Thermal gradients in a typical vertical ingot at successive times after the start of gas cooling, 12 liter/min.
computer calculations, Appendix B.3. This function is plotted in Figure 5.11.

5.4.2 Macrostructures

To investigate the solidification structure of vertically freezing aluminum-4.5 wt pct copper ingots, several series of ingots were partly frozen and then quenched. The experimental conditions and quench times for these ingots are listed in Table 5.1.

For convenience, a reference system has been adopted for locating points and identifying polished faces in the ingots, Appendix D. Except where noted, the photographs in this section show the \(-z\) face of the ingots, with the chill surface at the bottom, the \(x\) axis horizontal, and the \(y\) axis vertical.

**Series VA** - A series of ingots was frozen by a nitrogen gas flow of 12 liter/min from a starting temperature, \(T_{st}\), of 700\(^\circ\)C, and quenched at successively longer times after the start of cooling.

Figure 5.12, of ingot A-17, shows the early development of vertical liquid channels between groups of primary dendrite arms. These are the dark vertical lines (1) which appear on the photograph. This appearance is due to the presence in those regions of finely spaced dendrite arms which, because they have been rounded by the etchant, diffuse the incident light. The coarse dendrite arms which were already solid before the quench retain their flat polished
Fig. 5.11  Selected thermal gradients. It is assumed that the thermal gradient in ingot A-48 eight minutes after the start of gas cooling passed through the ingots unchanged from the start of solidification, for a gas flow of 12 liter/min.
### Table 5.1
Series of Aluminum-4.5 wt pct Copper Ingots Quenched at Various Times During Vertical Solidification

<table>
<thead>
<tr>
<th>series</th>
<th>ingot</th>
<th>gas flow liter/min</th>
<th>starting temp. °C</th>
<th>quench time min</th>
<th>tip location cm</th>
<th>heater current amp</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA</td>
<td>A-17</td>
<td>12</td>
<td>696.0</td>
<td>4.4</td>
<td>2.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>A-40</td>
<td>12</td>
<td>698.5</td>
<td>6.0</td>
<td>2.5</td>
<td>7.6*</td>
</tr>
<tr>
<td></td>
<td>A-16</td>
<td>12</td>
<td>697.5</td>
<td>6.3</td>
<td>3.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>A-15</td>
<td>12</td>
<td>698.0</td>
<td>6.3</td>
<td>3.2</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>A-19</td>
<td>12</td>
<td>698.0</td>
<td>10.0</td>
<td>6.6</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>A-18</td>
<td>12</td>
<td>698.0</td>
<td>none</td>
<td>complete</td>
<td>8.0</td>
</tr>
<tr>
<td>VB</td>
<td>A-41</td>
<td>12</td>
<td>718.5</td>
<td>8.1</td>
<td>1.5</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>A-43</td>
<td>12</td>
<td>718.0</td>
<td>10.1</td>
<td>3.2</td>
<td>7.6*</td>
</tr>
<tr>
<td></td>
<td>A-42</td>
<td>12</td>
<td>714.0</td>
<td>12.0</td>
<td>4.4</td>
<td>7.6</td>
</tr>
<tr>
<td>VC</td>
<td>A-14</td>
<td>48</td>
<td>703.5</td>
<td>4.0</td>
<td>2.5</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>A-20</td>
<td>48</td>
<td>696.5</td>
<td>8.3</td>
<td>6.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>A-44</td>
<td>48</td>
<td>718.0</td>
<td>10.1</td>
<td>3.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>

* In these experiments, the heater was turned on several minutes before reaching $T_{start}$. 
Fig. 5.12 The early development of vertical liquid channels. Ingot A-17, 1.5X.
faces and reflect the incident light. The irregular surface at the bottom was caused by the graphite cement which exuded onto the chill.

The structures of ingots A-40, A-16, and A-15, Figures 5.13 - 5.15 show the similarities and differences in the structure of ingots which were frozen under essentially identical conditions. A number of large vertical liquid channels formed between groups of primary dendrite arms (1). Some adjoining groups have the same orientations, while other adjoining groups have obviously differing orientations. In most cases the top of the group of dendrite arms is rounded, giving the appearance of a finger of solid pointing up into the melt. Even on a macroscopic scale, the solidification front is rough and diffuse.

The structure of ingot A-19, Figure 5.16, shows that the vertical liquid channels are maintained near the top of the columnar zone as solidification continues, but are frozen over nearer the chill. Thus the formation of channels must be associated with the advancing solidification front. Generally at greater distances from the chill, it was more difficult to maintain columnar solidification.

Ingot A-18 was frozen completely without any transverse quench, Figure 5.17. Its structure shows no remaining evidence of the vertical channels which were present during growth. The obvious worth of the slow freeze-transverse quench technique is that it demonstrates features of the solidification process which do not exist in the completely solidified
Fig. 5.13 Vertical liquid channels between groups of primary dendrites. Ingot A-40, 1.5X.
Fig. 5.14  Vertical channels between groups of primary dendrites. Ingot A-16, 1.5X.
Fig. 5.15  Vertical channels between groups of primary dendrites. Ingot A-15, 1.5X.
Fig. 5.16  Vertical channels after continued solidification. Ingot A-19, 1.5X.
Fig. 5.17  Completely solidified ingot. A-18, 1.5X.
ingot. The vertical channels leave no obvious "tracks", but the discernable columnar grains have the same size in the final structure as the groups of primary dendrite arms, or "fingers" had in the partly solidified ingots.

Series VB - A series of ingots was frozen from a starting temperature of approximately 720°C by a nitrogen gas flow of 12 liter/min, to determine the effect of superheat on the solidification structure.

Ingot A-41 was quenched shortly after solidification began, Figure 5.18. The structure shows a large number of small vertical channels within a group of primary dendrites which all have the same orientation (1), and a few larger channels between groups of primary arms (2). The number of differently oriented groups of primary dendrite arms is small.

The structure of ingot A-43 shows many distinct vertical channels both between primary dendrite arms and groups of primary dendrite arms, Figure 5.19. The four vertical sides of a section from this ingot are shown in Figure 5.20. Horizontal sections through this vertical section are shown in Section 5.4.4.

Air infiltration at the tip of ingot A-42 caused solidification at the top surface of the ingot A-42, Figure 5.21. Crystallites can be seen breaking off from the "roof" of the ingot and showering down onto the columnar zone. If slow solidification had been allowed to continue, the top half of the ingot would have consisted of randomly oriented, equiaxed grains.
Fig. 5.18  Early development of vertical channels. Ingot A-41, face +z, 1.5X.
Fig. 5.19  Vertical liquid channels. Ingot A-43, 1.5X. (a) Face -z. (b) Face +z.
Fig. 5.19, continued.
Fig. 5.20  Four faces of a section cut from ingot A-43. (a) Face \(-z\). (b) Face \(+x\). (c) Face \(+z\). (d) Face \(-x\).
Fig. 5.21 Crystallite falling from the "roof" of the ingot. Ingot A-42, 1.5X.
Series VC - Three ingots were solidified by a nitrogen gas flow of 48 l/min - two from a starting temperature of about 700°C, and one from a starting temperature of about 720°C.

No large vertical channels are visible in the structures of ingots A-14 and A-20, Figures 5.22 and 5.23. A number of fine vertical channels do occur, however. The columnar grains are larger and longer than in the ingots shown above. The structure of ingot A-44 shows one large vertical channel and more misalignment than was evident on the previous two ingots, Figure 5.24.

Shrinkage - This alloy shrinks about 5.5 pct when it solidifies. In those ingots in which a solid "roof" formed at the top of the ingot, the remaining liquid moved down to feed the solidification shrinkage at the bottom of the ingot and left a contracted area below the solid top. In some ingots, solidification shrinkage also occurred into the top of the columnar zone at the vertical graphite block (at x = 0.0 cm).

5.4.3 Distribution of Liquid in the Part Solid Region

The subject of this section is the volume fraction of the part solid region which consists of identifiable liquid channels, as a function of the vertical distance from the chill. The macroscopic features of the liquid channels have been described in the previous section, and their microstructural features are described in the following section. Thus, the locations of the liquid channels within the part solid regions are presented elsewhere, and only the overall features of the
Fig. 5.22 No large vertical channels are visible in ingot A-14. 1.5X.
Fig. 5.23 Only small vertical channels occurred in ingot A-20. 1.5X.
Fig. 5.24  Narrow vertical channels in ingot A-44.  1.5X.
volume fraction channels, $g_c$, and the surface area of channels per cm$^3$ of the part solid region, $\Sigma_c$, are considered here.

A liquid channel is defined in this study as a region which has a recognizably finer dendrite arm spacing than adjacent regions. In practice this definition was applied to ingots which had been ground on 400 grit paper and etched, Appendix C. They were viewed at 10X magnification. It is to be noted that a "liquid channel" thus defined could be as small as 0.005 cm, and could be completely surrounded by coarse dendrite arms.

The measurements were made by moving an ingot past the microscope objective on a moving stage, and counting the channel and total distances with a Hurlbut counter.\(^{(48)}\) The number of channels intersected was also counted. The measured lengths were converted to volume fraction channels by a computer program, Appendix E, according to the equation

$$g_c = \frac{l_c}{l_t} \quad (5.1)$$

where $l_c$ is the total linear distance on the trace which was occupied by channels, and $l_t$ is the total length of the trace. This equation thus equates the volume and linear fractions occupied by channels.\(^{(49)}\)

The surface area per unit volume (1/cm) of the part solid region, $\Sigma_c$, was calculated as

$$\Sigma_c = 4n_c \quad (5.2)$$
where \( n_c \) is the number of channels intersected per unit length of the trace. The factor 4 includes one factor of 2 to convert from the number of channels intercepted to the number of channel surfaces intercepted, and a second factor of 2 to convert from the number of surfaces intersected per unit length to the surface area per unit volume. (52)

Data from two ingots each from series VA, VB, and VC, Table 5.1, are shown in Figures 5.25-5.30. Each point represents the results from a trace about 1 cm long and parallel to the base of the ingot on the -z face. A vertical strip which appeared to be representative of the ingot was chosen for each set of traces.

The fraction channel, \( q_c \), is always small near the chill, and increases sharply within a centimeter of the solidification front. The increase is sharpest in ingot A-20, Figure 5.30, which was frozen by a nitrogen gas flow of 48 liter/min. The increase is not as sharp for ingots A-17, A-15, A-41, and A-43, which were frozen more slowly by a gas flow of 12 liter/min.

It is clear from the figures that the curve form moves upward with the solidification front as freezing proceeds. The surface area of the channels generally increases towards the solidification front.

The data from the ingots in series VA and VB should be contrasted with the curve shown in Figure 5.31. The volume fraction of the part solid zone which is liquid when the solidification front is 4.2 cm from the chill, has been
Fig. 5.25  Distribution of liquid in ingot A-17, series VA, as a function of distance from the base of the ingot.

Fig. 5.26  Distribution of liquid in ingot A-15, series VA.
Fig. 5.27  Distribution of liquid in ingot A-41, series VB.

Fig. 5.28  Distribution of liquid in ingot A-43, series VB.
Fig. 5.29  Distribution of liquid in ingot A-14, series VC.

Fig. 5.30  Distribution of liquid in ingot A-20, series VC. (The solidification front was at 6.25 cm.)
Fig. 5.31  Volume fraction liquid in the part solid region when the solidification front was 4.2 cm above the chill, for a gas flow of 12 liter/min.
calculated from the selected thermal gradient, Section 5.4.1, and Equation 6.3 for the volume fraction liquid, \( q_1 \), as a function of temperature.* It is evident that only a small fraction of the total liquid at any location in the part solid region formed distinct liquid channels during solidification.

5.4.4 Microstructures and Solute Gradients

Microstructures and electron microprobe analysis of ingots A-15 and A-43, which were frozen by a gas flow of 12 liter/min, are presented in this section. The microstructures demonstrate the continuous nature of the channels in three dimensions. Preparation of the samples is described in Appendix C.

The microprobe analysis shows the solute content of the liquid channels as a function of the distance from the dendrite tips at the tcp of the columnar zone. Complete details of the microprobe calculations are given in Appendix F. The method used to investigate local compositions within the liquid channels was presented at the Fifth National Conference on Electron Probe Analysis by Pielet, Saffir, and Elliott.\(^{(50)}\)

* The inflection in the curve is caused by the decrease in the thermal gradient near the solidification front. See Appendix E.
Ingot A-15 - A portion of ingot A-15 is shown in Figure 5.32. The section shown here is at the top of the columnar zone and can also be seen in Figure 5.15. As shown here, secondary arms protrude into the channel, forming small side channels perpendicular to the main channel. The secondary arms are round and coarse at their tips. This means that there was no solid within the channel before the quench, since such solid would have to have been connected to the secondary arms. Thus, before the quench, the channels were regions of pure unfrozen liquid, and not a mixture of fine solid dendrites and liquid. The apparent porosity resulted from polishing this sample with alumina rather than magnesia. Such porosity is not visible on the other, properly prepared, samples.

To determine the solute concentration of the liquid channel at various distances from the top of the columnar zone, the sample was translated at a rate of $9.6 \times 10^{-3}$ cm/min under the analyzing spot of an electron microprobe along the lines shown in the figure. As the sample moved, the intensity of the CuKα radiation measured by the microprobe was accumulated for 5.0 sec and the results were printed while the counters reset themselves. Using conversion factors which were determined by measurements on a series of standards, each accumulated intensity was converted to weight percent copper.
Fig. 5.32 Section of ingot A-15 showing the locations of microprobe traces across the liquid channel. 20X.
Each resultant data point therefore represents the concentration of a length of $9.6 \times 10^{-4}$ cm along the trace.

Because the dendrite arms have a low copper concentration, while the interdendritic eutectic has a high concentration of copper, Figure 5.2, the data points vary from one to thirty percent copper. These data points are then presented in three different ways to describe the composition of the liquid channel and the adjacent solid.* First, all of the data points in the portion of the trace across either the liquid or the solid region are averaged to determine the average concentration in the liquid or solid at that location. Since each data point represents a region of different density, the data points are "weighted" according to the formula for the room temperature density of aluminum-copper alloys given in Appendix G.1. The averages thus obtained are the numbers given for portions of the traces in Figure 5.33.** Generally, the liquid channel has a higher concentration of copper than the adjacent solid regions.

A second treatment of the data points is to average a few adjacent points at a time to investigate local composition gradients. The averaging procedure is required because, as mentioned, the coring of the dendrite arms and the high copper

* The solid region, as shown in Section 5.4.3, is really a partly solid dendritic region before the quench, but the simpler designation "solid" will be used.

** The microprobe data and many of the other figures were plotted on a cathode ray tube using the GRDMET plotting program. (51)
Fig. 5.33 Moving average concentration between two eutectic peaks. Ingot A-15, area A, face -z. (a) line A. (b) line C. (c) line D. (d) lines F, G, and H.
Fig. 5.33, continued.
content of the interdendritic liquid are reflected in wide local variations between adjacent data points, Appendix F, Figure F.3. Since, however, the dendrite arms across which the trace runs are not evenly spaced, a constant averaging distance does not result in consistent averaging and is therefore unsatisfactory. The averaging distance is therefore constantly adjusted to the dendrite arm spacing by a computer algorithm described in Appendix F. The lines shown in Figure 5.33 thus represent the moving average concentration of two adjacent dendrite arms.* The principal observation from these curves is that there is no consistent solute gradient within the liquid channel.

A third method of analyzing the data points is to simply reorder all the points for a liquid or solid portion of the trace from lowest to highest. Again correcting for density, the data can then be plotted against the cumulative weight fraction solid, Figure 5.34. If little or no diffusion of solute occurs during solidification within the solid dendrite arms\(^{(8)}\), this curve is in effect the concentration in the solid at the solid-liquid interface of a dendrite arm, \(C_s\), as a function of the weight fraction which has solidified, \(f_s\).

* By its nature, the moving average does not pertain to the very ends of the trace. Also, an average at the junction of a liquid and solid region includes data from both regions. From these reasons, there is occasionally an apparent discrepancy between the average concentration in a region (the number at the top of the figure) and the moving average in that region.
Fig. 5.34  Concentration in the solid at the freezing surface of a dendrite arm. Data from the trace across the solid and liquid portions of line A-A', ingot A-15.
The concentration in the liquid at the solid-liquid interface, is \( C_s/k \), by the definition of equilibrium partition coefficient

\[
k = \frac{C_s}{C_l}.
\]

Thus the curve is directly connected to the concentration of copper in the interdendritic liquid during freezing until the interdendritic liquid is of eutectic composition at \( f_s \) about 0.9.

The distortions introduced into this curve by the motion of the sample while the data was taken, and by the inclusion of regions with different average compositions are discussed in Appendix F. Because of the movement of the sample, each point is an average of a region of finite size, and thus the curve for the liquid region does not reach the eutectic composition. Regions of different compositions produce an irregular curve form.

The composition at low fraction solid reflects the composition in the liquid as solidification in a region begins. Back diffusion of solute into the dendrite arms increases this concentration slightly, but, as this effect is related to dendrite arm size \(^{(8,46)}\) it occurs to about the same extent in both the liquid and the solid regions.

Figure 5.34 shows the curves for the solid and liquid regions are nearly identical near the top of the columnar zone. The other curves of \( C_s \) versus \( f_s \) for ingot A-15 are placed in Appendix F.
The average concentrations measured in the liquid and solid regions are plotted in Figure 5.35 as a function of distance from the dendrite tips at the top of the columnar zone. To illustrate the uncertainty in the average composition, the traces were divided into regions no longer than 0.03 cm. Thus all of the data points have approximately equal weight.

The solid line shown on the data was calculated from the thermal gradient shown in Figure 5.11 and the equilibrium liquidus concentration. Equation G.1, and includes a correction for the vertical macrosegregation which, as shown in Section 5.4.5, existed before any solidification began. The positive segregation into the liquid which was measured by the microprobe is thus even greater than that predicted by the equilibrium phase diagram.

**Ingot A-43** - As shown in Figure 5.36, a section was cut from ingot A-43. The cut surface was tilted 4° from the vertical to parallel the apparent channel direction. The tilt of the channels is evident on Figure 5.19. The four vertical sides of this section are shown in Figure 5.20. The cuts through this section, illustrated in Figure 5.36 were tilted 14° from the horizontal to make them perpendicular to the channels. The intersections of the channel across which microprobe traces were made are marked by asterisks.

Photographs of successive cut faces are shown in Figures 5.37 - 5.39. Since the faces were not perpendicular to the growth direction, the edge at the bottom of each
Fig. 5.35  Average concentrations of traces 0.03 cm long in the liquid and solid regions of ingot A-15, area A. The solid line is the equilibrium liquidus composition from the phase diagram and the measured temperature distribution. (For ease of comparison, this graph and all the other graphs which relate the average concentration to the distance from the tips have been drawn to the same scale.)
Fig. 5.36 Section cut from ingot A-43 for microprobe analysis. The intersections of the liquid channel which was analyzed are indicated by asterisks.
Fig. 5.37  Cross section of vertical channels at the top of the columnar zone. Ingot A-43, area D, 20X.
Fig. 5.38 Cross section of vertical channels about 0.3 cm below the top of the columnar zone. Ingot A-43, area E, 20X.
Fig. 5.39 Cross section of vertical channels about 0.7 cm below the top of the columnar zone. Ingot A-43, area A, 20X.
photograph was farther from the chill than the edge at the top of each photograph and therefore the channels at the bottom of the photographs appear to be larger than the channels at the top of the photographs. Clearly, the size and volume fraction of the channels decreases with distance down from the top of the columnar zone. The channels occur in chains parallel to the z axis. If any specific shapes can be ascribed to the channel cross sections, they are "V" shaped or "diamond" shaped. (These sections were polished with magnesia powder, Appendix A, and exhibit very little microporosity.)

The results of microprobe analysis across the channel on area A are shown in Figure 5.40. There is positive segregation of copper into the liquid, but there are no evident solute gradients within the liquid regions. There is considerable scatter in the data. For example, the concentration of copper in the liquid at the intersections of lines A, E, and F, as measured on each trace, is 9.6, 7.6, and 10.4 wt pct. Line C was taken at the core of a coarse dendrite and the measured composition was one percent. Line D, taken across what appear to be tertiary dendrite arms, gave a concentration of 1.7 wt pct copper. This is much lower than the average composition, 4.5 wt pct. Thus much of the copper must be located between the secondary dendrite arms at the locations where the tips of the tertiary arms meet.

Area B, still farther from the top of the columnar zone (and thus closer to the chill), is shown in Figure 5.41. Again, the liquid regions occur in "chains" parallel to the
Fig. 5.40 Moving average concentration between two eutectic peaks. 
Ingot A-43, area A, face +y.
Fig. 5.41 Cross section of vertical channels about 1.55 cm below the top of the columnar zone. Ingot A-43, area B, 20X.
z axis. Their structure is clearly governed by the intrusion of secondary arms, and thus their sides are irregular and angular. Microprobe traces, presented in Figure 5.42 demonstrated considerable segregation into the channels. The variation of the results of two traces across the same liquid region is again several percent.

Average concentrations from the liquid and solid regions of this section are plotted in Figure 5.43 as a function of distance from the vertical center plane of the ingot. The average composition in the liquid is about 10.5 wt pct, and there is no marked variation from the center to the edge of the ingot.

The last area of this series is shown in Figure 5.44. The channels are less than 0.01 cm wide at this distance from the top of the columnar zone. Considerable coarsening of the dendritic structure occurred between the time when the solidification front passed this location and the structure was first formed, and the time at which further coarsening was halted by the transverse quench. As shown at (1) on the figure, a number of dendrite arms are completely surrounded by solid formed through the coarsening of the adjacent dendrite arms. The microprobe data from this section are placed in Appendix F.

All of the data for the solid and liquid regions on areas A, B, and C were reordered to obtain curves of the concentration as a function of the fraction solidified, Figure 5.45. For all three areas, the concentration at very
Fig. 5.42 Moving average concentration between two eutectic peaks. Ingot A-43, area B, face +y. (a) Lines A, B, C, and D. (b) Lines E and H.
DISTANCE, CM

(b)

Fig. 5.42, continued.
Fig. 5.43 Average concentrations of traces 0.03 cm long in the liquid and solid regions on area B of ingot A-43. The solid line is the equilibrium liquidus composition. There is no segregation from the vertical center plane to the edge of the ingot.
Fig. 5.44  Cross section of vertical channels about 2.25 cm below the top of the columnar zone. Ingot A-43, face C, 20X.
Fig. 5.45  Concentration in the solid at the freezing surface of a dendrite arm. Data from traces across the solid and liquid portions of ingot A-43. (a) Area A. (b) Area B. (c) Area C.
Fig. 5.45, continued.
low fraction solid is higher for the liquid region than for
the solid region. This means that when the liquid region
first began to solidify, its copper content was higher than
was the copper content of the solid region when it first
began to solidify.

At higher fraction solid, the curves for the solid
regions are all concave upwards, but the curves for the liquid
regions are slightly convex. This can be due to the inclusion
of regions of different real average compositions, as shown
in Appendix C, or an increase of copper content in the liquid
region during the quench.

Average concentrations from these three faces are
plotted against distance from the top of the columnar zone
in Figure 5.46. Though the data are scattered, the segregation
of copper into the liquid is evident. The equilibrium
liquidus concentration seems to be the lower limit of the
concentration in the liquid. The concentrations in the solid
are somewhat lower, on average, than the bulk composition.

5.4.5 Macrosegregation

Two types of macrosegregation were investigated.
First, vertical macrosegregation which existed in the melt
before solidification began was investigated by wet chemical
analysis. Second, the macrosegregation that might have
developed across the thickness of the ingot as a completely
liquid region solidified during the quench was investigated
by both wet chemical and electron microprobe analysis.
Fig. 5.46  Average compositions of traces 0.03 cm long in the liquid and solid regions of ingot A-43. The solid line is the equilibrium liquidus composition.
Vertical Macrosegregation - To determine what macrosegregation existed before solidification began, ingot A-66 was quenched before any solidification had occurred. It was ground flat, and then samples were taken with a 5/16 inch drill. The locations of the samples and the results for both this ingot and the liquid portions of ingot A-43 are shown in Figure 5.47. The compositions shown above each ingot are the concentrations of copper in the samples taken before and after the ingots were poured, Appendix A. The compositions are plotted as a function of distance from the bottom of the ingot in Figure 5.48. The straight line which is assumed to represent the initial macrosegregation is put through the average composition at about the mid-height of the ingot.

Macrosegregation Caused by the Quench - Next, the concentration across the thickness of the ingot from the surface to the interior was investigated. At two locations on ingot A-66, samples were taken first by drilling part way into the ingot from each face, and then by drilling through the remaining material. As shown on Figure 5.47, the two samples in each location, one from the surface and one from the interior, had nearly identical compositions - (4.28, 4.29) and (5.08, 5.01) wt pct copper.

This type of macrosegregation was also investigated by electron microprobe analysis. A section across the thickness of ingot A-15, about eight centimeters above the chill, is shown in Figure 5.49. This region was completely liquid until it was frozen by the water quench. The fine dendrite arms
Fig. 5.47 Locations and results (wt pct copper) of chemical analysis. The concentrations above the ingots are the compositions of samples drawn from the crucible before and after the ingot was poured.
Fig. 5.48  Initial vertical macrosegregation. All data was taken from regions which were liquid before the quench. Ingot A-66) no slow freezing. Ingot A-43) slow vertical freezing.
Fig. 5.49  Microstructure of a region which was completely liquid until the quench. The surface of the ingot is at right. Ingot A-15, area B, face +x, 20X.
therefore grew inward from the surface of the ingot. Three microprobe traces were made parallel to the vertical surface of the ingot, as shown. The results of those traces are shown as the moving average composition of two dendrite arms in Figure 5.50. Since the region was liquid of a single composition before the quench, the irregularities in this line must be caused by the measurement and averaging procedures. The data from all three traces were recorded, Figure 5.50b. The curve of concentration versus fraction solid is very smooth and is typical of the microsegregation expected in this alloy \((8,46)\). The averages from one-third of each trace, 0.03 cm, are plotted in Figure 5.51 as a function of distance from the vertical center plane of the ingot. There is no segregation at the surface of the ingot. The average of all of these traces is 4.2 wt pct copper, which is nearly the same as the value of 4.0 wt pct copper shown in Figure 5.48 for the initial bulk concentration eight centimeters above the chill.

5.5 **Summary**

A summary of the results and observations of vertical solidification is presented in this section. These results will be discussed and compared with the results of horizontal solidification in Chapter 7.

**Temperature Measurements** - Two thermocouples, separated vertically in the melt, gave the following information about the solidification process:
Fig. 5.50 Data taken from a region of ingot A-15 which was completely liquid before the quench. (a) Moving average composition. (b) Reordered data.
Fig. 5.51 Average compositions of traces 0.03 cm long in a liquid region near the top of ingot A-15. No segregation occurs at the surface of the ingot during the quench.
The melt cooled most rapidly at the bottom of the ingot, establishing a vertical thermal gradient in the liquid. Solidification began at the bottom, with no undercooling. The rate of cooling in the melt decreased after solidification began, since the advancing solidification front was always at the liquidus temperature.

The rate of advance of the dendrite tips was constant. For a gas flow of 12 liter/min, the rate was 0.9 cm/min.

Macrostructures - Examination of the structure of ingots which were partly frozen vertically and then quenched reveals a number of details of the solidification structure which are not visible in completely solidified ingots.

Large vertical liquid channels developed as freezing proceeded due to a gas flow of 12 liters per minute. These channels tend to occur between groups of primary dendrite arms which have different orientations. The grain structures of a completely solidified ingot have the same size as the groups of primary arms.

Small vertical liquid channels occurred in ingots frozen by a gas flow of 12 liter/min within groups of like-oriented primary dendrite arms.

The only apparent effect of increased superheat on the structure was a decrease in the number of differently oriented groups of primary dendrite arms.

The higher cooling gas flow of 48 liter/min produced ingots with no large vertical channels.
When the top surface of the ingot was allowed to freeze before solidification was complete, crystallites broke off from the "roof" of the ingot and fell onto the columnar zone. Solidification shrinkage left a contracted area under the top of such an ingot.

Similar experimental conditions produced similar macrostructures. That is, the results are reproducible.

Microstructures - Microscopic examination of finely polished and etched sections of the quenched ingots revealed additional information about the slow freeze-transverse quench technique and the solidification structure.

Regions which were entirely liquid before the quench appear distinctly as areas with a very fine dendritic structure on the polished sections.

Sections polished with magnesia powder do not exhibit any interdendritic microporosity.

Fine dendritic structure (liquid) is limited to regions between secondary and primary dendrite arms. That is, the smallest dendrite elements, tertiary arms, thicken during the quench without breaking down into finer dendrites.

The dendritic structure of sections near the chill is coarser than of sections near the dendrite tips.

The channels are continuous in the vertical direction. Their sides are irregular because of the intrusion of secondary arms.

A horizontal section shows that the vertical channels are arranged in distinct lines, or "chains".
On a coarsened section near the chill, some dendrite elements are surrounded by a ring of eutectic which is in turn completely surrounded by solid.

**Microprobe Analysis** - The solute concentrations of liquid and solid regions of the quenched ingots were investigated by electron microprobe analysis. The average compositions of the liquid and solid regions, the local compositions within the liquid channels, and the solute concentration at the freezing surface of a dendrite arm, were determined.

The average concentration of copper in the liquid is higher than both the initial concentration of copper in the melt, and the equilibrium liquidus concentration as determined from the temperature measurements and the phase diagram. This average concentration approaches the initial concentration near the dendrite tips at the top of the columnar zone, and increases with distance from the dendrite tips.

The average compositions of solid (actually part solid) regions adjacent to the liquid regions are slightly lower than the initial composition of the melt. The average concentration in a trace across several tertiary dendrite arms in the solid region was only 1.7 wt pct copper.

The moving local average composition within a liquid region was determined. It shows that there is no solute gradient across the liquid channels.

The standard deviation of the average concentration of a 0.03 cm long trace across a liquid region is approximately two
wt pct copper. Within this error, several measurements of the concentration of the same liquid region gave the same result.

The concentration of copper at the freezing surface of a dendrite arm was determined as a function of the weight fraction solid by reordering the microprobe data points. This concentration is higher in the liquid regions than in the solid regions at the cores of the dendrite arms, when the fraction solid is zero, which implies that, before the quench, the concentration of copper in the liquid regions was higher than the initial concentration of the melt. At higher fraction solid, the curve of concentration versus fraction solid from liquid regions is convex upwards. This may mean that the solute concentration increased during the quench.

**Distribution of Liquid in the Part Solid Region** - Near the chill, the volume fraction of distinct liquid channels is nearly zero. Within a centimeter of the solidification front, the volume fraction of liquid channels increases sharply.

The fraction channel near the chill is smaller and the sharpness with which the fraction channel increases with distance just behind the solidification front is greater, for the ingots which were frozen more rapidly by a higher gas flow.

The shape of the curve of volume fraction channel with distance is not a function of the distance solidified. The curve translates upwardly with the advancing solidification front.
Comparison of the data for the volume fraction channel with the calculated curve of the volume fraction liquid as a function of distance from the chill shows that only a small part of the liquid in the part solid region formed discrete, identifiable channels.

The specific surface of the liquid channels increases towards the solidification front.

**Macrosegregation** - Chemical analysis of portions of two ingots which had been quenched directly from the liquid state show that a vertical solute gradient existed in the melt before solidification began.

Both chemical analysis and electron microprobe analysis show that no solute gradient was produced across the thickness of the ingot by the quenching of a completely liquid region.
6. INVESTIGATION OF THE HORIZONTAL SOLIDIFICATION
OF ALUMINUM-4.5 wt pct COPPER

The slow freeze-transverse quench apparatus described in Section 5.2 was used for aluminum-4.5 wt pct copper ingots which were solidifying horizontally under various conditions. Natural convective flow can occur in these ingots because the thermal and solute gradients are at an angle to the gravitational force. Comparison in Chapter 7 of the structures of these horizontally solidifying ingots with the structures of the vertically solidifying ingots establishes the existence and nature of this convective flow.

6.1 Outline

To aid the comparison of vertical and horizontal solidification, this chapter is organized in exactly the same manner as Chapter 5.

Modifications are described to adopt the slow freeze-transverse quench apparatus for horizontal solidification of the aluminum-4.5 wt pct copper alloy.

Temperature measurements in the horizontally solidified ingots indicate that the solidification front advanced at a nearly constant rate.

Photographs of the quenched ingots show the presence of vertical liquid flow channels within the part solid region, and a large liquid region at the bottom of the part solid region. Ingots frozen under various conditions indicate the
effects of superheat and freezing rate on the solidification structure.

Measurements on the quenched ingots show that most of the liquid in the part solid region is distributed between secondary and tertiary dendrite arms.

Electron microprobe analysis of the liquid channels shows the presence of excess solute in the liquid but the absence of solute gradients across the width of the liquid channels.

Macrosegregation due to the flow of interdendritic liquid was determined by chemical analysis of ingots which were partly solidified and then quenched.

Discussion of the experimental results for both vertical and horizontal solidification is presented in Chapter 7.

Analysis of the permeability of the part solid region and a model of natural convective flow in the part solid region which correlates the results of this Chapter are presented in Chapter 8.

6.2 Apparatus and Materials

Several alterations were made to the apparatus which was described in Section 5.2, to adapt it for the study of horizontally solidifying ingots. Rings were formed from stainless steel shim stock and spot welded together, Figure 6.1(a). This assembly was inserted in the opening of the stainless steel plate (b), to limit the convection of air within this space without blocking the incoming water spray
Fig. 6.1 Modifications to the apparatus for horizontal solidification. Rings were joined together (a), and inserted in the mold window (b). The cooling gas tube was inserted at the vertical edge of the mold (c).
from the surface of the mold. The removable insulating brick and the cooling gas tube were placed at the vertical edge of the mold, instead of at the bottom of the mold, (c). The two thermocouples were located at mid-height in the ingot, one near the chill, and the other in the bulk liquid, Figure 6.2. The flow of water through each of the quenching spray nozzles was 8.7 liters per minute, or more than twice the flow rate used on the vertically solidifying ingots. The resultant cooling rate at the center of the ingot was $1000^\circ\text{C/min.}$

The same aluminum-4.5 wt pct copper alloy was used for both vertical and horizontal solidification. Its preparation is described in Appendix A.

6.3 Procedure

The construction of the ingot mold, pouring of the ingot, and insulation of the ingot are described in Section 5.2 for vertical solidification. With the exceptions mentioned in Section 6.2, the same procedure was followed for horizontal solidification. Remelting of the ingot in the resistance furnace was done in the manner described in Section 5.3 and illustrated in Figure 5.4. After remelting, the insulation unit containing the molten ingot was removed from the furnace and clamped between the two water spray nozzles, and the small resistance heater above the ingot was turned on. The unit cooled slowly in the air to the desired starting temperature, which was generally between $710^\circ\text{C}$ and $720^\circ\text{C}$. 
Fig. 6.2 Schematic diagram of an ingot freezing horizontally, showing thermocouple 1 near the chill and thermocouple 2 in the bulk liquid.
The insulating brick was removed from the vertical edge of the mold and the nitrogen gas cooling tube was inserted. The time between the removal of the insulation and the start of the gas flow was more critical for horizontal solidification than for vertical solidification because convection of air up the hot vertical chill surface caused some cooling of the melt. To avoid introducing an additional variable, the gas flow was always begun forty seconds after the insulation was removed.

After the solidification front had proceeded into the ingot, the sliding insulation bricks at the broad sides of the mold were raised and the water sprays were turned on to quench the unfrozen liquid. The subsequent preparation of the ingot for metallographic examination is described in Appendix C.

6.4 Results

The order used in Section 6.4 for the presentation of the experimental results is followed here as well. Separate sections are devoted to temperature measurements during solidification, macrostructures of the ingots, the distribution of unfrozen liquid within the part solid region, microstructures and electron microprobe analysis, and macrosegregation during solidification. Data on the dendrite arm spacing in horizontally solidifying ingots is presented in Chapter 8 in connection with the calculation of the permeability of the part solid region.

6.4.1 Temperature Measurements

The temperature distribution within the ingot during solidification was determined from measurements taken by two
thermocouples. In addition, the absence of turbulent convective flow ahead of the solidification front was determined from measurements taken with an intrinsic thermocouple.

**Temperature Distribution** - The horizontal thermal gradient at mid-height in a solidifying ingot was examined in detail. Measurements were taken from two thermocouples located as shown in Figure 6.2. Thermocouple 1, being closest to the chill, always registered the lowest temperature.

Figure 6.3 shows the temperatures within ingot A-64 as it froze horizontally. Thermocouple 1 was 1.3 cm from the vertical chill face, and thermocouple 2 was 6.4 cm from the chill. At point A, the insulation unit with the molten ingot had been removed from the resistance heating furnace, clamped in place between the spray nozzles, and the small heater at the top of the ingot turned on. (The heater was turned on earlier for horizontal solidification than for vertical solidification.) At point B, when the melt had cooled to the starting temperature, there was a horizontal temperature gradient of approximately 0.4 °C/cm. The vertical temperature gradient at this time was measured in one experiment by thermocouples which were placed vertically, as shown in Figure 5.6 and found to be 0.5 °C/cm. This is about half of the vertical thermal gradient observed for vertical solidification.

The insulating block was then removed from the chill face, B, the nitrogen cooling gas probe was inserted, and the gas flow turned on, C. For this ingot, the gas flow rate was 12 liters per minute. The cooling rate in the ingot, as shown
Fig. 6.3 Temperature measured in an aluminum-4.5 wt pct copper ingot as it froze vertically. T.C.1 was 1.3 cm from the vertical chill face, and T.C.2 was 6.4 cm from the chill. The dashed lines were interpolated for imaginary thermocouples located 3.0 cm and 4.7 cm from the chill. (See Appendix B.)
in Figure 6.3, was doubled by the cooling gas. As in vertical solidification, the rate of cooling increased more quickly near the chill than in the bulk liquid. As the superheat was extracted from the melt, the horizontal thermal gradient increased to about 2.4 °C/cm.

Solidification then began at the chill, D, and since the solidification front remained at the liquidus temperature, \( T_{l,0} \), the thermal gradient decreased rapidly. Solidification proceeded past thermocouple 1, E, and then past thermocouple 2, F, into a liquid of nearly constant temperature. The liquidus arrest temperature measured during horizontal solidification was several degrees higher than that measured during vertical solidification.

Generally, an ingot was quenched between times E and F, when the solidification front was in the central portion of the ingot. The cooling rate due to the water spray quench was about 1000 degrees per minute.

**Rate of Solidification** - The details of the method of calculating the rate of solidification from the thermocouple measurements and measurements on the quenched ingots are given in Section 5.4.1 and Appendix B. As shown there, data on the location of the dendrite tips as a function of the time from the start of slow gas cooling can be obtained both from measurements on quenched ingots and from thermocouple data. This data, corrected to an equivalent starting temperature of 710°C, is plotted in Figure 6.4, for several different gas flow rates. The time at which solidification initiated is
Fig. 6.4 Position of the solidification front for horizontal solidification as a function of the time after the start of nitrogen gas cooling. Open symbols represent measurements made on etched ingots. Solid symbols are from thermocouple data. All of the data has been corrected to an apparent starting temperature of 710°C.
directly related to the cooling gas flow, but the solidification rate is only slightly affected by the gas flow. The solidification rate due to a gas flow of 12 liter/min is taken to be constant, 1.1 cm/min.

**Thermal Gradients** - Thermal gradients during solidification can be found by combining the thermocouple measurements, Figure 6.3, with the solidification rate, 1.1 cm/min, as described in Appendix B. The results, Figure 6.5, show that superheat is lost more rapidly in horizontal solidification than in vertical solidification. The general form of the horizontal thermal gradient in horizontal solidification is the same as the form of the vertical thermal gradient in vertical solidification. The equivalent thermal gradients in ingot A-51, which was frozen by a gas flow of 96 liter/min, show that the average thermal gradient in the part solid region was three times as large for ingot A-51 as for ingot A-64, which is described here.

**Selected Thermal Gradient** - As shown in Figure 6.5, the superheat was nearly completely dissipated before solidification began, and the form of the thermal gradient in the part solid region remained unchanged as solidification progressed. Since the thermal gradient in only the part solid region is required in subsequent sections, it is assumed that the thermal gradient shown for eight minutes after the start of gas cooling moves through the ingot unchanged during solidification. In other words, whatever the distance solidified, this temperature curve is translated so that the locations of
Fig. 6.5 Thermal gradients in a typical horizontal ingot at successive times after the start of gas cooling, 12 liter/min.
the dendrite tips coincide. A tabular function representing this curve was constructed, Appendix B, and is shown in Figure 6.6.

Turbulent Convection - Turbulent natural convection is accompanied by local oscillations of temperature. Measurements were made with an intrinsic thermocouple to determine the presence of such convection. The thermocouple was made from 0.01 cm chromel-alumel wire, and a high-speed, high-sensitivity recorder was used.

As shown in Figure 6.7, the two wires of the thermocouple were exposed so that the electrical circuit was completed through the melt. This direct contact with the melt makes the measurement more sensitive than one taken with a coated thermocouple. In addition, such a thermocouple is sensitive to changes of temperature at either contact. This thermocouple, of course, could not be used to determine the exact temperature where a thermal gradient exists. In test measurements in a melt of aluminum-4.5 wt pct copper, this thermocouple showed fluctuations only when the alloy was stirred, Figure 6.8. Measurements with this thermocouple during horizontal solidification show that no turbulent convection occurred, Figure 6.9.

6.4.2 Macrostructures

To investigate the effects of superheat and freezing rate on horizontally solidifying ingots, several series of ingots were frozen from various starting temperatures at different gas flow rates, as shown in Table 6.1.
Fig. 6.6 Selected thermal gradient. It is assumed that the thermal gradient in ingot A-64 eight minutes after the start of gas cooling passed through the ingots unchanged from the start of solidification, for a gas flow of 12 liter/min.
Fig. 6.7  Intrinsic thermocouple for measurement of local thermal gradients.
Fig. 6.8 Trace from an intrinsic thermocouple showing local thermal fluctuations introduced by stirring a melt of aluminum-4.5 wt pct copper.
Fig. 6.9 Trace from an intrinsic thermocouple showing only very slight changes in the local thermal gradient in the bulk liquid during the horizontal solidification.
Table 6.1
Series of Aluminum-4.5 wt pct Copper Ingots Quenched at Various Times During Horizontal Solidification

<table>
<thead>
<tr>
<th>series</th>
<th>ingot</th>
<th>gas flow liter/min</th>
<th>starting temp. °C</th>
<th>quench time min</th>
<th>location of tips cm</th>
<th>heater current amp</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>A-57</td>
<td>12</td>
<td>711</td>
<td>5.6</td>
<td>1.9</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>A-52</td>
<td>12</td>
<td>720</td>
<td>6.5</td>
<td>2.9</td>
<td>0.0</td>
</tr>
<tr>
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<td>12</td>
<td>706</td>
<td>7.6</td>
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<tr>
<td></td>
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<td>12</td>
<td>714</td>
<td>8.3</td>
<td>4.1</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>A-64</td>
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<td>none</td>
<td>complete</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>A-54</td>
<td>12</td>
<td>711</td>
<td>none</td>
<td>complete</td>
<td>7.6</td>
</tr>
<tr>
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<td>A-32</td>
<td>12</td>
<td>726</td>
<td>7.7</td>
<td>1.8</td>
<td>3.0</td>
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<td>4.0</td>
<td>3.0</td>
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<td>711</td>
<td>5.2</td>
<td>5.1</td>
<td>7.6</td>
</tr>
</tbody>
</table>
Series HA - The ingots in series HA were frozen from about 710°C by nitrogen gas at 12 liter/min, and quenched at increasing times after the start of freezing. Ingot A-57, Figure 6.10, shows distinct flow channels developing in the lower half of the ingot. Most remarkably, the dendrites do not rest on the bottom of the mold, near the interface, but are above a distinct liquid channel (1). Small liquid channels can be seen along the primary dendrite arms (2), and larger channels which cross the primary dendritic structure are visible as well (3). A large channel is seen on the opposite face of the ingot (4) which crosses the dendrite structure for the most part, but which also contains projections of primary arms. Higher on this face (5), small channels between primary arms are visible.

Ingot A-52, Figure 6.11, shows the increasing development of trans-dendritic channels with increasing solidification. Again, there is a liquid channel at the bottom (1). The size of this channel increases where it is joined by the vertical flow channel. This vertical channel is primarily trans-dendritic (2). Small vertical channels are visible at mid-height on the ingot (3), and small horizontal channels can be seen between the tips of primary arms in the upper portion of the ingot (4).

The start of a transition to equiaxed growth is seen in ingot A-46, Figure 6.12, but it is not clear whether the misoriented crystals causing equiaxed growth (1) formed first at the top of the ingot (2) or from the columnar zone itself.
Fig. 6.10  Faces of ingot A-57, 1.5X, showing initial development of flow channels.  (a) Face -z.  (b) Face +z.
Fig. 6.10, continued.
Fig. 6.11  Ingot A-52, 1.5X, showing channels primarily across dendrite arms. (a) Face -2.  (b) Face +z.
Fig. 6.12  Ingot A-46, 1.5X, showing transition to equiaxed structure. (a) Face -z. (b) Face +z.
Fig. 6.12, continued.
Since no disturbance of the columnar zone is evident (3), the former mechanism is more probable. Channels in the growth direction between primary arms are particularly evident (3) in this ingot. The shrinkage which occurs in all horizontal ingots ahead of the columnar zone is very noticeable here (4).

Ingot A-49, Figure 6.13 was frozen with exactly the same conditions as ingot A-46. Their macrostructures are very similar. The flow channels, however, are more clearly visible on ingot A-49. As they appear on the two faces of the ingot, the flow channels are somewhat dissimilar. Those on the -z face are more inclined from the vertical and appear to follow the dendrite arms more closely than does the channel on the +z face (2).

To complete the series, ingot A-64, Figure 6.14 was frozen completely, without any quench. The vertical channels (1) and the bottom surface (2) show much shrinkage porosity, indicating that liquid rich in solute occupied those regions before the completion of solidification. Other than the shrinkage, however, the process by which the flow channels and the bottom channel developed, is entirely obscured by the continued solidification of the ingot.

Another completely solidified ingot, A-54, Figure 6.15, shows an earlier transition to an equiaxed zone. This was due to the absence of a heater at the top of this ingot during solidification.

Series HA' - A different remelting procedure from that described in Section 5.3 was used for several ingots.
Fig. 6.13  Ingot A-49, 1.5X, is nearly the same as A-46.  (a) Face -z.  (b) Face +z.
Fig. 6.13, continued.
Fig. 6.14 Ingot A-64, 1.5X, showing shrinkage porosity in a completely solidified ingot. (a) Face -z. (b) Face +z.
Fig. 6.14, continued.
Fig. 6.15 Ingot A-54, 1.5X, showing a more rapid transition to equiaxed solidification than ingot A-64.
As shown in Figure 5.4 and Figure 5.7, the usual practice was to reheat the ingot to a temperature above the desired starting temperature, and to begin gas cooling after the ingot had cooled back down to the starting temperature. For the ingots in this series, the insulation unit was removed from the remelting furnace while the temperature of the ingot was still below the desired starting temperature (point D in Figure 5.4), and gas cooling was begun as soon as the temperature in the ingot rose to the starting temperature.

(The purpose of this procedure was to attempt to prevent the breakdown of columnar solidification by beginning solidification while heat was still entering the mold from the insulating bricks. In fact, the only effect of this procedure was to delay the start of solidification a few minutes while the heat added by the bricks was dissipated. The standard procedure, therefore, was used for all the other ingots.)

The structures of two ingots reheated in this way, and frozen by a gas flow of 12 liter/min are shown in Figures 6.16 and 6.17. These two ingots also were sectioned horizontally as shown in Figure 6.18. Such sections, Figures 6.19 and 6.20 show that the liquid channels change from a set of many irregular liquid pools to a few large round flow channels, as solidification proceeds.

**Ingot A-58** - An ingot was frozen from a lower starting temperature to show the effect of superheat on the solidification structure, Figure 6.21. There is no clear difference from series HA, except the increased presence of equiaxed grains
Fig. 6.16  Ingot A-32, 1.5X, showing flow channels between the dendrite arms.
Fig. 6.17  Ingot A-31, 1.5X, showing flow channels across the dendrite arms.
Fig. 6.18 Several horizontally solidified ingots were sectioned horizontally at their mid height. Photographs were then taken of the exposed +y faces. The arrow indicates the direction of solidification.
Fig. 6.19  Horizontal section of ingot A-32, 4X, showing many irregular flow channels.

Fig. 6.20  Horizontal section of ingot A-31, 4X, showing three large, round flow channels.
Fig. 6.21  Ingot A-58, 1.5X, showing a number of equiaxed grains ahead of the interface.
in the melt ahead of the interface. Fine channels along the dendrite arms are visible in several areas.

**Series HC** - To find the effect of the cooling gas flow rate on the solidification structure, ingot A-65, Figure 6.22, was frozen with a gas flow rate of 2.4 liter/min, and ingot A-51, Figure 6.23, was frozen with a flow rate of 96 liter/min. The slower flow rate produced an ingot with visible flow channels and only a short columnar zone due to the interruption of the directional growth by crystallites falling from a "roof" at the top of the ingot. Figure 6.23, on the other hand, shows a long, columnar zone with large regions of constant orientation. The bottom channel is smaller than in the previous ingots, and no vertical flow channels are visible.

**Shrinkage** - A distinct contraction of the thickness of the ingot occurs from one half to one centimeter ahead of the dendrite tips near the top of the quenched ingots. This contraction must occur during the quench, since it was always found just ahead of the interface. It appears to have been caused by solidification shrinkage into the part solid region. It might also have been due, however, to hindering of downward solidification shrinkage in the center of the ingot by the dendrite tips.

6.4.3 Distribution of Liquid in the Part Solid Region

Data were taken on the volume fraction channel, \( g_c \), and the specific surface of channels, \( \Sigma_c \), in the part solid region from a number of horizontally solidified ingots. The
Fig. 6.22  Ingot A-65, 1.5X, showing a short columnar zone due to slower solidification.
Fig. 6.23  Ingot A-51, 1.5X, showing a long columnar zone with large regions of constant orientation.
data were taken by translating the etched ingots on a microscope stage, as described in Section 5.4.3. The measurements were converted to values of $g_c$ and $E_c$ according to Equations 5.1 and 5.2, respectively.

The ingots of series HA, Table 6.1, were sectioned at 3/4, 1/2, 1/4, and 1/8 the ingot height, as shown in Figure 6.24. Photographs of these sections of ingot A-49 are shown in Figure 6.25. The vertical flow channels, which appear as the dark spots on the photographs, are visible only on faces D and E, in the bottom half of the ingot. They occur within the ingot and not just at the surface. Photographs of ingots A-57, A-52, and A-46 are shown in Appendix E.

Linear traces were taken across the width of the sections parallel to the z axis (i.e. perpendicular to the growth direction) at varying distances from the chill. The values of $g_c$ and $E_c$ found from these traces are shown in Figure 6.26. In (d), at 1.4 cm from the chill, the presence of the large flow channels markedly increases the volume fraction channel. The fraction channel increases sharply, and fairly smoothly, near the dendrite tips. The data on the specific surface of the channels are very scattered, but it appears that the specific surface increases toward the dendrite tips.

In Figure 6.27, all of the data (including that given in Appendix E for ingots A-57 and A-52) have been translated to the same location of the dendrite tips. All of the data fall on one curve, which means that the curve fraction
Fig. 6.24  Photographs were taken of the top faces of sections through the ingot at 3/4, 1/2, 1/4, and 1/8 of the ingot height. The heavy arrow indicates the direction of solidification.
Fig. 6.25  Horizontal sections of ingot A-49, 3X.
Fig. 6.26  Distribution of liquid as a function of distance from the chill for four horizontal sections in ingot A-49, series HA. (a) Section B. (b) Section C. (c) Section D. (d) Section E.
Fig. 6.26, continued.
Fig. 6.27 Data from ingots A-57, A-52, and A-49, transposed to the same tip location.

Fig. 6.28 Volume fraction liquid in the part solid region when the solidification front was 4.6 cm from the chill, for a gas flow of 12 liter/min.
channel versus distance from the dendrite tips is not a function of the actual distance solidified. For comparison, the volume fraction liquid, $g_1$, is plotted in Figure 6.28. This curve was calculated from Equation G.3 for $g_1$, and the selected thermal gradient, Section 6.4.1.

At any distance from the dendrite tips, the fraction of the ingot which is composed of liquid channels is markedly smaller than the fraction of the ingot which was unfrozen liquid. Most of the liquid in the part solid region must have been distributed between secondary and tertiary dendrite arms, and not as distinct liquid channels. That liquid cannot be differentiated on the quenched ingot since the dendrite arms around it froze by thickening during the quench and not by breaking down into finer dendritic structures.

Data was also taken at mid-height on ingot A-51, Figure 6.29. This ingot, from series HC, was frozen by a gas flow of 96 liter/min. The fraction channel in this ingot is zero until about one centimeter from the chill, then increases more sharply than did the data from the ingots in series HA.
Fig. 6.29  Distribution of liquid in ingot A-51, series HC.
6.4.4 Microstructures and Solute Gradients

Sections were taken from ingots A-57 and A-49 (series HA, section 6.4.2), and prepared for microprobe analysis by the procedure described in Appendix C. The locations of the sections from ingot A-49 are shown in Figure 6.30. Photographs of faces from these sections are identified by the letter of the section and the sign and direction of the outward normal to the surface described, as explained in Appendix D.

**Vertical Flow Channel** - As can be seen from the \( +z \) surface of this ingot (the back side), Figure 6.13(b), a large vertical flow channel passes through sections K, L, M, and N. Faces from these sections are presented with corresponding microprobe data.

Figure 6.31 shows the \(-y\) face of section K. The lower edge of the microstructure corresponds to the surface which was photographed for Figure 6.13(b). The channel is thus much larger below that surface. The channel itself is rounded, indicating that the intruding solid dendrites have been dissolved. The fine dendrite arms within the channel are smaller than their counterparts in Section 5.4.4 because the spray quench which was used for the horizontally solidifying ingots was twice as effective as that used for the vertically solidifying ingots.
Fig. 6.30  Locations of sections cut from ingot A-49.
Fig. 6.31  Vertical flow channel seen on ingot A-49, section K, face -y.  20X.
Two adjacent microprobe traces were made across this channel, and the moving average copper concentration is plotted in Figure 6.32.* There is no marked composition gradient across the channel. The average copper concentrations in the solid portions of the trace vary considerably, but the average compositions in the liquid, 11.3 and 11.7 pct, are nearly the same. Scatter in the averages for the solid regions should be larger than for the liquid regions both because the portions of the traces across the solid regions are smaller than across the liquid regions, and because many fewer dendrite units are included from the solid regions.

The curve of concentration versus fraction solid from this area is representative of all such curves from the horizontally solidifying ingots. As shown in Figure 6.33 the concentration of copper in the channel at the start of freezing is much higher than the bulk composition (cf. the discussion of Figure 5.34). The convex form of the curve at low fraction solid indicates either the accidental inclusion of regions with a low average concentration, or an increase in the solute content of the channel during the quench.

The same vertical flow channel is shown as it intersects the bottom face (z-y) of section L, Figure 6.34. The dark areas within the channel are caused by the selective darkening of

* The electron microprobe methods used for this section are the same as those used in Section 5.4.4, and are described in detail in Appendix F.
Fig. 6.32 Moving average concentration of copper between two peaks. Ingot A-49, section K, face -y.
(a) Line A. (b) Line B.
Fig. 6.33 Concentration in the solid at the freezing surface of a dendrite arm. Reordered data from lines A and B, ingot A-49, section K, face -y.
Fig. 6.34 Vertical flow channel on the -y' face of section L, ingot A-49. 20X.
certain groups of fine dendrite arms within the channel by
the etch. They do not represent microporosity. There are
several smaller channels adjacent to the larger one. Their
surface is irregular rather than rounded. There is apparently
some infiltration of the part solid region by the liquid in
the channel (1 on the photograph). Results of microprobe
analysis across the channel are given in Figure 6.35.

The top face (+y) of section M shows several vertical
flow channels, Figure 6.36. It was not ascertained whether
the channel shown at (1), or those shown at (2) represents the
continuation of the previous channels. The results of
microprobe analysis, Figure 6.37, show distinctly the increase
in copper concentration at each channel, compared to the
surrounding partly solid regions. (This face is also shown
in Figure 6.25, face E.)

The junction of this vertical flow system with the
channel at the bottom of the ingot is shown on face +z,
section N, Figure 6.38 (cf. also Figure 6.13(b)). The size
of the bottom channel increases markedly where the vertical
flow channel enters (1). Small vertical channels (2) can be
seen at the bottom of the solid zone.

The increase of solute in the liquid channels is
apparent from the microprobe results, Figure 6.39. The
smaller channel has a slightly lower average solute content
(9.9 pct) than the larger (11.2). The bottom channel has a
concentration of 10 pct (see below) at this location. The
moving average concentration across the larger channel shows
a flat solute profile.
Fig. 6.35 Moving average concentration from the probe trace on face -y, ingot A-49, area L.
Fig. 6.36 Vertical flow channels on face $+y$, section M, ingot A-49. 20X.
Fig. 6.37  Moving average concentrations, face +y, section M, ingot A-49.
Fig. 6.38  Confluence of vertical flow system with bottom channel. Face -z, section N, ingot A-49. 20X.
Fig. 6.39 Moving average concentrations across vertical flow channels. Face -z, section N, ingot A-49.
The concentrations in these sections are plotted as a function of distance from the chill, \( x \), in Figure 6.40. The averages have been taken for lengths along the trace of about 0.03 cm, to demonstrate the statistical scatter of the data more clearly. The data show a slight decrease in copper concentration in the channel with distance from the chill (and with height, since the channel is at an angle to the vertical). The concentrations in the solid regions adjacent to the channel average about 6 pct copper.

**Bottom Channel** - Microprobe analysis of the bottom channel in ingot A-49 on sections N, P, and Q were made to find the variation of concentration as a function of distance from the chill.

Results of trace B, Figure 6.38, are given in Figure 6.41.

A section through the width of the ingot, face \(-x\) of section P, is shown in Figure 6.42. Small vertical channels at the bottom of the solid zone (1) are again evident. The bottom surface of the partly solid region is macroscopically flat and microscopically rough. The results of microprobe analysis, Figure 6.43, show an average solute concentration in the liquid, of 7.7 pct from each trace.

A portion of the ingot near the dendrite tips, face \(-z\) of section Q, is shown in Figure 6.44 (cf. also Figure 6.13(b)). The small vertical channels are again visible (1), as are similar channels (2) in what is an equivalent location higher in the ingot, since that region is also open to the bulk
Fig. 6.40  Average concentrations of traces 0.03 cm long in the liquid and partly solid regions of the vertical flow system of ingot A-49, sections K, L, M, and N. The solid line represents the equilibrium liquidus concentration.
Fig. 6.41 Moving average concentration from face -z, section N, ingot A-49.
Fig. 6.43  Moving average composition from face -x, section P, ingot A-49.  (a) Line A.  (b) Line C.
liquid near the interface (3). Microprobe results are shown in Figure 6.45.

Averages for the liquid and solid regions at the bottom of ingot A-49, taken from the preceding areas, are plotted in Figure 6.46. Each point represents approximately 0.03 cm of a trace. There is a clear decrease of solute in the channel towards the interface. The high values of solute concentration in the solid regions at -2.1 cm come primarily from line C of section P.

As shown in Figure 6.30, sections G, H, I, and J form a series slightly above mid-height in the ingot. The +x faces of these sections were prepared for microprobe analysis. This region was chosen, since from Figure 6.13, the structure in the area is similar to that of some of the vertical ingots of Chapter 5.

The +x face of section G is shown on Figure 6.47. There are a large number of scattered liquid pools. They seem to be separated, rather than contiguous.

The average composition of the liquid region on line A is 6.5 wt pct copper.

The fraction of liquid pools on face +z, section H, Figure 6.48, is much smaller than on the previous face. A series of liquid pools across the width of the ingot were analyzed and the results are plotted in Figure 6.49. There is no marked difference of segregation from the center to the edge of the ingot.
Fig. 6.45  Moving average composition on face -$z$,
section $Q$, ingot A-49.
Fig. 6.46  Average concentrations of traces 0.03 cm long in the liquid and solid regions at the bottom of ingot A-49. The solid line is the equilibrium liquidus composition.
Fig. 6.47 Liquid pools on face +x, section G, ingot A-49. 20X.
Fig. 6.48  Liquid pools on face +x, section H, ingot A-49.  20.3X.
Fig. 6.49 Average concentrations of traces 0.03 cm long in the liquid and solid regions on face +x, section H, of ingot A-49. Distance is taken from the vertical center plane of the ingot. The solid line is the equilibrium liquidus concentration.
Still closer to the chill, face +x of section I, Figure 6.50, shows a number of very small liquid pools. The microprobe trace gives a concentration of copper in the liquid region of 9.2 wt pct.

The +x face of section J, Figure 6.51, shows virtually no liquid regions.

The solute concentrations (again for 0.03 cm trace lengths) from these sections are plotted in Figure 6.52. The decrease in concentration with decreasing distance from the dendrite tips and the difference in concentration between the solid and liquid regions is again evident.

The developing flow system of ingot A-57, Figure 6.10(a), and Appendix F, was examined by sectioning as shown in Figure 6.53. Face +y of section F, shows a number of small vertical flow channels, Figure 6.54, and probe traces across these channels show concentrations of copper in these channels of from 8 to 13 wt pct.

The interface between the part solid zone and the bulk liquid can be seen on face +y of section G, Figure 6.55. The centerline (l) formed by the junction of fine dendrites which grew from each side of the ingot during the spray quench is also clearly visible. Probe data was taken on a channel near the interface and in the bulk liquid.

Concentration as a function of distance from the chill is plotted in Figure 6.56, and shows that the concentration in the liquid near the interface is the same as that in the bulk liquid.
Fig. 6.50 Very small liquid pools occur on face +x, section I, ingot A-49. 20X.
Fig. 6.51  Face +x, section J, ingot A-49.  20X.
Fig. 6.52  Average concentrations of traces 0.03 cm long in the liquid and solid regions of sections G, H, and I in ingot A-49. The solid line is the equilibrium liquidus concentration.
Fig. 6.53 Location of sections cut from ingot A-57.
Fig. 6.54  Small vertical flow channels on face +y, section F, ingot A-57. 20.3X.
Fig. 6.55  The interface between the part' solid and liquid regions of ingot A-57, face +y, section G.  20.3X.
Fig. 6.56: Average concentrations of traces 0.03 cm long in the liquid and solid regions of sections P and G of ingot A-57. The solid line is the equilibrium liquidus composition.
6.4.5 Macrosegregation

Since flow of solute rich liquid through the part solid zone implies the building up of a degree of macrosegregation, 1 gm samples were drilled from the ingots in series A and analyzed chemically. The locations of the samples, and the results are shown in Figure 6.57. The numbers shown above each ingot are the concentrations of the samples taken from the melt before and after each ingot was poured, Appendix A. Except for ingot A-64, which was solidified completely, all the samples were taken from the region of the ingot which was liquid before the quench.

The results are plotted as a function of distance from the base of the ingot in Figure 6.58 and show a slight increase in vertical macrosegregation with the progress of solidification.

6.5 Summary

A summary of the results and observations of horizontal solidification is presented here. These results will be discussed and compared with the results of vertical solidification in Chapter 7. In Chapter 8, the results of horizontal solidification are extended and developed into a model of flow in the part solid region.

The language of this section is often similar to the language of section 5.5, as many results are the same for both vertical and horizontal solidification.
Fig. 6.57 Locations and results in wt pct copper of chemical analysis. The concentrations above the ingots are the compositions of samples drawn from the crucible before and after the ingot was poured. Ingots A-57 and A-49 were partly solidified and then quenched. Ingot A-64 was solidified completely without any quench.
Fig. 6.58 Vertical macrosegregation in horizontally solidifying ingots. Macrosegregation increased as the distance of the dendrite tips from the chill increased. Ingot A-57, S = 1.9; A-49, S = 4.1; A-64, S = 7.7.
Temperature Measurements - Two thermocouples, separated horizontally at mid-height in the melt, gave the following information about the solidification process:

The melt cooled most rapidly at the vertical chill face, establishing a horizontal thermal gradient in the liquid. Solidification began at the chill face, with no measurable undercooling.

The rate of cooling in the melt decreased after solidification began, because the advancing solidification front was always at the liquidus temperature.

The measured liquidus temperature, \( T_{1,0} \), was approximately 650°C.

The rate of advance of the dendrite tips was constant. For a gas flow rate of 12 liter/min, it was 1.1 cm/min.

The rate at which superheat was removed was increased by an increase in the flow rate of the cooling gas.

The rate of advance of the solidification front was increased only slightly by an increase in the flow rate of the cooling gas.

Turbulent convection did not occur in the melt during horizontal solidification.

Macrostructures - The structures of quenched and etched ingots showed a number of features which are not visible on completely solidified ingots.

The bottom of each ingot was completely liquid beneath the part solid region. The height of this "liquid channel" increased with distance from the chill. The height of the
channel was decreased by an increase in the gas cooling rate. An increase in the channel height occurs wherever a vertical flow channel joins the bottom channel.

Flow channels, both between and across the primary dendrite arms, occurred in ingots which were frozen by gas flows of 2.4 and 12 liter/min. They did not occur in the ingot which was frozen by a gas flow of 96 liter/min.

The downward flow of interdendritic liquid occurred initially between primary dendrite arms, then across the dendrite arms without destroying the dendrites, and finally across the dendrites in open tubular channels. These channels were confined to the lower half of the ingots, and were only found near the chill.

Channels occurred in the horizontal growth direction, between primary arms with the same orientation. These were usually in the upper portion of the ingot.

No channels were observed in the horizontal growth direction between groups of dendrite arms.

Both a decrease in the gas flow rate and a decrease in the superheat shortened the columnar zone.

The crystallites which interrupted columnar growth came from the partly frozen top of the ingot, and from sections of the solidification front whose growth had already been interrupted. No crystallites were specifically seen to result from the breakup of the advancing tips of the columnar zone.

Solidification shrinkage during the quench caused a contraction of the ingot thickness about a centimeter ahead of
the solidification front.

Similar experimental conditions produced similar macrostructures, demonstrating that the results are reproducible.

Microstructures - Micrographs of sections from the quenched ingots yield additional information about the slow freeze-transverse quench technique and the channels which occur during horizontal freezing.

Regions which were completely liquid before the quench are readily distinguished on the micrographs by their fine dendritic structure.

No general microporosity is visible on the micrographs. The quench did not produce a fine dendritic structure between tertiary dendrite arms.

Sections nearer the chill have a coarser dendrite structure than sections near the dendrite tips.

Well developed flow channels are tubular, with a smooth wall and a round cross-section. The dendrite structure around them is continuous.

The lower edge of the part solid region, which defines the bottom channel, is macroscopically flat. Small vertical channels lead from the part solid region into the bottom channel.

The liquid regions in the upper part of the ingots, as seen on a vertical section, are not continuous in the vertical direction.
**Microprobe Analysis** - The compositions of liquid and solid regions of the quenched ingots were investigated by electron microprobe analysis. The average compositions, the local compositions, and the compositions during freezing were determined.

The average concentration of copper in the liquid is higher than both the initial concentration of the melt, and the equilibrium liquidus concentration as determined from the temperature measurements and the phase diagram. This average concentration approaches the initial concentration near the dendrite tips at the solidification front, and increases with distance from the dendrite tips for the three types of regions which were investigated. These were the liquid pools in the upper part of the ingot, the large vertical flow channels, and the liquid region at the bottom of the ingot.

The average composition of the solid regions adjacent to the liquid pools and channels are slightly lower than the initial composition of the melt.

The moving average composition across the liquid regions show that no significant solute gradients exist across any of the liquid regions.

The standard deviation of the average concentration of a 0.03 cm long trace across a liquid region is approximately two wt pct copper. The averages of two 0.1 cm long traces across the same liquid region agreed to within 0.4 wt pct copper.
The concentrations in the solid and liquid regions during freezing are illustrated as the concentration at the surface of a solid dendrite versus weight fraction solid. Since this concentration at zero fraction solid is higher for liquid regions than for solid regions, some segregation of solute into the liquid must have occurred before the quench. The form of the curve at higher fraction solid is convex upwards, which may mean that the solute concentration in the liquid increased during the quench.

**Distribution of Liquid in the Part Solid Region** - Near the chill, the volume fraction of the part solid region which consists of distinct liquid channels is almost zero. Within a centimeter of the solidification front, the volume fraction of liquid channels increases sharply.

The fraction channel near the chill is smaller, and the sharpness with which the fraction channel increases with distance just behind the solidification front is greater, for an ingot which was frozen by a higher gas flow.

The curve of volume fraction channel with distance moves forward with the solidification front.

Comparison of the data for the volume fraction channel with the calculated curve of the volume fraction liquid as a function of distance from the chill shows that only a small part of the liquid in the part solid region formed separate, identifiably large channels.

The specific surface of the liquid channel increases towards the solidification front.
The tubular flow channels increase the fraction liquid several times over the fraction liquid of adjacent areas in which there are no such channels.

**Macrosegregation** - Chemical analysis of a series of ingots which had been partly frozen for successively longer times shows an increase in the solute content of the liquid near the bottom of the ingot as horizontal solidification proceeds.
7. DISCUSSION OF THE SOLIDIFICATION OF ALUMINUM-4.5 WT PCT COPPER

The results of the studies of the vertical and the horizontal solidification of aluminum-4.5 wt pct copper alloys are discussed and compared in this chapter. The solidification of any ingot involves almost the entire field of solidification, from the nucleation of the solid phase to the nature of the macrostructure. Some attempt has therefore been made to limit the discussion and concentrate it on those features of the experiments which are most directly related to the interaction of solidification structure and natural convective in the part solid region.

Further development of the results for horizontal solidification is undertaken in Chapter 8 to construct a mathematical model of convective flow in the part solid region. The worth of the slow freeze-transverse quench technique is discussed in Chapter 11.

7.1 Outline

The results of vertical and horizontal solidification are discussed and compared in essentially the same order in which they were presented in Chapters 5 and 6.

The temperature distributions are shown to be representative of slow, unidirectional solidification. The rate of advance of the solidification front is less influenced by an increase in the gas flow rate than is the rate of loss of the superheat.
The macrostructures and microstructures are discussed. The different types of liquid channels which occur in vertical and horizontal solidification show that convective flow of liquid through the part solid region occurred only during horizontal solidification. Two different views of the origin of dendrite arm spacing are compared with the results of this study. Two new models are proposed to account for the coarsening of the dendritic structure after the solidification front has passed.

The results of microprobe analysis are analyzed. It is shown that segregation of solute into the liquid channels must have occurred both during slow freezing and during the quench. Since no better data are available, it is assumed that the concentration of copper in the liquid channels during the quench is always the equilibrium liquidus concentration.

It is shown that the vertical macrosegregation which existed before solidification began did not strongly affect the solidification structures which occurred.

The possibility of gross mistakes in the experimental procedure is considered and rejected.

7.2 Temperature Measurements

The temperature measurements, as expressed by the curves for the location of the dendrite tips as a function of time, and the thermal gradients at successive times must be analyzed as a whole. In particular, it is an interesting and not immediately understandable result that the rate of advance of the solidification front was not strongly affected by the
cooling gas flow rate, while the time at which solidification began and the solidification structures which were observed were functions of the gas flow rate.

To begin with, the conditions of this experiment were distinct from the usual industrial solidification process. There, superheated liquid metal usually is poured directly into a cold mold. In this experiment, the metal was melted in the mold to avoid the momentum convection which accompanies pouring. Heat extraction, therefore, is governed by the cooling gas flow, rather than by the rate of absorption of heat by the mold walls. The result that the superheat is lost quickly agrees, however, with comments made by Nelson (17) and Tenenbaum (6) on temperatures in steel ingots.

The absence of undercooling in the center of the melt before the start of solidification is also typical of industrial practice. There, the size of the ingot and the presence of foreign matter in the melt prevents any slight undercooling which may occur at the chill from causing undercooling in the center of the melt. Experiments on the directional solidification of aluminum-copper alloys (8) also showed no undercooling within the melt. Experiments on smaller ingots, however, consistently show undercooling throughout the melt before solidification begins. (22)

It is understandable that an increase in the flow rate of the nitrogen cooling gas caused solidification to begin more quickly, but explanation is required for the fact that the rate of advance of the dendrite tips was nearly independent
of the gas flow rate. Examination of the thermal gradients in an ingot which was frozen by a gas flow of 96 liter/min showed that the temperature near the chill was much lower than in an ingot which was frozen by a gas flow of 12 liter/min, for equivalent locations of the dendrite tips. This meant that the average thermal gradient in the part solid region was three times greater in the ingot for which the gas flow was higher. Thus, although the dendrite tips advanced at the same rate, considerably more heat had been removed from the ingot which had been frozen by the larger gas flow. A computer simulation of the solidification process by Campagna, also showed that the rate of advance of the dendrite tips is relatively insensitive to the rate of heat extraction. (53)

The location of the dendrite tips as a function of time was measured in two different ways, which gave the same results for the rate of advance of the solidification front. One measurement was the time at which a thermocouple at a given distance from the chill registered a temperature below the liquidus temperature. The other measurement was the distance the tips had progressed from the chill at the time of the quench. This was obtained directly from the etched ingot. Thus, the assumption which is generally made, that the progress of solidification can be observed from the temperatures registered by a series of thermocouples in the ingot, is supported by these measurements.

The rate of advance of the dendrite tips was constant for both vertical and horizontal solidification. This differs
from the results which have been reported for steel ingots, in which the progress of the solidification front is a linear function of the square root of time.\(^{(17,19,54)}\) As mentioned, however, these ingots were cast against a cold metal chill, while for this experiment, the rate of heat extraction was governed by the transfer of heat to the nitrogen gas.

The heat input from the heater was designed to prevent freezing at the top of the ingot by adding as much heat as was otherwise lost at the top of the ingot. That is, the power of the heater was calculated as the product of the mass of solid at the top of the ingot when the heater was not used, and the heat of fusion of the alloy. Therefore, the heater merely prevented heat losses at the top of the ingot and did not alter the character of the unidirectional solidification.

The higher liquidus arrest temperature which was measured during horizontal solidification is explained in terms of the measured vertical macrosegregation. For horizontal solidification, the thermocouples were placed at the mid-height of the ingot, while for vertical solidification, the liquidus arrest was often measured only by the lower of the two thermocouples. Because of the vertical solute gradient, the bottom of the melt has a higher copper content, and a lower liquidus temperature than the top of the melt.

Since the measured liquidus temperature was within several degrees of the value on the phase diagram, and since there is good correspondence between the location of the
solidification front as measured by the thermocouples and as measured on the quenched ingots, it is assumed that the measured temperatures are correct to two degrees. The temperature gradient, which is a relative measurement between two thermocouples is accurate to 0.25 °C/cm.

The absence of local temperature fluctuations during horizontal solidification shows the absence of turbulent convection, but some convection in the melt is still expected. For example, Stewart and Weinberg, using a radioactive tracer technique, have demonstrated the existence of natural convection in tin with a thermal gradient in the melt as low as 0.2 °C/cm. (55) The physical arrangement which they used was similar to that of the mold in this experiment.

In summary, the thermal gradients obtained in these experiments are self-consistent and reasonable for slow solidification by gas cooling. The selected thermal gradient for horizontal solidification is used in Chapter 8 to calculate the velocity of flow in the part solid region.

7.3 Solidification Structures

The solidification structures of sections 5.4.2, 5.4.4, 6.4.2, and 6.4.4 are discussed here. Each type of solidification structure is discussed separately, and a comparison is made for each between the results for vertical solidification and the results for horizontal solidification.

It must be noted that in fact the results of vertical solidification are not strictly comparable to the results of
horizontal solidification. This is because the thermal gradients and rates of solidification are not the same for the two types of solidification. They are similar, however, and in any case it would not be possible to obtain identical thermal gradients and solidification rates without the use of a gradient furnace. Therefore, it is assumed that the results of vertical and horizontal solidification can be compared generally. However, it is not claimed that vertical solidification due to a specific gas flow rate is the exact counterpart of horizontal solidification due to the same gas flow rate.

7.3.1 Liquid Channels

The most dramatic result of this study is that four distinct kinds of liquid channels occurred during solidification:

- Liquid channels in the growth direction between groups of primary dendrites.
- Liquid channels in the growth direction between similarly oriented primary dendrites.
- Tubular flow channels.
- Bottom flow channel.

The fact that different kinds of channels are found in horizontally solidified ingots than in vertically solidified ingots is direct evidence that fluid flow caused by the gravitational force affected the solidification structure during horizontal solidification. The characteristics of each kind of channel and the differences between vertical and horizontal solidification implied by each are discussed here.
Liquid Channels in the Growth Direction Between Groups of Primary Dendrites - In ingots frozen slowly in the vertical direction, distinct vertical channels, which were large compared to the primary dendrite arm spacing, developed between differently oriented groups of primary dendrite arms. Secondary dendrite arms grew into these channels as solidification proceeded. Observation of the structure of a completely solidified ingot shows that these groups of primary dendrite arms are the basis of as-cast grain structure in the completely solidified ingot.

As solidification continued, the solidification front became less smooth, as a series of round "fingers," separated by vertical liquid channels, proceeded upwards into the melt. It is not quite clear whether these groups of dendrites with rounded tops are the same as the "superdendrites" observed by Cole and Bolling (56) in decanting ("dumping") experiments. It is tempting to speculate that just as, with decreasing thermal gradient ahead of the solid-liquid interface, and with increasing rate of solidification, a planar solidification front breaks down, first to cellular growth and then to dendritic growth, so also a dendritic solidification front may take several forms, depending on the growth parameters. At slow growth rates, with low thermal gradients, the solidification front is uneven, composed of "fingers," while at higher growth rates all of the primary dendrite arms form a flat solidification front.
These large channels occurred only in vertically frozen ingots and were entirely absent in horizontally frozen ingots. There are two possible explanations for this fact. The first emphasizes the horizontal components of flow into the part solid region at the top of a horizontal ingot and out into the bulk liquid at the bottom of the ingot. The second emphasizes the vertical component of flow down through the part solid region.

Flow into the part solid region in the upper part of the ingot brings "fresh" liquid between the primary dendrite arms. Because this liquid has the initial bulk composition, rather than the higher solute concentration of the liquid which it replaces, the solute segregation which stabilizes large channels in the growth direction is eliminated. Secondary dendrites can then grow into, and eliminate any large channels which form in the growth direction. The counterpart of this inward flow in the upper part of the ingot is an outward flow at the bottom of the ingot. The additional solute carried by this flow should stabilize channel formation. In fact, the channel at the bottom of the ingot might be considered a large liquid channel in the growth direction.

The second explanation for the absence of large channels in the growth direction between groups of primary dendrites in horizontal solidification, is the effect that the downward component of flow in, and ahead of the part solid region can have on the interaction of the solid dendrites and the interdendritic liquid. Within the part solid region, the downward flow can sweep the rejected solute from between the dendrite
arms and also improve the thermal contact between the solid
dendrites and the interdendritic liquid. Both of these
effects would destabilize channel formation. Ahead of the
interface, the thermal boundary layer which "leads" the
growing dendrites (57) probably also is swept away by the
downward flow of liquid.

In the actual case, both components of flow exist. Thus
both explanations may be involved in preventing the formation
of liquid channels in the growth direction between dendrite
groups during horizontal solidification.

**Liquid Channels in the Growth Direction Between Similarly
Oriented Primary Dendrites** - In both vertical and horizontal
solidification, small liquid channels occurred between
identically oriented primary dendrite arms. All of the primary
arms advanced together, with their tips touching the plane of
the solidification front. This type of growth has been shown
by Jackson et al. (26) to occur in transparent materials which
freeze dendritically. Bower, Brody, and Flemings, (8) using
a decanting technique, have shown an array of primary dendrite
arms which protruded individually into the liquid as they grew.
Glicksman and Shaefer have also observed similar separated
primary dendrites on the top surface of a horizontally
solidifying alloy. (29)

The sides of such a channel are irregular since they
are defined by the intrusion of the secondary dendrite arms
which grew into the channel from the two adjacent primary
dendrite arms. A cross section taken through a number of these
channels which had formed in a vertically solidifying ingot shows that they developed in a regular linear array. Bower(58) has shown that linear eutectic patterns can be seen on sections of completely solidified aluminum-copper ingots. The linear patterns must therefore represent the locations of liquid channels which existed between the primary arms during solidification.

**Tubular Flow Channels** - The most striking difference between vertical and horizontal solidification, and the most specific proof that convective flow occurs during horizontal solidification, is the occurrence of tubular flow channels only in horizontally solidified ingots. From the series of ingots which were quenched after increasing amounts of horizontal solidification, it is clear that convective flow first moved in many small channels around the dendrite arms which had been formed by the passage of the solidification front. Later, continued flow dissolved the solid dendrites in a few channels, forming large tubular flow channels with smooth, walls.

Channels of this type have been presented elsewhere in the literature. Marburg, (16) as well as Mayo(59) and Elliott, (60) have described such "pencil" segregate streaks at the top of steel ingots. (Since the segregate in a steel ingot is less dense than the melt, convective flow would move upwards through the part solid region.) McDonald and Hunt have modeled these segregates with an "alloy" of ammonium chloride and water. (61)
Giami and Kear\textsuperscript{(43)} have described vertical "freckles" in vertically solidified nickel-base superalloys, and Copley et al.\textsuperscript{(42)} have modeled these with the ammonium chloride-water system. They demonstrated that these "freckles" are flow channels which occurred because the rejection of solute during freezing caused a density inversion in the interdendritic liquid. This inversion was relieved when the lighter liquid at the bottom of the columnar zone spurted upwards through a series of tubular, vertical channels.

Mehrabian, Keane and Flemings\textsuperscript{(45)} have reported a tubular flow channel in a completely solidified aluminum-copper ingot which is nearly identical to the ones shown here. They conclude that the channel was formed within the part solid region on the basis of their mathematical model of convective flow in the part solid region. That conclusion is supported by the results of this study.

All of the vertical flow channels occurred near the chill. Interestingly, the channel shown by Mehrabian, Keane, and Flemings was also near the chill. It is possible that once the flow channels are formed, their presence stabilizes the flow and relieves the driving force for channel formation farther from the chill. The origin and nature of these channels is discussed further in Chapter 8, in which a model is presented for the calculation of flow velocities in the part solid region.

**The Bottom Flow Channel (Horizontally Solidifying Ingots)** - The tubular flow channels empty into a liquid region
at the bottom of the part solid region. At these "deltas", the height of the bottom channel increases, indicating that fluid flow was indeed responsible for the existence and maintenance of the bottom channel. The small vertical channels at the flat bottom of the part solid region imply that a general downward flow also emptied into the bottom channel.

This channel, of course, does not occur in vertical solidification, and is a clear distinction between the two solidification directions. It could be seen at the bottom of a completely solidified ingot only because of solidification shrinkage due to incomplete feeding. This presents the possibility that channels of this type may occur whenever a horizontal aluminum-copper casting is made in mold as high as 10 cm.

7.3.2 Effects of Superheat

The variable of superheat was examined because the amount of superheat is usually associated with the length of the columnar zone.\(^{(62)}\) It was therefore thought possible that the superheat might affect the solidification structure and thus cause the transition from columnar to equiaxed growth. In this study, however, the primary effect of increased superheat was merely to delay the start of freezing. A secondary effect appeared to be increased suppression of the
formation of crystallites at the top surface of the melt. This may have been due to the increased heat content of the insulation unit which could have prevented nucleation of solid at the top of the ingot.

7.3.3 Effects of Cooling Rate

An increase in the gas flow rate affected all four types of liquid channels, and in fact affected them all in the same way. Liquid channels of all types were made smaller, or eliminated by an increase in the rate of cooling.

The large channels which formed between groups of dendrite arms during slow vertical solidification were greatly reduced in size by an increase in the gas flow rate. As mentioned previously, while the rate of advance of the dendrite tips did not alter much with an increase in the gas cooling rate, the temperature gradient in the part solid region did increase significantly. Thus the increased heat extraction from the part solid region must have provided the driving force for secondary dendrite arms to grow sideways into what would otherwise have been large channels between groups of dendrites.

The vertical flow channels which formed during slow horizontal solidification were prevented from forming by an increase in the cooling gas flow. Qualitatively, this must be due to the increased rate of growth of the dendritic structure within the part solid region at higher cooling rates. This result is in agreement with the simulation
experiments of McDonald and Hunt (39) and Copley et al. (42) who found that the occurrence of flow channels in the ammonium chloride-water system could be reduced or eliminated by increasing the rate of solidification. Similarly, Mehrabian, Keane, and Flemings (45) increased the solute content and decreased the rate of cooling to cause the formation of a channel segregate in a horizontally solidified aluminum-copper ingot. This was done in accordance with their mathematical model (44) in which the local freezing rate is calculated as a function of the local cooling rate and the local velocity of flow. There is thus agreement that convective flow channels can be eliminated by increasing the rate of cooling.

The bottom channel occurred in horizontally solidifying ingots even when the rate of cooling was high enough to prevent the formation of vertical flow channels. It was, however, smaller. This indicates that a general downward flow of interdendritic liquid occurred throughout the part solid region even during more rapid solidification.

7.3.4 Dendrite Arm Spacing

As illustrated by Bower, Brody and Flemings (8) the average distance between dendrite arms in an aluminum-copper alloy decreases with decreasing local solidification time (the time between the initiation of solidification at some point in the ingot and the completion of solidification at that point). An alternate view of the same phenomenon is
presented by Rohatgi and Adams (63-65) who describe dendrite arm spacing as being a function of the maximum local freezing rate. In other words, although there is agreement on the final dendrite arm spacing in a completely solid ingot, there are several opinions of the path by which this spacing is achieved during solidification.

One objective of this study was to determine if all of the part solid region was filled with fine dendrite arms, or if liquid regions existed between primary or secondary dendrite arms. That liquid does separate the primary and secondary dendrite arms is evident in the aqueous models of Jackson et al. (26) but no correlative work on metals was available when this study was begun.

From the macrostructures and microstructures shown in Chapters 5 and 6 it is clear that primary, secondary, and tertiary dendrite arms all grew by continuous extension of their tips, and that two adjacent arms of any type were separated by liquid. Thus, all of the part solid region was not filled with tertiary dendrite arms. This fact is of importance to the calculation of flow velocities in the part solid region since the presence of liquid channels in part solid region reduces the resistance of the structure to convective flow.

A specific viewpoint on the achievement of a final dendrite arm spacing is obtained from this study. Any type of dendrite arm grows into the liquid by extension of its tip. The spacing of adjacent tips adjusts constantly to the
solidification rate at the tips. For example, an increase in the solidification rate must cause some tertiary dendrites to grow rapidly to the size of primary dendrite arms, decreasing the spacing of the primary dendrite arms. Conversely, when the solidification rate is decreased, some primary arms do not survive, and the arm spacing increases. Both of these mechanisms have been demonstrated in transparent modeling materials by Jackson et al. (26)

After their formation, the spacing of the dendrite arms decreases continuously by the coarsening mechanisms described below during the entire local solidification time. An ingot which has been frozen slowly and then quenched demonstrates that both the local solidification time and the maximum local solidification rate determine the dendrite spacings in an ingot. The large dendrites clearly have coarsened during the entire local solidification time. The fine dendrites in the liquid channels reflect the maximum local solidification rate.

7.3.5 Coarsening of the Dendritic Structure

In ingot solidification, the local solidification time is shortest at the chill and largest in the center of the ingot, because the heat of solidification must be removed through the part of the ingot which has already solidified. In the experiments shown in Chapters 5 and 6, however, the ingots were quenched before solidification was completed at the chill. In this case, then, the local solidification time was longest at the chill and shortest at the dendrite tips.
Correspondingly, etched sections near the solidification
front have a finer dendrite structure than sections near
the chill. This demonstrates that coarsening of the dendrite
structure occurred after the passage of the solidification
front.

Three different physical models for isothermal
coarsening are shown in Figure 7.1.* They have been analyzed
mathematically under the assumption that a dendrite or a
portion of a dendrite with a radius of curvature which is
smaller than that of neighboring dendrites has a lower melting
temperature than its neighbors and "remelts" as the surrounding
arms increase in size. The first model, Model I, assumes that
the smaller dendrite arm at the center remelts along its
entire length as the adjacent arms thicken. This model has
been analyzed by Kattamis, et al. (66) In the second model,
Model II, the root of the center dendrite "melts off" because
of its small radius. This model has been considered by
Chernov, (67) Klia, (68) and Kattamis, et al. (66) The third
model, Model III, assumes that smaller dendrite arms "melt
back" to the root because of the small radius of curvature at
their tips. (69)

Observations made of vertical and horizontal
solidification suggest the addition of two more models of
coarsening to the previous three. First, electron microprobe

* Figure 7.1 and the description of Models I, II, and
III have been taken from lecture notes by Flemings. (1)
Fig. 7.1  Three models of isothermal coarsening which have been analyzed by other authors.
analysis shows that copper is segregated into the liquid channels. These channels formed between primary and secondary dendrite arms.

Second, on a section near the chill of a vertically solidified ingot, which had coarsened considerably, some dendrite arms were completely surrounded by a ring of eutectic which was in turn entirely surrounded by solid.

To account for these observations, two additional models of coarsening are presented. The first of these, which relates to the first observation would operate both for isothermal coarsening and for coarsening during solidification. The second, which accounts for the second observation would only operate during solidification.

One criticism of the three models shown in Figure 7.1 is that they account only for coarsening of the dendrite arms which are shown, but not for the simultaneous coarsening of the dendrite arm from which they grew. The first model proposed, Model IV is shown in Figure 7.2. It is based on the assumption that the complex dendrite surface tends to relax to a smooth surface with a minimum surface area. The driving force for this relaxation is the interfacial energy which, like a sheet of rubber tends to pull in any protrusions. The result of isothermal coarsening by this mechanism is to displace the liquid from between the dendrite arms. The action of this mechanism during solidification is dependent on the local freezing rate. If freezing occurs slowly, compared to the rate of diffusion of solute in the liquid between the dendrite
Fig. 7.2 Two new models of coarsening which are proposed to account for the results of this investigation.
arms, the liquid may still be displaced as the dendrite arms coarsen. If freezing is more rapid, this mechanism only slows the intrusion of dendrites into the liquid.

To explain how dendrite fragments can be completely surrounded by solid, it is necessary to invoke both Model II and its counterpart Model V. As shown in Figure 7.2, as solidification proceeds, some dendrites impinge and others "melt off." Subsequently, reduction of the surface area results in a round dendrite fragment which is entirely surrounded by solid. It is noted, however, that Model V involves more conjecture than Model IV.

7.3.6 Origin of the Equiaxed Crystallites

When any cooling occurred at the top surface of the melt, a solid "roof" formed across the top of the ingot. Pieces several millimeters in diameter separated from this solid and moved down in the melt. Where the columnar dendrites impinged on these falling crystallites, a disorganization of the solidification front occurred, resulting in the cessation of columnar growth.

The effect of crystallites falling from the top of the mold on the macrostructure of horizontal sand castings has been described by Gray(70), the Melting and Metallurgical Committee of the British Iron and Steel Research Association(71), and West(72). Tenenbaum(6) has described the formation of a solid crust at the top surface of steel ingots. More recently, Southin(15) has shown that coarse dendritic areas can be found
in each of the equiaxed grains of a steel casting. He assumes that these coarse areas are crystallites which have fallen from the solidified upper surface of the ingot. Jackson et al.²⁶ have demonstrated the operation of this mechanism in an aqueous simulation.

They have also suggested that equiaxed grains may be produced by "melting off" of some of the dendrite arms from the columnar dendrites. The operation of this mechanism in aluminum-copper alloys has been confirmed in several studies.⁹,⁷³ In this study, however, no evidence was found of dendrite segments separating from the columnar zone. All of the crystallites in the melt ahead of the solidification front could be related either to solid at the top surface of the ingot, or to other crystallites in the melt which in turn had fallen from the top of the melt. This was somewhat surprising since when the study was begun, it was assumed that the breakdown of the columnar zone by this mechanism would be observed.

7.4 Distribution of Liquid in the Part Solid Region

Throughout most of the part solid region, the volume fraction of liquid channels, $g_o$, was less than one-tenth of the volume of the part solid region. In contrast, for the slowly frozen ingots from series VA, VB, and HA the volume fraction of unfrozen liquid, $g_1$, was nowhere less than four-tenths before they were quenched. Evidently, most of the liquid in the part solid region was distributed between secondary and tertiary dendrite arms during freezing.
These dendrite arms were so close together that they continued freezing during the quench with a smooth surface. Since their surfaces did not "break down" into fine dendrite arms during the quench, the amount of liquid that was between them cannot be determined from the microstructure of the quenched ingot.

This continued solidification must also have decreased the apparent size of the liquid channels. From the micrographs, however, it is clear that any liquid region which was larger than 0.01 cm would have been solidified during the quench as fine dendrites. Since most of the liquid channels were several times this minimum size, the measured values of \( g_c \) should not be more than ten percent less than the actual values in the freezing ingot.

It is of no consequence that liquid regions smaller than 0.01 cm may not have been measured, since a distinction would in any case have to be made between liquid in "channels" and liquid between dendrite arms. Conveniently, the quench method makes the distinction by itself.

The fact that the curve of \( g_c \) with distance "moved forward" with the solidification front is evidence that the formation of liquid channels is a steady state process which occurs at the solidification front. The existing liquid channels are continued at the advancing dendrite tips, and get smaller after the solidification front has passed as secondary dendrite arms extend into them.
The analysis of the data from the horizontal ingots is continued and extended in Chapter 8, where the permeability of the part solid region is calculated. The velocity of convective flow in the part solid region is then calculated from the permeability and from the selected thermal gradient and the equilibrium liquidus composition.

7.5 Solute Gradients in the Part Solid Region

The basic result of electron microprobe analysis is that a solute gradient exists in the liquid channels in the growth direction, but not across the channels in a direction perpendicular to the growth direction. The measured segregation into the channels, however, is greater than the maximum equilibrium liquidus concentration, as determined from the measured temperature gradient and the phase diagram.

Those mechanisms which operate to increase the solute concentration of the liquid during slow solidification are described first. Additional mechanisms for solute segregation which can operate during the quench are described. They increase the concentration of solute in the liquid above the maximum expected value of the equilibrium liquidus concentration. The possible sources of error in the microprobe results are then described, and the results of other investigations are presented. The discussion justifies the assumption which is used in Chapter 8 that the solute concentration in the liquid is always the equilibrium liquidus concentration.
7.5.1 Results Which Indicate Segregation of Solute into Liquid Channels

Both directly and indirectly, the results of this study show that copper is positively segregated into the liquid channels* within the part solid region. In addition, some of the results indicate that part of this segregation occurred during the quench.

The indirect evidence for segregation is the visible appearance of the microstructures. The eutectic lines between tertiary dendrite arms are very fine, while the eutectic between secondary and primary arms is coarser and therefore darker on the microstructures. Microprobe analysis across a number of tertiary dendrite arms confirmed the low average concentration in that area.

The average measured concentration of copper in liquid channels increases with distance from the tips of the columnar dendrites. The average concentrations of the adjacent solid regions are slightly lower than the initial concentrations of the melt. Thus, on the quenched ingots, there is considerable evidence of positive segregation of copper into the liquid channels. The maximum solute content of any liquid channel is the equilibrium liquidus concentration on the phase diagram at the temperature which equals the temperature of the liquid in the channels.

* Note that, as before, a liquid channel is defined as any area in the part solid region with a dendritic structure which is recognizably more closely spaced than that of the surrounding areas.
As shown in Chapters 5 and 6, however, the measured solute concentrations in the liquid channels considerably exceed this maximum concentration.

The curves of concentration as a function of fraction solid which were derived from the microprobe data show that the solute content of the liquid channels was higher than the initial melt composition at the beginning of the quench. In addition, the form of the curve indicates the possibility that the copper concentration of the liquid channels increased during the quench.

Finally, the local average composition showed no distinct variation across any type of liquid channel. The implications of these results for partitioning solute rejection between the slow freeze and transverse quench portions of solidification are discussed below.

7.5.2 Mechanisms for Solute Segregation During Slow Freezing

There are three mechanisms by which the solute content of the liquid channels can be increased during slow freezing. The first is a physical mixing process, and the other two are diffusion processes. For all of these, the result is the transfer of copper from the surfaces of the freezing dendrites, where it was rejected into the interdendritic liquid, out into the liquid channels at the tips of the secondary dendrite arms.

First of all, this movement can be accomplished by any liquid motion which stirs the liquid at the surfaces of the dendrite arms into the larger liquid regions. Macroscopic
fluid flow due either to solidification shrinkage, or to
natural convection can cause this kind of mixing. The highest
copper concentrations, however, are adjacent to solid surfaces,
and viscous forces prevent the motion of liquid close to
stationary solid surfaces.

The second segregation mechanism is the diffusion of
solute from between tertiary dendrite arms into the liquid
between secondary dendrite arms and then into the liquid
channels at the tips of the secondary dendrite arms.

In addition to these two methods, coarsening of the
dendritic structure actually changes the locations of the
interfaces between dendrite arms and the surrounding liquid. As
shown by Model IV, Section 7.3.5, the penetration of dendrite
arms into the liquid channels is limited by the attempt of the
system to reduce its interfacial area. This results in more
compact solid areas with lowered solute concentration and
larger liquid regions of higher solute concentration.

These three methods operate during the entire course
of solidification. The last two, however, being diffusion
processes, will be more effective during slow freezing than
during the quench.

7.5.3 Mechanisms for Solute Segregation During the
Transverse Quench

Segregation of copper into the liquid channels can
continue during the transverse quench both by diffusion of
solute from the surfaces of dendrite arms and by the physical
processes which are accentuated by the drastic quench.
The quench was rapid, but not instantaneous, and examination of the microstructures shows that solidification during the quench occurred from existing solid dendrite arms. Thus some continued solute rejection and diffusion must have occurred during the quench.

The physical motions which occurred during the quench, however, are more likely to have redistributed the solute effectively than diffusion in the ten seconds during which final solidification took place. The most important motion during the quench was fluid flow to feed solidification shrinkage. For horizontal ingots, the contraction of the ingot thickness which occurs about a centimeter ahead of the solidification front indicates motion of liquid either into the part solid region or down to the bottom of the ingot. Conversely, the grains of fine dendritic material due to the quench are more numerous at the center of the ingot, which indicates that some concentration of water at the center of the quench spray caused more rapid solidification at the center of the broad faces of the ingot than at the edges of the ingot. Since, in any case, solidification was almost instantaneous at the surface of the ingot and proceeded towards the centerline, flow due to solidification shrinkage should have been largest at the centerline and negligible at the surface.

Another type of physical motion during the quench is the cooling contraction of the solid dendrites. Adams\(^{74}\) has shown that the interdendritic liquid can be pushed from
between the dendrites by this shrinkage. Such motion of interdendritic liquid during the quench would increase the average solute content of the liquid channels.

7.5.4 Sources of Error in the Microprobe Analysis

A short digression is made at this point to discuss the considerable scatter of the microprobe data. Three types of errors are considered. They are the constant error introduced by the measuring technique, random error caused by the trace technique, and random error caused by the trace location within the sample.

The first kind of error is that introduced by the microprobe analysis itself. As shown in Appendix F, the measured intensities were corrected for background, for instrument drift, and for interactions between the copper and aluminum atoms to convert them to copper concentrations. These methods, however, are well understood, and the total relative error introduced by these corrections was less than five percent. A more important source of error was the averaging of areas of different compositions by the sample motion which occurred during the taking of each data point. Because the curves of density and relative intensity with composition are nonlinear, this averaging introduced some error into each data point. As shown in Appendix F, the data from the measured AlKα intensities were discarded for this reasons. (They yielded average compositions which were some 20 percent lower than the corresponding values for CuKα radiation.) The
best estimate of the errors introduced by this averaging is obtained by comparing the microprobe results for regions which were ahead of the solidification front with the chemical analyses of the melt and of similar regions of quenched ingots. The results of these two different methods of analysis agree to within 0.5 wt pct copper. Thus the relative error which sample motion introduced into the CuKα measurements is less than 10 percent.

The trace technique can introduce random errors into the results. In part, this is due to the fact that the surface of the sample cuts through each dendrite arm or group of dendrite arms differently. It is expected that the average compositions of different section planes through a dendrite arm will be different. Obtaining a correct average is thus dependent on sectioning adjacent dendrite arms differently to obtain an "average" distribution of section planes, as well as averaging a large number of individual dendrite arms. In fact, average concentrations in the solid regions, which involve few dendrite arms, are more scattered than the average concentrations of the liquid regions, which contain more dendrite arms.

The other error introduced by the trace technique is caused by the "dead time" during which the integrated intensities were printed by the microprobe. Since the sample motion continued during this time, only a fraction of the trace was involved in the averaging (5/6 in most cases). The distribution of this fraction in relation to the dendrite arms and
interdendritic eutectic therefore introduces some uncertainty into the measurement.

The final kind of error is the possibility of real differences of composition within the sample. Segregation need not be uniform, particularly in view of the relative motion of solid and liquid during the quench. The total of these random errors, both real and artificial can be estimated from the data presented in Chapters 5 and 6 as approximately two wt pct copper for a trace 0.03 cm long.* In several instances, data from similar or identical regions along a trace 0.1 cm long were in agreement to within 0.4 wt pct copper.

Thus, considering all of the experimental errors, there is no doubt, then, that there was segregation of copper into the liquid channels in the quenched ingots. The allocation of this segregation to the slow freezing or to the transverse quench remains a problem.

7.5.5 Results of Other Investigations

The segregation of solute ahead of an advancing dendritic interface has been the subject of a number of investigations. A distinction has been made between forward segregation in the growth direction at the tips of the columnar dendrites, and sideways segregation within the part solid region.

* For consistency, each trace was divided only at eutectic peaks of composition. Thus all of the averages shown contain the same number of dendrite arms as interdendritic spaces. Additional error would have been introduced if the points on the structure at which the divisions of the trace fell were not always the same.
Thermocouple measurements ahead of the solidification front by Backerud and Chalmers\(^{(22)}\) and by Doherty and Feest\(^{(75)}\) indicate that partial solute rejection at the tips of primary dendrite arms depresses the freezing temperature of metal alloys which are freezing dendritically.

At the other extreme, Flemings and coworkers\(^{(8,46)}\), successfully calculated microsegregation with the assumption that the liquid between the finest dendrite arms in an ingot was completely mixed by solute diffusion. Hellawell\(^{(76)}\) has supported this assumption.

The solute gradients investigated in this study are between secondary dendrite arms, and thus intermediate in nature between the two cases outlined above. Wojciechowski and Chalmers\(^{(73)}\) have demonstrated an increase in the solute concentration at the junction between columnar and equiaxed grains of an aluminum-copper alloy. As seen from the macrostructures in Chapters 5 and 6, such a junction is similar to the large channels in the growth direction between groups of dendrite arms. Kohn and Philibert\(^{(20,21)}\) have found a solute gradient at the surfaces of equiaxed grains in an aluminum-copper alloy which was frozen slowly and then quenched. Hellawell\(^{(76)}\) questions the validity of such results because of the transition region which must occur during the quench. In addition, their result was obtained with a defocused microprobe spot, and the energy distribution of such a spot is uncertain.\(^{(77)}\) Thus the literature indicates that some segregation is expected between the secondary dendrite arms. The exact extent of that segregation, however, is uncertain.
7.5.6 Assumed Solute Segregation

The assumed solute gradient in the liquid channels thus must be determined by apportioning the measured segregation to the slow freezing and the transverse quench on the basis of the results of this and other investigations. It is shown that the most reasonable assumption is that the liquid channels are completely mixed and contain the equilibrium concentration of solute.

First, there is specific proof that segregation did occur during slow freezing. The fact that the cores of the dendrites in the liquid channels have a higher solute content than the cores of the larger dendrites in the adjacent part solid regions demonstrates that segregation of copper into the liquid channels had already occurred before the quench. In addition, the mere existence of liquid channels implies positive segregation of copper into those channels. Only the presence of additional copper in the liquid channels could lower the freezing temperature of the liquid and prevent the rapid penetration of the channels by dendrite arms.

Proof of segregation during the quench is ambiguous. The shape of the curve of concentration as a function of fraction solid might be due to segregation during the quench. If segregation does occur during the quench, three specific results might be expected. First, at the same locations, the smaller channels might have a higher concentration of copper than the larger liquid channels. Second, the solute
concentration near the part solid region might be higher than at the center of the liquid channel. Third, the average solute concentration of a liquid channel near the surface of an ingot, which solidifies at the start of the quench, should be different from the average concentration of a channel at the mid-plane of the ingot, which is the last area to solidify.

Examination of the microsections shown in Chapters 5 and 6 shows no evidence that the smaller channels have a higher copper concentration than the larger channels. No evidence was found of gradients across the liquid channels or across the thickness of the ingot. Thus there is no real evidence for continued segregation during the quench, except that the measured concentrations are higher than the equilibrium liquidus composition.

Finally, it must be considered that the measured segregation, ten to fifteen wt pct copper, is much closer to the equilibrium liquidus concentrations of five to ten wt pct copper than to the maximum concentration of 33.2 wt pct.

Considering all of the above, it is concluded that the concentration of copper in liquid channels is most reasonably assumed to be the equilibrium liquidus concentration. The data simply do not justify any more complex an assumed solute gradient.

7.6 Macro segregation

The vertical macrosegregation found in an ingot which had been quenched from above the liquidus temperature is an
unexpected result. Since the ingot was liquid for more than twenty minutes, and since thermal gradients were produced in the melt by both the heating process in the resistance furnace and the cooling process both prior to and during freezing, it was expected that the melt would be thoroughly mixed. The origin of the vertical macrosegregation must be the casting and remelting procedure which preceded the start of slow freezing.

The ease with which the nucleation and growth of solid occurred at the top surface of the melt is probably due in part to the fact that liquid at the top of the ingot had a lower copper concentration and therefore a higher freezing temperature than liquid at other locations in the melt. Because the solute gradient was low, however, (0.15 wt pct/cm) it is assumed that the solute gradient did not significantly affect the solidification structure. The segregation of copper into the liquid channels produced much steeper solute gradients (1.5 wt pct/cm) and therefore this natural segregation must have a much stronger influence on the solidification structure.

Even though vertical macrosegregation existed at the start of solidification, the data show an increase of the copper concentration at the bottom of the bulk liquid of about 0.03 wt pct during horizontal solidification. This segregation was caused by convective flow through the part solid region. Models for both the flow and the resulting macrosegregation are presented in Chapter 8.
No macrosegregation was found in the liquid or in the liquid channels across the thickness of the ingot. This means that the amount of material ground from the surface to prepare the ingot for etching is not a critical parameter. It also means that the location within the ingot thickness of the liquid channels chosen for microprobe analysis is not an important variable.

7.7 Reality of the Results

The possibility that the results are merely artifacts caused by the slow freeze-transverse quench itself or by mistakes in the experimental procedure is considered here. The possibility that the structures are unreal, caused by tearing the structure apart by the quench, by shrinkage of the solid dendrites during the quench, by the presence of thermocouples in the melt, or by other errors in the technique or its application are discussed and rejected.

The effect of the vertical macrosegregation in the melt on the solidification structure was discussed in the previous section. The segregation of copper into the liquid channels produced solute gradients several times the solute gradient in the melt. It is therefore likely that the vertical macrosegregation in the melt did not affect the solidification structure in any significant way.

The liquid channels in the growth direction represent regions of separation between adjacent dendritic regions, and it might be thought that such structures could have occurred by
a physical motion of the dendrites during the quench. Several features of the structures indicate the reality of their existence before the quench. First, the groups of dendrites and the individual dendrites between which the liquid channels occur, are rounded at the solidification front. Second, the tips of the secondary arms which grew into the channels are rounded and appear to have coarsened. Third, the dendrite structures on the two sides of the channels do not match. For all these reasons, the possibility that rupture of the solidification structure by the quench caused the liquid channels in the growth direction is rejected.

There are two possible artificial methods which could have cause the bottom channel in horizontally solidifying ingots. First, shrinkage of the solid dendrite structure during the quench might have raised the bottom surface of the part solid region. This would account for the smooth surface which is found at the bottom of the part solid region. This possibility is rejected, however, because such shrinkage would surely have caused some large sections of the part solid region to fall off at the bottom, and would also be expected to cause some horizontal "cracks" in the part solid region at higher locations in the ingot. Also, it is not at all clear that shrinkage of this type would cause the bottom channel to be larger near the solidification front than near the chill.

A more likely artificial cause of the bottom channels is that heat retained in the graphite block at the bottom of the mold prevented solidification of the alloy at the base of
the ingot. While some such consideration might in fact have stabilized the formation of the bottom channel by convective flow, the efficiency with which heat is transported in the metal alloy implies that a slight retardation of the solidification front, rather than a long liquid channel would have been the result of any addition of heat from the bottom of the mold. In addition, the reality of convective flow, both through the part solid region, and into the bottom channel, is proven by the tubular shape and the location of the vertical flow channels.

The presentation and analysis of the results assumes that both heat flow and solidification were unidirectional. The fact, however, that slow cooling of the melt occurred even before the nitrogen cooling was begun shows that the insulation unit was not completely effective. The solidification front, however, generally did not show any curvature, either on the vertical surface of the ingot, or on sections through the ingot thickness. In addition, the presence of long columnar dendrites which were aligned in the heat flow direction also indicates that growth and heat flow were essentially unidirectional.

The presence of thermocouples and gas bubbles in the melt might also have influenced the structure. Structural features, however, were continuous across the thermocouples and were unchanged from ingots in which the part solid region did not reach the thermocouples. Gas bubbles were most pronounced in ingots which were cast on humid days and experimentation was
therefore limited to relatively dry days. As a rule, structural features were not associated with gas bubbles. In addition, some gas is usually present in commercial castings\(^{(78)}\) and is therefore "natural".

Finally, it is recalled that, as shown throughout this chapter, all of the structural features except the bottom channel in horizontal solidification have counterparts in other investigations. Thus although the physical environment of the ingot and the procedures used in this study are unique the results are representative of unidirectional solidification in general.

7.8 Summary

The major result of this study is that horizontal solidification results in a different solidification structure than vertical solidification, and that this difference is caused by natural convective flow of the unfrozen liquid in the part solid region during horizontal solidification. In addition the parameters required to calculate the velocity of this flow - the temperature gradient, the solute gradient, and the distribution of the unfrozen liquid - have been determined. The calculation is done in Chapter 8.

The major differences in the solidification structures of vertical and horizontal solidification are the different types of liquid channels which are formed. These channels also provide specific evidence for the presence of convective flow in horizontal solidification. Channels in the growth direction between groups of dendrites formed only in vertical
solidification. The irregular sides of these channels were caused by the inward growth of the secondary dendrite arms. Channels in the growth direction between like-oriented dendrites were formed between primary arms in both vertical and horizontal solidification. Indeed these channels may be a necessary corollary of columnar dendritic growth.

On the other hand, tubular flow channels and the bottom channel formed only during horizontal solidification. The development of the convective flow system from general flow around the existing dendrites to smooth tubular flow channels shows that convective flow during horizontal solidification altered the solidification structure. The flow moved down through the part solid region, across the bottom of the mold, and into the bulk liquid, carrying liquid with a high solute content and causing macrosegregation.

The selected temperature distribution and the assumption that the unfrozen liquid at any location in the part solid region contains the equilibrium concentration of solute are combined in the next chapter with a more complete analysis of the distribution of liquid in the part solid zone to model the flow velocities and macrosegregation.

In this study, vertical and horizontal flow have been examined separately. In most industrial processes, however, the two occur simultaneously in a casting or ingot. To see how the two types of solidification interact, one ingot was frozen bi-directionally. Using two cooling gas tubes, slow freezing was begun from both the bottom and the side of the ingot.
The resulting structure is shown in Figure 7.3, and has characteristics of both vertical and horizontal solidification. Both large and small liquid channels formed in the growth direction at the bottom of the ingot. Convective flow through the portion of the ingot which was freezing horizontally could not continue to the bottom of the ingot, however, because of the resistance provided by the part solid region at the bottom of the ingot. Therefore, there is no bottom channel. Instead, convective flow left the part solid region in the upper part of the ingot. Thus, a tubular flow channel is seen at (1) in the upper part of the ingot.

The conclusion to be drawn from this experiment is that bidirectional solidification can be viewed as a combination of vertical and horizontal solidification.
Fig. 7.3 To illustrate the interaction of vertical and horizontal solidification, one ingot was frozen from both the side and the base. 1.5X. (a) Face -z. (b) Face +z.
Fig. 7.3, continued.
8. CALCULATIONS AND MODEL OF FLOW

The primary concern of this chapter is whether the flow of interdendritic liquid in the part solid region of a horizontally solidifying ingot can be calculated from the thermal and solute gradients which were measured, and the solidification structure which was observed by the slow freeze-transverse quench technique. To do this, the permeability of the part solid region is calculated. This allows the calculation of the convective flow velocities in the part solid region. It is then possible to construct a simple model of flow to account for the measured macrosegregation which occurred during horizontal solidification.

8.1 Outline

The basic relations of fluid flow in porous media are introduced.

Two permeabilities in the part solid region are calculated and compared. One is due to the liquid channels and pools in the part solid region. The other is due to the interdendritic liquid which is distributed between tertiary dendrite arms.

The flow of interdendritic liquid through the part solid region is calculated from the permeability, the assumed solute gradient, and the assumed temperature distribution.

It is shown that flow through the tubular flow channels must be restricted by the resistance to flow of the part solid region at the top of the ingot.
The time constant for flow in the part solid region is calculated and shown to be negligibly small.

A simple model is constructed to calculate the macro-segregation caused by the transport of solute from the part solid region by liquid flow.

The results of the calculations are discussed, both as they are developed, and at the end of the chapter.

8.2 Fluid Flow in a Packed Column

The subject of fluid flow in a packed column (packed bed, porous medium) is presented in a number of texts.\(^{79,80}\) One of the basic relations in this field is D'arcy's Law, which is the equivalent of Ohm's Law for electricity. It is written

\[ v = \frac{K}{\mu} \Delta p, \]

where \( v \) is the apparent velocity of flow, \( \Delta p \) is the driving force, or potential drop per unit length, and the ratio of \( K \), the permeability, to \( \mu \), the viscosity, is the conductance of the material.

The most widely accepted analysis of this type of flow develops an analogy with flow through a set of distorted capillary tubes. The porous material is assumed to contain many small, tangled tubes, through which liquid can flow. Using this analogy, the Kozeny equation relates the permeability, \( K \), to the volume fraction of the pores in the material (the volume fraction of interdendritic liquid, \( g_1 \),
for the part solid region), and the surface area of the pores per unit volume of porous material, \( \Sigma \),

\[
K = c g^3_1/\Sigma^2
\]  \hspace{1cm} (8.2)

Bird, Stewart, and Lightfoot\(^{(81)}\) accept the value of 0.24 for the constant \( c \). As they demonstrate, the quantities \( g_1 \) and \( \Sigma \) may also be used when the real physical nature of the porous medium is that of a column packed with regular or irregular particles. The concept of capillary tubes in a solid material is then only a convenient analogy.

8.3 **Permeability in the Part Solid Region**

As seen in Chapter 6, there are two distinct factors which contribute to the permeability of the top half of the part solid region of the ingots. First, there are pools and channels of liquid, identifiable as the fine dendritic structure in the quenched sample. This will be called the "channel permeability." Second, the rest of the interdendritic liquid is dispersed between the dendrite arms throughout the solid regions. This results in an "interdendritic permeability". The different permeabilities associated with two types of liquid areas in the part solid region are calculated separately, and then compared. It is found that the interdendritic permeability determines the velocity of flow.

8.3.1 **Channel Permeability**

The permeability due to pools and channels, \( K_c \), is found from the Kozeny equation (8.2) as
\[ K_C = 0.24 \frac{q_C^3}{\Sigma_C^2}, \quad (8.3) \]

where the volume fraction of channels, \( q_C \), and the surface area of channels, \( \Sigma_C \), are determined from the lineal analysis data on the quenched ingots of Series HA. These data were presented in Chapter 6 as \( q_C \) and \( \Sigma_C \) versus distance from the chill for sections from different ingots.

Using the location of the tips of the columnar dendrites, and the assumed thermal gradient, all of these data may be combined and plotted as a function of temperature, Figure 8.1 and Figure 8.2. As seen in Figure 8.1, the channels represent a large volume fraction only where the temperature is greater than \( 645^\circ C \). The form of the data is similar to the volume fraction liquid in the solidification of an alloy with a very narrow freezing range. The data were therefore compared visually to a series of equations with the form of the Scheil equation for solidification with no diffusion in the solid, which is,

\[ f_1 = \left( \frac{T_M - T_{1,o}}{T_M - T} \right)^{1 - k} \quad (8.4) \]

where \( f_1 \) is the weight fraction liquid, \( T_M \) is the melting temperature of the pure solvent, \( T_{1,o} \) is the liquidus temperature of the alloy, and \( k \) is the equilibrium partition ratio. The best fit of the function to the data was obtained by taking \( T_M \) equal to 647.1, and \( k \) equal to zero. The function plotted in Figure 8.1 for \( q_C \) is therefore
Fig. 8.1  Data values of volume fraction channel from horizontal aluminum-4.5 wt pct copper ingots A-57, A-52, and A-59. The solid line is the assumed functional relation.

Fig. 8.2  Data values of the surface area of channels per cm$^3$ from horizontal aluminum-4.5 wt pct copper ingots A-57, A-52, and A-49. The solid line is the assumed functional relation.
\[ g_c = \frac{(647.1 - 647)}{(647.1 - T)}, \]  

(8.5)  

where the liquidus temperature has been taken to be 647°C.  

These values indicate that the slope of the assumed liquidus is very small, and that there is no solubility of the solute element in the solid. This is, of course, only an analogy.  

Similarly, the specific surface is assumed to be

\[ \Sigma_c = \frac{1}{2} \times \frac{(648.6 - 647)}{(648.6 - T)} \times 100. \]  

(8.6)  

The permeability due to channels, \( K_c \), is then calculated from Equation 8.3, and is shown in comparison with the permeability of the dendritic regions in Section 8.3.3, Figure 8.6.  

8.3.2 Interdendritic Permeability

The dendritic areas between liquid pools and channels also contain interdendritic liquid which is dispersed between the dendrite arms. The permeability of these areas may also be calculated from the Kozeny equation as

\[ K_d = 0.24 \frac{g_d^3}{\Sigma_d^2}, \]  

(8.7)  

where \( K_d \) is the permeability of the dendritic region, \( g_d \) is the volume fraction of liquid within the dendritic areas, and \( \Sigma_d \) is the surface area of the dendrite arms per unit volume of the dendritic region. The volume occupied by the liquid channels is specifically "removed" from the part solid region for this analysis.
The volume fraction of interdendritic liquid in the dendritic areas, \( g_d \), is found as the ratio of the volume fraction of liquid which is within the dendritic region to the volume fraction of the part solid region which contains no channels:

\[
g_d = \frac{g_1 - g_c}{1.0 - g_c}. \tag{8.8}\]

The assumption that \( g_1 \) applies to the total volume of the part solid region and not just the dendritic area results from the assumption that the interdendritic liquid is completely mixed.

As seen on Figure 8.3, the volume fraction of liquid within the dendritic areas is much higher than the overall volume fraction of liquid in pools and channels**.

The number of dendrites crossed per unit length of a linear trace across several finely polished samples from ingots A-57 and A-49 produced data on the average size of dendrite arms, \( \bar{d} \), in dendritic areas at different distances from the chill. The traces were along either the \( z \) or \( y \) axes. Although in some areas the dendritic structure was highly oriented, check lines in directions other

* Equations for the calculations of \( g_1, f_1, C_1, \rho_S, \rho_L, \) and \( \mu \) for the aluminum-4.5 wt pct copper alloy are given in Appendix G.

** To better demonstrate the nature of the functions, the curves in this chapter are plotted as if the chill surface was at -6.0 cm and the tips of the columnar dendrites were at +4.63 cm. Since many of the functions are undefined at exactly the tip location, evaluation of the functions is not continued as far as 4.63 cm.
Fig. 8.3 Comparison of the volume fraction of unfrozen liquid in the dendritic region, $g_d$, with the volume fraction of liquid channels, $g_c$. 
than y and z indicated that a random distribution of dendrite orientations could be assumed. Data from less well polished samples was found to be inaccurate since fine dendrite arms near the tip of the columnar zone could not be resolved.

The distances from the tips of the columnar region were calculated and converted to local solidification time in seconds, \( \theta_f \), assuming that the rate of advance of the tips was 1.08 cm/min. The converted data are compared in Figure 8.4 to the inverse of the dendrite arm spacing relation reported by Bower, Brody, and Flemings.\(^{(8)}\) The equation which is plotted is

\[
\frac{1}{d} = \left( \frac{10^4}{7.5} \right) \theta_f^{-0.39}
\]

where \( d \) is the secondary dendrite arm spacing in centimeters. The slope of the data agree well with the exponent -0.39, however the values are uniformly lower. The average dendrite size, \( \bar{d} \), is larger than \( d \), which is in essence the minimum distance of secondary arm packing. The relation which is obtained for the average number of dendrites per centimeter is thus,

\[
\frac{1}{\bar{d}} = \left( \frac{10^4}{19.6} \right) \theta_f^{-0.39}.
\]

\( (8.9a) \)

\( S \) is defined as the distance of the dendrite tips from the chill, and \( s_c \) is defined as the distance of any point in the part solid region from the chill. The local solidification time (sec) in the part solid region during solidification is then found by dividing the distance from the tips (cm),
Fig. 8.4  Number of dendrites per centimeter. Points - Data taken from polished ingots. Dotted line - Inverse of secondary dendrite arm spacing. (8) Solid line - Inverse of assumed average dendrite arm spacing.
(S - s_c), by the rate of advance of the solidification front, 0.018 cm/sec,

θ_f = 55.6(S - s_c)

The inverse of the dendrite arm spacing (cm) is therefore related to the distance from the tips by

\[ \frac{1}{\bar{a}} = 107.0 (S - s_c)^{-0.39} \]  \hspace{1cm} (8.9b)

The measured specific surface area of the interdendritic liquid in dendritic regions of the quenched sample, Σ_{d,f}', is found from

\[ Σ_{d,f} = 4.0/\bar{a}. \]  \hspace{1cm} (8.10)

The factor 4.0 contains two factors of 2.0. On a linear trace there are 2.0 intersections with interdendritic liquid for each dendrite arm, and multiplying by 2.0 converts the number of intersections to the specific surface. \((49)\)

A correction, however, must be applied to this value since the surface of interest existed in a partly liquid ingot and has increased as the dendrite arms solidified during the quench. As shown in Appendix H.1, the specific surface of solid particles which increase their size but not their number as they freeze is

\[ Σ = (1 - g_1)^a B, \]  \hspace{1cm} (8.11)

where \(a\) has the value 2/3 for spheres and 1/2 for infinitely long rods, and \(B\) is a constant which depends on the number
and shape of the particles. At some point during freezing
the particles (here the dendrite arms) will impinge on one
another and their surface area will stop increasing. Assuming
an exponent of 0.6 in Equation 8.11, and also assuming that
the surface cannot expand after \( g_d \) has decreased to 0.3, the
original specific surface, \( \Sigma_d \) is calculated from the measured
specific surface, \( \Sigma_{d,f} \), by

\[
\Sigma_d = \left( \frac{1 - g_d}{1 - 0.3} \right)^{0.6} \Sigma_{d,f}
\]  

(8.12)

\( \Sigma_{d,f} \) is found from Equation 8.10. As seen in Figure 8.5, the
specific surface in the dendritic areas is much larger than
the specific surface of channels in the entire volume. The
change of slope of \( \Sigma_d \) which occurs at -3 cm is a result of the
restriction mentioned above that no correction is applied to
\( \Sigma_{d,f} \) if \( g_d \) is less than 0.3.

The permeability of dendritic areas, \( K_d \), is then
calculated from Equation 8.7. It is compared to the channel
permeability in Figure 8.6, below.

8.3.3 Total Permeability

The overall permeability due to channels, \( K_c \), and the
permeability of the dendritic regions between channels, \( K_d \),
calculated from Equation 8.3 and Equation 8.7 are shown in
Figure 8.6. Clearly, the dendritic regions have a much higher
permeability than that caused solely by channels. For this
reason, the small contribution of the channels to the total
permeability is ignored and the total permeability is
calculated from Equations 8.12, 8.8, and 8.7 as
Fig. 8.5 Comparison of the surface area per cm$^3$ of the freezing interface within dendritic regions, $\Sigma_d$, with the surface area per cm$^3$ of liquid channels, $\Sigma_c$. 
Fig. 8.6 Calculated permeabilities. $K_C$ - due to liquid channels. $K_d$ - due to interdendritic liquid. $K_t$ - assumed total permeability.
\[ K_t = 0.24g_1^3[0.7/(1 - g_1)]^{1.2}d_{\text{eff}}^{-2}, \]  

which is also plotted in Figure 8.6.

8.3.4 Discussion

From Equations 8.13 and 8.10, the total permeability may be expressed as

\[ K_t = 0.24g_1^3 0.7^{1.2} (1 - g_1)^{-1.2}d^2/16 \]  

\[ = 9.78 \times 10^{-3} d^2 g_1^3/(1 - g_1)^{1.2}. \]

Piwonka and Flemings\(^{(82)}\) have measured the permeability of an aluminum-4.5 wt pct copper alloy by measuring the flow of liquid lead and gaseous nitrogen which were forced through a partly solidified alloy, Figure 8.7. They assumed the relation

\[ K_t = \gamma g_1^2, \quad g_1 < 0.3. \]

Using the capillary tube flow analogy described in Section 8.2, they assumed that the number of channels per unit area and the tortuosity of the channels did not change during solidification. Since \( \gamma \) in the tube analogy includes only constants, the number of channels per unit area, and the tortuosity, it could also be assumed to be constant. Equation 8.15 is shown as the dotted line on the figure. Piwonka and Flemings assumed that their data was in error for fraction liquid greater than 0.3, because channeling within the part solid region made D'arcy's Law inapplicable.
Fig. 8.7 Comparison of permeability functions with the experimental data of Piwonka and Flemings, (82) obtained by passing liquid lead (X) and nitrogen (O) through a partly solidified aluminum-copper alloy.
Assuming that all of their experiments were performed after the same local solidification time, the average dendrite size, $\bar{d}$, would be constant for all of their data. Thus by Equation 8.14, $K_t$ is only a function of the volume fraction liquid, $g_l$. To plot Equation 8.14 the average dendrite size, $\bar{d}$, was taken to be 15 microns. (This parameter shifts the curve vertically, but does not change its form.)

Piwonka and Flemings used the value 0.045 poise for the viscosity of the liquid aluminum. This is three times the value which is currently accepted, Appendix G. To correct their data, all of the values of permeability should be divided by three. The value of $\bar{d}$ which would then correlate their data with Equation 8.14 is about 9 microns. Their reported dendrite arm spacing was somewhat more than 10 microns. The curve shown on the figure to represent Equation 8.14 therefore represents their data better than the straight line which they used.

Mehrabian, Keane, and Flemings (44, 45) have developed a model for the flow of interdendritic liquid which takes account of both flow due to the feeding of solidification shrinkage, and flow due to gravity-induced convection. They have used this model to calculate the expected macrosegregation in a horizontally solidified ingot.

To test their model, they solidified several aluminum-4.5 wt pct copper ingots under experimental conditions which were similar, but not identical to the conditions under which the ingots of Series HA in this work were solidified. They
then chose the value $6.0 \times 10^{-7} \text{ cm}^2$ as the value of $\gamma$ in Equation 8.15 which best correlated with the macrosegregation which they measured.

Since the value which they used for viscosity was twice the average value used here, Appendix G, it is apparent from Equation 8.1 that the value $3 \times 10^{-7} \text{ cm}^2$ should be used for comparison of the permeability which they found with the permeability obtained here. Figure 8.8 shows that the permeability obtained here is about ten times that obtained by Mehrabian, Keane, and Flemings. At the tips of the part solid region the permeability, $K_t$, becomes very large, whereas $K_F$ increased only to $3 \times 10^{-7}$. The reason $K_t$ does not decrease below $K_F$ with decreasing fraction liquid, as in Figure 8.7, is that the surface area per unit volume decreased towards the chill, as coarsening of the dendrite arms proceeded.

In summary, the permeability found in this work solely from information on the structure of dendritic solidification in an aluminum-4.5 wt pct copper alloy is different in form, but not inconsistent with the experimental data of Piwonka and Flemings, and approximately ten times the permeability which was assumed by Mehrabian, Keane, and Flemings.

8.4 Flow of Interdendritic Liquid in the Part Solid Region

The driving force for convective flow in the mushy zone is the difference of the density of the bulk liquid and the density of the interdendritic liquid. Assuming that the
Fig. 8.8 Comparison of the permeability obtained in this study with that found by Mehrabian, Keane, and Flemings. (44, 45)
interdendritic liquid is completely mixed on a local scale, its concentration at any point may be found from the selected temperature distribution, Section 6.4.1, and the concentration of the liquidus line at each temperature, Figure G.1, Appendix G. Assuming that the bulk liquid is at the liquidus temperature, and has the initial concentration,

$$\Delta p = g(\rho_1(T_1, C_1) - \rho_1(T_1, C_0))$$ \hspace{1cm} (8.16)

$$g = 980 \text{ cm/sec}^2$$

$$T_1 = 647^\circ\text{C}$$

$$C_0 = 4.5 \text{ wt pct copper},$$

which is plotted in Figure 8.9. The calculation of density as a function of temperature and concentration is given in Appendix G. Dividing the driving force for flow by the viscosity, \(\mu\), does not appreciably affect the form of the driving force, Figure 8.10.

From D'arcy's Law, Equation 8.1, and Equation 8.16, the velocity of flow can be calculated as

$$v = K \cdot \frac{(g/\mu)(\rho_1(T, C_1) - \rho_1(T_1, C_0))}{g}$$ \hspace{1cm} (8.17)

which, as shown in Figure 8.11 has a maximum approximately 1.3 cm behind the tip of the columnar zone. The existence of a maximum velocity is a corollary of the fact that the driving force for flow is zero at the tips, where the permeability is a maximum, and the permeability is very small near the chill, where the driving force is a maximum.
Fig. 8.9  The driving force for flow in the part solid region, caused by the density difference between the bulk and interdendritic liquids.

Fig. 8.10  Dividing the driving force for flow by the viscosity does not change the form of the function.
Fig. 8.11  Velocity of flow down through the part solid region.

Fig. 8.12  Mass flow rate of excess copper down through the part solid region, per unit length of the part solid region, for an ingot 1 cm thick.
The rate of motion of excess solute per unit length and thickness of the mushy zone is

\[ w = v \cdot \rho_1 (C_1 - 4.5)/100, \quad (8.18) \]

which is plotted in Figure 8.12. The maximum of the flow rate of solute is farther from the interface than the maximum of the flow velocity.

**Summary** - Flow through a part solid region will generally exhibit a maximum velocity and a maximum rate of solute motion which will occur at different distances from the advancing solidification front.

8.5 **Tubular Flow Channels**

The tubular flow channels which occur in the bottom halves of horizontally solidified ingots in Series HA, are considered specifically in this section. It is shown that the channels did not form according to a criterion for "freckle" formation which has been proposed. It is also demonstrated that flow through channels must have been restricted by the resistance to flow of the part solid region in the upper part of the ingots.

8.5.1 Development of Tubular Flow Channels

Mehrabian, Keane, and Flemings\(^{44}\) have suggested a criterion for the development of stable flow channels which, for horizontal solidification, involves the variable
\[ \bar{V} = v_s (\frac{dI}{dx})/(dT/dt) \]
\[ = v_s/(ds/dt) \]

(8.19)

For flow towards the chill, \( v_s \) is negative and \( \bar{V} \) is positive, and no channels form. For \( \bar{V} \) greater than -1.0 (slow flow away from the chill) channels which form neither grow nor freeze, and for \( \bar{V} \) less than -1.0 any perturbation will cause the growth of a channel. Evaluation of \( \bar{V} \) for the conditions of solidification for the ingots in Series HA gives

\[ \bar{V} = v_s/0.018. \]

Since, from Chapter 6 flow in the tubular channels dissolved dendrite arms and increased the size of the channels, these channels are of the unstable type. The criteria proposed by Mehrabian et al then requires that \( v_s \) be at least 0.018 cm/sec. From Figure 8.11, however, the maximum vertical velocity is only one fifth (and using their smaller permeability the maximum vertical velocity would be only one fiftieth) the horizontal velocity required for the formation of unstable channels.

**Discussion** - The formation of tubular flow channels does not agree with the criterion presented above. Their development does, however, correlate well with two facts shown by the derivation of the flow rate in the part solid region in Section 8.4. First, the channels formed some distance back from the interface, which corresponds well to the location of the maximum flow rate. Second, new channels were not produced near the interface as solidification continued.
This might be because the flow of solute at the location of the channels continued to increase, Figure 8.12, as the solidification front advanced. This would have kept the channels open, and their existence may have relieved the flow which would otherwise have formed new channels closer to the tips of the columnar zone.

8.5.2 Restriction of Flow Through the Tubular Flow Channels

The tubular flow channels might have provided less resistance to flow than the dendritic region above them. In that case, flow through the channels would have been restricted by the smaller flow rate down through the upper region of the ingot.

Considering a channel with a radius of 0.05 cm, and assuming a difference in density of 0.03 gm/cm$^3$ between the channel location and the bulk liquid, the average unrestricted velocity in each channel would then be (83)

$$v = \frac{g \Delta pr^2}{8 \mu} \quad (8.20)$$

$$\begin{align*}
&= 980 \cdot 0.03 \cdot 0.05^2/8 \cdot 0.0146 \\
&= 0.63 \text{ cm/sec,}
\end{align*}$$

or nearly two hundred times the flow rate in the dendritic region. Thus the flow from an area two hundred times as large as the channel would be required to feed unrestricted flow through such a channel. Taking the total cross sectional area of the round, vertical flow channels as 0.02 cm$^2$, the flow from an area of 4.0 cm$^2$, or the entire part solid region,
would have to be concentrated in the vertical flow channels to allow flow in the channels to proceed at an unrestricted rate. The microstructure of the bottom of the part solid region, however, shows that liquid flowed into the bottom channel from all parts of the part solid region. Flow in the tubular channels, therefore, must have been restricted by the resistance of the part solid region in the upper part of the ingot.

8.6 **Time Constant of Flow**

All of the calculations have assumed that flow is at steady state through the mushy zone. Thus it is important to examine the time constant for time variant flow. For a tube of radius \( r \), (84)

\[
\tau = \frac{0.2r^2}{\mu}
\]

\[
= (0.2 \cdot 2.58/0.0145)r^2
\]

\[
= 35.6r^2.
\]

Thus the time constant for flow in a tube of radius 0.05 cm is 0.0875 sec. Flow in the interdendritic region and probably in the vertical flow channels as well may be assumed to be at steady state.

8.7 **Model of Macrosegregation**

A very simple model is developed to account for the macrosegregation which developed during the horizontal solidification of the ingots shown in Chapter 6 as Series HA.
From the results of Section 8.4, the downward flow of solute through the part solid zone can be calculated from the thermal gradient and the rate of advance of the solidification front. In the model presented here, this calculation of flow is coupled simply to the still liquid portion of the ingot to predict the macrosegregation.

The Model - Figure 8.13a illustrates the physical model which is assumed for the calculation of macrosegregation. It is assumed that the interdendritic liquid flows vertically down into the liquid channel at the bottom of the ingot. Shrinkage flow and the bending of the flow lines at the bottom of the ingot are ignored. Fluid enters this region with various volocities and concentrations. It is assumed, however, that the flow from the part solid region mixes completely in the bottom channel before entering the bulk liquid. Thus the flow rate from the part solid region*, \( W_{ps} \), is

\[
W_{ps} = \int_{0}^{s} \rho_{v} v_{ds}
\]

and the concentration of the fluid which enters the bulk liquid is

\[
\bar{C}_{ps} = \int_{0}^{s} \rho_{C} c_{vds}/\int_{0}^{s} \rho_{v} v_{ds}.
\]

* All flow rates are taken per unit thickness of the ingot.
Fig. 8.13 Model of macrosegregation. (a) Schematic diagram of a solidifying ingot. (b) Equivalent stirred tank.
The mixing region is defined by the advancing columnar zone and an assumed height, \( H \). Fluid enters the mixing region from the bottom channel, Equation 8.22, and leaves in two ways. First, solidification decreases the size of the mixing region, which is equivalent to removing liquid at a rate

\[
W_{\text{SOL}} = \rho_1 \frac{ds}{dt} \quad \text{(8.24)}
\]

Since the interface velocity, from Section 6.4.1, is constant

\[
B = \frac{ds}{dt} = 1.08 \text{ cm/min} = 0.018 \text{ cm/sec} \quad \text{(8.25)}
\]

the weight of the mixing region is

\[
W_{\text{MIX}} = \rho_1 H(L - Bt) \quad \text{(8.26)}
\]

The liquid which flows into the mixing region from the bottom channel displaces liquid upwards in the mixing region. It is assumed that liquid equal to the entering fluid leaves the top of the mixing region with the average concentration, \( C_{\text{MIX}} \). The stirred tank equivalent of this physical model is shown in Figure 8.13(b).

A simple stepwise computer simulation, Appendix G.2, is used to calculate macrosegregation. The excess copper in the mixing region and the average excess concentration of copper in the flow into the bottom channel are plotted in Figure 8.14 as a function of the length of the part solid region, \( S \), for an assumed height of the mixing region of 5 centimeters. The calculation is not valid past 6.0 centimeters.
Fig. 8.14 Calculated values of the excess copper concentrations in the bottom channel, $C_{ps}$, and the lower half of the bulk liquid, $C_{mix}$, from a model of a horizontally solidifying ingot, as a function of the distance solidified. Each interval represents the distance frozen in 10 seconds.
because when solidification reached that location the bulk liquid was filled with equiaxed dendrites which impeded flow.

Discussion - The results of the flow model, Figure 8.14, agree with the macrosegregation shown in Section 6.4, of about 0.3 wt pct copper. This agreement demonstrates that the calculated permeability is correct to an order of magnitude. The assumption of vertical flow is balanced on the one hand by ignoring shrinkage flow, and on the other by disregarding the obvious outward slant of the vertical flow channels. From considerations presented in Section 8.6, the assumption of steady state flow would appear to be quite reasonable.

The assumption that the fluid which enters the bottom channel is mixed and then enters the bulk liquid immediately means that the transport lag through the bottom channel was ignored. Including it would shift the curve for $C_{MIX}$ forward about half a centimeter.

8.8 Discussion

The significance of the calculations done in this chapter are discussed here in the same order in which they were presented. Some discussion of the accuracy of each calculation has already been given in the previous sections.

Permeability - That the distinct liquid channels and pools contribute so little to the total permeability, Section 8.3.3, is at first a curious result. It is more understandable
if the permeability of a solid material with a constant volume fraction of liquid is considered. From Equation 8.2,

\[ K = c g^{3/2} \]

it is apparent that by increasing the surface area without changing the fraction liquid, the permeability may be decreased without limit. Thus the reason is that the fraction liquid in the dendritic region, which is much greater than the fraction of channels in the whole of the ingot, more than compensates for the higher surface area per unit volume in the dendritic regions.

The fact that the permeability of the part solid region is governed almost entirely by the permeability of the dendrite arms means that the part solid zone may be considered to be homogeneous. This has been assumed by Flemings, Nereo, and Mehrabian. (35-37)

The calculation of the surface area of the dendrite arms in a freezing ingot from the fraction liquid and the local solidification time is a useful result. As shown in Figure 8.4, the average dendrite spacing found on the horizontally solidified ingots for which these calculations are made was about twice the secondary dendrite arm spacing observed by other investigators. This is reasonable, since those measurements are taken in a "close packed" direction. The equation derived for the variation of surface area with fraction liquid, Figure 8.7, is different from, but not inconsistent with the interpretation given by Piwonka and
Flemings to their data. Thus the surface area of dendrites in a partly frozen ingot can be calculated from Equations 8.9 and 8.12.

The importance of all of this is that the permeability of a freezing alloy can now be calculated using only the thermal gradients and the rate of advance of the solidification front. The surface area is a function only of the fraction liquid and the local solidification time, and the fraction liquid is found from the temperature and the phase diagram.

The difference between the total permeability obtained here, and that found by Mehrabian, Keane, and Flemings, Figure 8.8, is significant in the sense that a discrepancy of an order of magnitude will occur when they are both used to calculate flow velocities. Considering, however, that the conditions of the two experiments were not identical, and that the third power of fraction liquid and the second power of surface area occur in the calculation of permeability, the disagreement is not large.

Calculation of Flow - The form of the curves for the flow velocity, Figure 8.11, and flow of excess solute, Figure 8.12, result from the nature of the permeability and the driving force for flow. The permeability, or conductance, becomes larger near the tips, while the composition and thermal differences which cause the density difference decrease. This results here in a maximum in the flow velocity. For an ingot in which the superheat was lost
quickly and flow in the melt was quickly damped, this maximum has a physical reality.

If, however, a thermal gradient exists ahead of the advancing solidification front, convective flow downward will occur in the bulk liquid, just ahead of the interface. It is apparent that this flow will then match up with the convective flow shown in Figure 8.11, and thus penetrate the part solid region for some small distance. In this case, there will not actually be a maximum of the flow velocity within the part solid region.

**Tubular Flow Channels** - The development of the tubular flow channels in the bottom half of these ingots does not agree with the criterion offered by Mehrabian, Keane, and Flemings. They do, however, state that channels may form from flow instabilities which can arise with much slower flow rates. That statement must be invoked in this case. This study does, however, confirm the prediction by their criterion that flow channels are less likely to develop at higher solidification rates. This is shown by the absence of tubular flow channels in the more rapidly frozen ingots shown in Chapter 6, ingot A-51.

It should be noted that the flow channels form at approximately the distance from the solidification front given by the location of the maximum of the flow velocity. The continued existence of these channels even when the location of the maximum flow velocity has moved forward might reflect the continuous increase in the flow rate of excess solute, Figure 8.12.
The presentation in Section 8.5.2 indicates clearly that the flow of interdendritic liquid in the flow channels at the bottom of an ingot was restricted by the smaller permeability of the dendritic regions in the upper part of the ingot.

**Time Constant for Flow** - The calculations here all assume steady state flow. Since, as shown in Section 8.6 the time constant for flow is much less than a second, this assumption is justified.

**Model of Macrosegregation** - The model presented to account for the measured macrosegregation during horizontal solidification is admittedly a very simple one. In part this was necessitated by the complicated boundary condition at the bottom of the part solid region. The shape of the vertical flow channels demonstrates that the fluid flow lines were curved out into the liquid. On the other hand, most of the flow must have fed into the bottom channel. For that reason, the simplifying assumption was made that the liquid flowed straight down through the part solid region. The transport lag was ignored primarily to keep the model simple.

From the above considerations, it is apparent that only qualitative agreement with the measured macrosegregation should be expected from this type of model. Its simplicity, however, makes it a useful tool for making qualitative calculations.
Summary - The velocity of liquid flow in the part solid region has been calculated from the measured temperature and solute distributions and the dendrite arm spacing. Figure 8.11 which illustrates the maximum which occurs in the flow velocity is thus in some ways the heart of this study. Finally, it is noted that the calculation of the permeability of the part solid region from the physical characteristics of the dendritic structure is a direct method of calculation. If it can be developed successfully, it will be possible to calculate the expected macrosegregation in any proposed casting solely by combining the appropriate thermal analysis with data on the dendrite arm spacing of the alloy.
9. INVESTIGATION OF THE VERTICAL SOLIDIFICATION OF IRON ALLOYS

With the experience gained by working with the aluminum-copper alloy, apparatus was designed for applying the slow freeze-transverse quench technique to iron-copper and iron-carbon alloys. The results are, in some ways, similar to the results for the vertical solidification of the aluminum-copper alloy.

9.1 Outline

Apparatus is described for application of the slow freeze-transverse quench method to iron alloys. A moving induction coil and susceptor could be raised quickly from a fused silica crucible, exposing the crucible to the water quench.

Distinct vertical channels can be seen on the micrographs of the ingots.

From the temperature measurements, it is apparent that only a small part of the unfrozen liquid was contained in distinct channels.

9.2 Apparatus and Materials

Completely new apparatus was built to melt and quench the iron alloys. The iron alloys were melted in fused silica crucibles by a water-cooled induction coil around a graphite susceptor.
As shown in Figure 9.1, the coil and susceptor could be raised together, thus exposing the partly solidified ingot to the water spray quench. A cross-sectional view of the apparatus, Figure 9.2, shows the induction unit in a partly-raised position. Two 0.025 cm platinum/platinum-10 wt pct rhodium thermocouples, in 0.32 cm alumina sheaths (1) were placed in the melt (2). Approximately 350 gm of alloy was contained in a fused silica crucible (3), which had a 0.025 cm wall. A sheet of molybdenum, 0.15 cm thick, was placed inside the graphite susceptor (4). The susceptor (5) was insulated with bubble grain alumina (6) poured between it and a tube of pyrex glass (7). The induction coil (8), and the transite support (9), were attached to a sliding back plate. This allowed the coil and the susceptor to be raised and lowered around the crucible. The crucible was supported by a kaolin mat (10) and by high-temperature insulating bricks (12). Nitrogen gas was directed to the bottom of the crucible by a fused silica tube (11).

Each alloy was prepared differently, Appendix A. Rods of Armco iron and either rods of OFHC copper or a carbon-saturated iron alloy were placed in the mold together with small additions of silicon (0.2 wt pct) to prevent solution of the crucible, and of aluminum (<0.1 wt pct) to limit undercooling of the melt.

Temperatures were plotted on a chart recorder with a 10 mv scale using a rotating switch and a 5 mv per step voltage suppression box, Appendix B.
Fig. 9.1 Apparatus for applying the slow freeze-transverse quench method to iron alloys. The induction coils and susceptor were lowered over the crucible for melting and slow cooling (a), and raised to expose the crucible to the water sprays (b).
Fig. 9.2 Diagram of the apparatus for vertical freezing and quenching of iron alloys, 0.8X.
The water quench consisted of four spray jets located symmetrically on the horizontal mid-plane of the crucible, Figure 9.1. Each produced a fan shaped spray of 3.8 liter/min.

9.3 Procedure

The mold was preheated at 400°C for two hours. The materials were then placed in the mold. The unit was assembled and the vertical alignment of the sliding induction unit was checked.

After assembly, 5 kw of power in the induction coil melted the solid alloying elements and raised the temperature of the melt to approximately 1550°C to ensure complete solution and mixing. By lowering the power, the temperature was lowered to about 100°C above the liquidus temperature of the alloy. The power was adjusted to maintain a constant temperature. Nitrogen gas was then flowed onto the bottom of the crucible to cause slow vertical solidification.

When solidification had progressed upwards into the ingot, the power was turned off and the assembly of coil, insulation, and susceptor was raised. The water sprays were then turned on to quench the ingot.

The ingots were sectioned, polished, and etched in nital as described in Appendix C. The appearance of the ingot indicated that complete solution and mixing had occurred when the separate components were melted.
9.4 Results

The results for the vertical solidification of an iron-copper alloy and an iron-carbon alloy are presented here in a manner similar to the presentation of the results on the aluminum-copper alloy. First, the results of temperature measurements are given, then the solidification structures of the ingots are shown. The volume fraction of liquid channels within the part solid region is then considered. The results for each alloy are presented separately.

The experimental conditions and the distance of the dendrite tips from the chill for the four ingots to be discussed are given in Table 9.1. Because the preparation of the iron-carbon alloy was subject to some error, Appendix A, the composition of the alloy was determined by comparing the liquidus arrest temperature which was measured during freezing with the liquidus line on the iron-carbon phase diagram. The "starting temperature" and the "quench time" are not listed because the very slow cooling rate, and fluctuations of the power in the induction coil make such data meaningless. The time from the start of gas cooling to the onset of solidification varied from thirty minutes to two hours.

9.4.1 Iron-50 wt pct Copper

The iron-50 wt pct copper alloy was chosen because it solidifies over a large range of temperature. As shown on the phase diagram, Figure 9.3, the freezing range is more than
Table 9.1
Iron Alloy Ingots Solidified Vertically and then Quenched

<table>
<thead>
<tr>
<th>ingot</th>
<th>composition</th>
<th>cooling gas flow, liter/min</th>
<th>tip location, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-9</td>
<td>50% Cu</td>
<td>4.7</td>
<td>2.7</td>
</tr>
<tr>
<td>S-10</td>
<td>50% Cu</td>
<td>4.7</td>
<td>1.3</td>
</tr>
<tr>
<td>S-11</td>
<td>-2.5% C</td>
<td>7.1</td>
<td>2.7</td>
</tr>
<tr>
<td>S-12</td>
<td>-2.9% C</td>
<td>4.7</td>
<td>2.5</td>
</tr>
</tbody>
</table>

300°C. In addition, as is shown in Figure 9.3(b), the fraction liquid remains greater than 45 wt pct for the entire freezing range. Large liquid channels would be expected in an alloy of this type.

Temperature Measurements - The power was adjusted to maintain a constant temperature of 1550°C. The nitrogen gas flow was begun at a rate of 4.7 liter/min, and the melt cooled at a rate of approximately 3°C/min. There was a vertical temperature gradient in the melt of about 5°C/min during cooling. Instabilities in the power supply caused fluctuations in the temperature curves over several minutes.

The melt undercooled about 10°C before solidification began. The time at which the temperature rose due to recrystallization was taken as the start of solidification at the base of the ingot. Once the solidification front passed the
Fig. 9.3  (a) Phase diagram for the iron-copper system. (85)
(b) Weight fraction solid as a function of temperature for an iron-50 wt pct copper alloy. (86)
lower thermocouple, its temperature decreased at a rate of 2.7°C/min, while the upper thermocouple recorded a nearly constant temperature until the solidification front passed it as well. The measured liquidus temperature was 1440°C for both ingots, 10°C higher than the value from the phase diagram, Figure 9.3. The cooling rate due to the quench was about 1200°C/min.

The locations of the dendrite tips on the quenched ingots have been plotted against the time of the quench after recalculation, Figure 9.4. The locations of the thermocouples have been plotted on the same figure against the time after recalculation at which they recorded a temperature below the liquidus temperature. These data on the motion of the solidification front are all consistent. The rate of advance of the solidification front was 0.15 cm/min. The data do not extrapolate to zero because solidification during recalculation was more rapid than later solidification. (This is because the heat of fusion had already been removed by undercooling, and recalculation is a "catching up" process.)

The measured thermal gradients at the time of the quench are shown in Figure 9.5. The average thermal gradient was 30-35°C/cm. Thus the thermal gradient was much higher and the rate of advance of the solidification front much lower than for the vertically solidified aluminum-copper ingots.

**Solidification Structures** - The cylindrical ingots were cut in half and the exposed vertical face was polished,
Fig. 9.4 Position of the solidification front for vertical solidification of iron-50 wt pct copper alloy as a function of the time after recalescence. The open symbols represent measurements made on the etched ingots. The solid symbols are from thermocouple data.
Fig. 9.5 Temperature distribution in vertically solidifying iron-50 wt pct copper ingots at the time at which they were quenched. The arrows indicate the distance of the dendrite tips from the chill on the etched ingot. The circles are the temperatures measured by the thermocouple.
etched, and photographed, as described in Appendix C. Photographs of the solidification front of ingot S-9 are shown in Figure 9.6. Liquid channels in the growth direction are visible between the primary dendrite arms at the dendrite tips (1), and within the part solid region (2). Shrinkage porosity formed during the quench (3). Long, fine extensions of the dendrite tips (4) are plainly artifacts formed during the transverse quench, as they are oriented in a different direction from the coarser dendrites from which they grew.

A number of equiaxed crystallites are present in the center of the ingot (5). Since they have not interrupted vertical solidification, they must have formed during the quench. The solidification front in this, and in the other vertically solidified iron ingots is slightly concave, indicating that there was some loss of heat from the sides of the mold.

The solidification front of ingot S-10, in which the part solid region is twice as high as for ingot S-9, is shown in Figure 9.7. Many large channels have formed between groups of primary dendrites. The quench artifacts (1) grew up towards the fine dendrites growing inwards due to the quench (2). They meet along a line (3) above the real solidification front.

**Distribution of Liquid in the Part Solid Region** — As shown in Figure 9.5, the lowest temperature in these ingots before the quench was 1350°C. From Figure 9.3(b), the weight fraction of liquid in the part solid region was therefore not
Fig. 9.6 The solidification front of ingot S-10 as seen on a vertical section through the center of the ingot. (a) Left edge. (b) Center. (c) Right edge. 10X.
Fig. 9.7  The solidification front of ingot S-9 as seen on a vertical section through the center of the ingot.  (a) Left edge.  (b) Right edge.  10X.
less than 0.5. From Figures 9.6 and 9.7, however, it is evident that the volume fraction of the part solid region which is occupied by distinct liquid channels is nearly zero at any distance farther than 0.3 cm from the dendrite tips. Thus, as was the case for the aluminum-copper alloy, most of the liquid was distributed between the secondary and tertiary dendrite arms.

9.4.2 Iron-Carbon

The iron-carbon phase diagram is shown in Figure 9.8. The preparation of the alloy, was designed to produce a composition with the maximum freezing range, two wt pct carbon. The first step in the preparation of the alloy was to saturate liquid iron with graphite and cool the melt slowly enough to reject the excess carbon along the liquidus line of the graphite-liquid region. The resulting ingot was assumed to contain 4.24 wt pct carbon, and was correspondingly diluted with pure iron to yield a final ingot whose carbon content would be 2.0 wt pct. However, some additional graphite was apparently trapped in the carbon-saturated ingot, thus increasing the carbon content of the final alloy, Appendix A. The carbon contents of the iron-carbon ingots were therefore determined by comparing the liquidus temperature measured during vertical solidification with the liquidus line of the $\gamma$-liquid region.
Fig. 9.8 The iron-carbon phase diagram. The dashed lines represent the metastable equilibrium with cementite. (87)
Temperature Measurements - The power was adjusted to maintain the melt at a temperature of 1450°C, and the nitrogen gas cooling was begun. Since the measured liquidus temperature was about 100°C lower than expected, the slow rate of cooling had to be maintained for several hours before solidification began.

The melt undercooled about 10°C before solidification began. The time at which the temperature rose due to recalescence was taken as the start of solidification. The rate of cooling due to the quench was 500°C/min. The progress of the solidification front, taken from measurements on the quenched ingots and from the temperature measurements is shown in Figure 9.9. With an increase in the gas flow rate from 4.7 to 7.1 liter/min, the rate of advance of the solidification front increased from 0.09 cm/min to 0.26 cm/min. The thermal gradients in the two ingots at the time of the quench are shown in Figure 9.10. The average gradient, about 17°C/cm, was approximately the same for the two ingots.

Solidification Structures - The solidification front on the vertical center plane of ingot S-12 is shown in Figure 9.11. Liquid channels formed between the primary dendrite arms in the part solid region (1). Continued vertical solidification during the quench, an artifact, is evident at the dendrite tips (2). Massive shrinkage porosity due to the quench occurred at the center of the ingot within the part solid region (3). Small pools of liquid are also visible in the part solid region (4).
Fig. 9.9 Position of the solidification front for vertical solidification of the iron-carbon alloy as a function of the time after recalescence. The open symbols represent measurements made on the etched ingots. The solid symbols are from thermocouple data.
Fig. 9.10 Temperature distributions in vertically solidifying iron-carbon ingots at the time at which they were quenched. The arrows indicate the distance of the dendrite tips from the chill on the etched ingot. The circles are the temperatures measured by the thermocouple.
Fig. 9.11 The solidification front of ingot S-12 as seen on a vertical section through the center of the ingot. (a) Left edge. (b) Right of center. 10X.
The solidification front of ingot S-11, which advanced more rapidly than the solidification front of ingot S-12 is shown in Figure 9.12. It shows no distinct channels. Some pools of liquid are visible within the part solid region (1).

**Distribution of Liquid in the Part Solid Region**

Assuming that the diffusion of carbon in austenite is rapid enough to prevent any solute gradient across the dendrite arms, the weight fraction of liquid at any temperature can be calculated from the lever rule. From the phase diagram, Figure 9.8, an iron-2.5 wt pct carbon alloy would be more than one half liquid by weight until its temperature decreased to 110°C below its liquidus temperature. Although the temperature in ingots S-11 and S-12 was always within 100°C of the liquidus temperature, the volume fraction of liquid decreases nearly to zero within 0.5 cm of the solidification front. Again, the explanation must be that most of the liquid was distributed between the secondary and tertiary dendrite arms, and not as distinct liquid channels.

**9.5 Discussion**

The apparatus and the experimental results on the iron-copper and iron-carbon ingots are discussed here. The solidification structures which were found correspond in general to the results of the vertical solidification of the aluminum-copper alloy.
Fig. 9.12  The solidification front of ingot S-11 as seen on a vertical section through the center of the ingot. (a) Near the left edge. (b) Right edge. 10.1X.
Apparatus - After development, the apparatus could be assembled with reasonable facility and operated smoothly during the quenching procedure. Observation of the temperature during this procedure showed that the rate of temperature decrease accelerated only slightly during the time between turning off the power and initiating the water quench (~10 sec).

The maintenance of the power input to the susceptor, it should be noted, was required because the heat loss with the power off was itself as great as that desired for the slow unidirectional solidification. Rapid fluctuations of the power input from the induction unit were absorbed by the heat capacity of the susceptor, but longer fluctuations in the average power input (longer than a minute) appeared as fluctuations in the temperature record.

The voltage induced on a coil of copper wire placed within the graphite susceptor showed that the susceptor attenuated only half of the magnetic field produced by the coil. Published information,\(^{(88)}\) however, is that the depth of penetration of the field from a spark-gap convertor into a graphite susceptor is less than one centimeter. This, and the fact that the solidification structures do not seem to have been disturbed by any fluid motion implies that no significant induction stirring occurred in the melt.

Temperature Measurements - The absence of any thermal gradient in the melt above the solidification front means that these results are comparable to solidification in an ingot after its superheat has been dissipated. The result for
the iron-carbon ingots that the rate of advance of the solidification front increased with an increase in the cooling gas flow while the thermal gradient was unchanged is the opposite of the results for the aluminum-copper alloy. Since, however, the result for the iron-carbon alloy is determined by only one experiment, and since the ratio of the power input to the gas cooling was uncertain, no definite conclusion can be made.

**Structure** - The large amount of shrinkage porosity at the center of the ingots is a result of solute motion during the quench. Because of this movement of liquid, probe work was not done on these ingots. Presumably, however, liquid motion was limited near the surface of the mold.

The vertical liquid channels are most pronounced near the walls, and their appearance, particularly in Figure 9.7 might lead to the assumption that they were caused by some motion of the dendrite arms. This cannot be the case, as only an outward motion of the crucible could make room for a liquid channel, and as seen on the photograph, the vertical surface of the ingot shows no such discontinuity. Thus formation of the channels must have arisen from the solidification process itself.

The primary question is the degree to which these iron alloys solidify in a manner similar to the vertically solidified aluminum-copper alloys.

The results for the iron alloys and for the aluminum-copper alloy have two features in common. First, the
solidification front advances by extension of the primary dendrite arms, which have spaces between them. Second, liquid channels between primary dendrite arms comprise only a small fraction of the liquid, most of the liquid being in the smaller interstices between secondary and tertiary dendrite arms. Both of these observations have been made in transparent systems which have been used to model the solidification of metal alloys. Figure 9.13 shows dendritic solidification in one such transparent system,\(^{(26)}\) and the resemblance to Figure 9.23 is quite pronounced. Thus these two characteristics are general features of dendritic growth.

Another similarity between the iron and aluminum ingots is the method of channel development. The development of channels with increased solidification time and distance shown from ingots S-10 (1.3 cm solid) and S-9 (2.7 cm solid) in Figures 9.6 and 9.9 parallels the results of Chapter 5. Also, the closing of the channels at higher freezing rates from ingot S-12 (.10 cm/min) to S-11 (.26 cm/min) in Figures 9.11 and 9.12 is the same result found for aluminum-copper ingots with an increase in the cooling gas flow. It should be noted that neither of these two results has been reported from observations of transparent media.

In those media, it appears that a change in growth rate produces a nearly immediate change in dendrite arm spacing, and that the channels at the tips of primary dendrite arms change accordingly, somewhat as if the magnification of the photograph had been changed.\(^{(89)}\) This
Fig. 9.13 Liquid channels between the tips of the primary dendrite arms in a cyclohexanol-fluorescein medium. 75X. Copied from Ref. 26.
may be because solidification of transparent media has usually been done with an imposed thermal gradient, while the dendrites in this study grew freely into a melt of nearly constant temperature.

In summary, the solidification structures of the vertically solidified iron alloys are similar to the structures found in the aluminum-copper alloy. Liquid channels between the tips of primary dendrites and the finding that most of the unfrozen liquid is situated between secondary and tertiary dendrite arms are general features of dendritic solidification. The development, during solidification of large liquid channels between groups of primary dendrites has not been reported in transparent media.
10. INVESTIGATION OF THE HORIZONTAL SOLIDIFICATION
OF AN IRON-CARBON ALLOY

The apparatus described in the previous chapter for
vertical solidification of iron alloys was modified to allow
horizontal solidification.

The structure of one ingot shows that the method will
be feasible once the proper gas cooling probe is designed.

Apparatus - The apparatus for applying the slow
freeze-transverse quench technique to the vertical solidification
of iron alloys, Section 9.2, was modified for horizontal
solidification. In place of the cylindrical fused silica mold
and graphite susceptor, a rectangular mold, similar in shape
to the mold for the aluminum-copper experiments and a rectangular
susceptor were substituted. The two thermocouples
were displaced horizontally to measure the progress of the
solidification front. The nitrogen cooling gas was introduced
through a fused silica tube at the bottom front edge of the
mold. It passed out through a hole at the top of the
susceptor.

To keep the flat sides of the mold from sagging outward,
sifted bubble grain alumina was poured into the space between
the susceptor and the mold walls. A steel rod was inserted
through the top of the susceptor just before the induction coils
and susceptor were raised, to hold down the mold. The two spray
nozzles were placed facing the flat sides of the mold. The
water flow from each was 8.7 liter/min.
Fig. 10.1  The solidification structure of an iron-2.0 wt pct copper alloy freezing from the bottom corner of the mold.
As discussed in Appendix A, the initial preparation of the alloy differed slightly from the preparation of the iron-carbon alloy in the vertical study. The carbon saturated ingot was melted with pure iron, a one gram addition of aluminum, and a 0.2 wt pct addition of silicon, in a magnesia crucible, and then poured into a graphite mold which had been machined to the interior dimensions of the rectangular fused silica mold. Thus the silica mold could be filled with more alloy than if separate pieces of carbon saturated iron and pure iron rod had been placed directly into the silica mold.

Procedure - Since the alloy had already been diluted and no pure iron had to be melted, the temperature of the melt was raised only to 1450°C. This limited the softening of the fused silica mold. The power was adjusted to maintain constant temperature, and a gas cooling flow of 7.1 liter/min was begun.

When the melt cooled to 1394°C, a tungsten wire was pushed down into the melt along the chill face. Recalescence began immediately (or had already begun), indicating that the composition was close to 2.0 wt pct carbon. The measured quench rate was 1200°C/min.

Results - The macrostructure of the bottom part of the ingot (which was 1 cm thick, 7 cm long, and 3 cm high) is shown in Figure 10.1. The ingot froze from the corner of the ingot, rather than with a vertical solidification front. Small liquid channels are visible between the tips of primary
dendrites (1). A number of crystallites separated from the part solid region (2). There seem to be liquid regions within the part solid region (3).

Discussion - The inclination of the solidification front shows that the cooling gas must be introduced along the entire height of the chill face, rather than at the bottom of the ingot.

The separation of dendrites from the part solid region in this ingot is the only instance in this study where this mechanism has definitely occurred.

The visibility of the solidification structure shows that the experiment will be practical once a suitable cooling gas tube is designed.
11. DISCUSSION OF THE SLOW FREEZE-TRANSVERSE QUENCH TECHNIQUE

The effectiveness of the slow freeze-transverse quench technique and the limitations of the technique are discussed. A comparison is then made between this method and others which have been used to study the solidification process.

Effectiveness of the Technique - The technique makes a clear distinction between liquid pools and channels, and dendritic areas, within the part solid region of a solidifying ingot. The delineation of the solidification front was not as clear. This is because the dendrites at the solidification front did not have time to coarsen. Also, solidification continued from the existing solid during the quench. Thus the dendrite arm spacing grades continuously from coarse to fine across the solidification front. This makes the delineation of the liquid regions between the dendrite tips at the solidification front more difficult than the delineation of liquid channels and pools between the coarse dendrite structures deeper within the part solid region.

Restrictions on the Rate of Slow Freezing - The slow freeze-transverse technique places both an upper limit and a lower limit on the rate of slow freezing which may be used. The maximum rate of slow solidification must be enough less than the quench rate that a good distinction is obtained between the coarse dendrites from the slow solidification and the fine dendrites from the quench. In this study good
definition of the liquid regions was obtained when the spacing of the coarse dendrites was three or more times as large as the spacing of the fine dendrites. The dendrite spacing is related to approximately the one-half power of the local solidification time. The local solidification time for slow freezing must therefore be at least ten times the local solidification time due to the quench.

The minimum rate of heat extraction for slow solidification must be enough greater than the rate of heat loss through the insulation that unidirectional solidification can be obtained. This is probably a somewhat subjective criterion, but certainly the rate of heat extraction at the chill should be several times the rate of heat loss from the sides of the mold.

**Motion of the Liquid During the Quench** - As was seen most markedly in the vertically solidified iron alloy ingots, considerable motion of the liquid within the part solid region can occur during the quench. This happens when the volume of the liquid decreases as it freezes during the quench, and the unfrozen liquid from other parts of the part solid region move through the part solid region to prevent the formation of any voids. The true composition of the liquid as it existed in the partly solidified ingot cannot then be measured.

At the vertical surfaces of the mold, however, the unfrozen liquid should freeze before it can move to feed solidification shrinkage. Thus, at least at the mold walls, the liquid in the part solid region is retained in place.
Continued Solute Rejection During the Quench - The continued rejection of solute during the quench also makes measurement of the true liquid composition impossible. It is likely, but not certain that a faster quench would limit the extent to which solute continues to be rejected during the quench. The microprobe analyses of the concentration of copper in the liquid channels of the aluminum-copper ingots were nearly all above the equilibrium liquidus concentration. Some of the values, however, were close to the equilibrium composition. It is possible that the concentration in the channels ranges from the equilibrium concentration to higher values, the low values occurring in regions where continued segregation was slight.

Comparison with Other Methods - This method of delineating the structure of a solidifying ingot is in some respects more useful, and in other respects less useful than other methods which can be used to study the nature of the solidification process. In Table 11.1, the slow freeze-transverse quench method is compared with a number of other techniques which were described in the survey of the literature, Chapter 3. The methods are ordered by the amount of interference which is required with the normal solidification process. Thus the study of a completely solidified ingot or the addition of a radioactive tracer to the melt during solidification disturb the casting process hardly at all. Dumping out the unfrozen liquid or displacing it with a heavier liquid requires no interference with the casting process until the
**Table 11.1**

Comparison of Methods of Studying the Solidification Process

<table>
<thead>
<tr>
<th></th>
<th>1*</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete solidification</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radioactive tracer</td>
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<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ingot dumping</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td></td>
<td>yes</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Liquid replacement</td>
<td>yes</td>
<td>yes</td>
<td></td>
<td>yes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parallel quench</td>
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<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transverse quench</td>
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<td></td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transparent media</td>
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<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td></td>
</tr>
</tbody>
</table>

*1. Is the ingot mold stationary?  
2. Can the structure of a partly solidified ingot be viewed?  
3. Can a wide range of freezing rates be used?  
4. Can an arbitrary mold shape be used?  
5. Can the method be used with existing commercial processes?  
6. Is the unfrozen liquid in the part solid region retained and identifiable?  
7. Is the method equally effective at all locations in the ingot?  
8. Are the dendrite tips visible at the solidification front?
ingot is inverted. Quenching the ingot either in the established heat flow direction or in a direction transverse to the growth direction (this study) ordinarily requires that casting be done in specially designed molds. The last method, the use of transparent media to simulate dendritic solidification is the furthest from the commercial casting of a metal, but it allows considerable freedom of mold and experiment design.

From the table, it is apparent that some of the techniques will be more useful than others in any particular study. For the study of the solidification process in large commercial castings, the radioactive tracer technique will probably be the most useful, as almost no interference with the solidification process (or the plant personnel) is required. For study of the specific details of the solidification structure and the distribution of liquid in the part solid region of a solidifying ingot, the slow freeze-transverse quench technique, though not the simplest, may well be the most useful method.

Summary - The slow freeze-transverse quench technique is an effective way to determine the distribution of unfrozen liquid within the part solid region. It is a useful way of determining the structure of the solidification front. In this study, it was of limited help in determining the solute content of liquid channels within the part solid region. Other methods, however, have been useful only in
determining the structure of the solidification front.

On balance, then the slow freeze-transverse quench technique is probably the best method now available for studying the solidification process on a laboratory scale.
12. SUMMARY AND CONCLUSIONS

A slow freeze-transverse quench technique was developed which makes visible the solidification structure of a partly frozen ingot. This method has been utilized in an investigation of the interaction of solidification structure and convective flow in an aluminum-4.5 wt pct copper alloy. The usefulness of the method for the study of the freezing process in iron alloys was also demonstrated. Four different types of liquid channels were found in the part solid region of aluminum-4.5 wt pct copper ingots:

(a) Liquid channels in the growth direction between groups of primary dendrites. These formed only during vertical freezing.

(b) Liquid channels in the growth direction between similarly oriented primary dendrites. These formed during both vertical and horizontal solidification.

(c) Tubular flow channels formed only in the bottom half of horizontally solidified ingots.

(d) A liquid flow channel formed at the bottom of all of the horizontally solidified ingots.

The driving force for convective flow in the part solid region is the increase of the liquid density with increasing solute content and decreasing temperature. The permeability of the dendritic structure measures the resistance to the liquid flow.
Measurements were made of the volume fraction and the specific surface of liquid channels in the part solid region of horizontally solidifying ingots. These were used to calculate the permeability of the part solid region to liquid flow. Because only a small portion of the unfrozen liquid in the part solid region comprised distinct liquid channels, the permeability of the part solid region was not appreciably increased by the presence of the liquid channels. Thus the permeability of the part solid region was a function only of the dendrite arm spacing and the volume fraction of unfrozen liquid. The velocity of convective flow in the part solid region was then calculated from the measured temperature distribution, the calculated permeability, and the equilibrium liquidus composition. The flow velocity had a maximum value of 0.004 cm/sec at a distance of about 1.3 cm behind the solidification front.

In the bottom half of the ingot, the convective flow system developed from general flow through the existing dendrite arms to concentrated flow through smooth tubular channels from which the dendrites had been dissolved. This was shown clearly by a series of ingots which were quenched at successive times after the start of slow horizontal freezing.

Apparatus was developed to apply the slow freeze-transverse quench method to both vertical and horizontal solidification of iron alloys. The solidification structures which were observed were similar to the structures which have been found in transparent media which are used to simulate dendritic freezing.
13. SUGGESTIONS FOR FURTHER WORK

The slow freeze-transverse quench technique is a way to "look inside" an ingot as it solidifies. Given the apparatus for using this technique, quite a large number of studies could usefully be carried out.

**Alloys with a Low Melting Temperature** - The aluminum-copper system was investigated at only one composition. It and other systems as well could be studied across a range of compositions to investigate the effects of solute content on the structure of the part solid region. In particular, the finding of Cole and Bolling (56) that the nature of the columnar to equiaxed transition undergoes a discrete change at "anomalous" compositions (other than eutectic compositions) in the lead-tin and lead-antimony systems should be investigated.

**Iron Alloys** - The apparatus for the application of the slow freeze-transverse quench technique to the vertical solidification of iron alloys should prove to be especially useful. It has a certain basic simplicity. Although assembling the apparatus for an experiment is a complex task, it is not overly time consuming or expensive to operate. This is particularly true considering that no experiments of this kind have been done on high temperature alloys. Besides studying the solidification structures of iron alloys, the apparatus should be useful for studying the mechanisms of the formulation of blowholes and inclusions.
The Quench Technique - A further study of the slow freeze-transverse quench technique may also be in order. The effect of the quench rate on the delineation of the solidification front and on continued segregation during the quench could be investigated. The motion of the unfrozen liquid to feed solidification shrinkage could also be determined.

Other Geometries - Except for the one aluminum-copper ingot which was solidified both from the bottom and from a vertical chill face, all of the ingots in this study were solidified from a flat chill face. The effect of the shape of the mold on the structure of the part solid region and on convective flow should be studied.
LIST OF SYMBOLS

a  correction constant for the conversion of relative intensity to concentration

B  rate of advance of the solidification front, dS/dt, cm/sec

c  constant factor in the Kozeny equation (Equation 7.2)

C_e  eutectic composition, wt pct copper

C_l,C_s  concentration at the freezing surface of a dendrite arm, in the liquid, in the solid, wt pct copper

C_mix  average concentration of the mixing region, wt pct copper

C_o  initial composition of an alloy, wt pct copper

C̅  average concentration of a number of microprobe data points, wt pct copper

C̅_{ps}  average composition of the flow out of the part solid region, wt pct copper

C̅_{s}  average composition of a solid dendrite arm

d  secondary dendrite arm spacing, cm

̅d  average dendrite arm spacing, cm

f_l  weight fraction liquid

f_s  weight fraction solid

g_c  volume fraction of liquid channels in the part solid region

g_d  volume fraction of interdendritic liquid in a dendritic area of the part solid region

g_l  volume fraction liquid

H  height of the mixing region in the model of macrosegregation, cm

I'  intensity of CuKα radiation, corrected for background, from a sample of material i, counts/sec
k equilibrium partition ratio, $C_l/C_s$
K permeability of a porous material, cm$^2$
K relative intensity (Appendix F only)
K$_c$ permeability of the part solid region due to liquid channels, cm$^2$
K$_d$ permeability of a dendritic area of the part solid region, cm$^2$
K$_f$ permeability of the part solid region assumed by Mehrabian, Keane, and Flemings (44)
K$_t$ total permeability of the part solid region, cm$^2$
l$_c$ length of a linear trace which is occupied by liquid channels, cm
l$_d$ length of a linear trace which is occupied by dendrites, cm
l$_t$ total length of a linear trace, cm
L length of the ingot, cm
n$_c$ number of channels crossed per unit length of a linear trace, l/cm
N$_i$ measured intensity of CuK$_\alpha$ radiation from a sample of material $i$, counts/sec
r radius, cm
s$_c$ distance from the chill, cm
S distance of the solidification front from the chill, cm
t time, min
t$_c$ counting time, sec
t$_p$ printing time, sec
t$_q$ quench time, measured from the start of gas cooling, min
T temperature, ºC
T$_e$ eutectic temperature, ºC
T$_{1,0}$ liquidus temperature of the initial alloy composition, ºC
\( T_{st} \)  
temperature of the ingot at the start of slow gas cooling, \(^\circ\)C

\( v \)  
apparent velocity of flow in the part solid region, cm/sec

\( v_s \)  
flow velocity away from the chill, cm/sec

\( V \)  
velocity of the sample under the microprobe beam, micron/min

\( \vec{v} \)  
vector flow velocity, cm/sec

\( W_{MIX} \)  
weight of the mixing region in the model of macrosegregation, for an ingot of unit thickness, gm

\( W_{ps} \)  
mass flow rate out of the part solid region per unit thickness of the part solid region, gm/sec

\( W_{sol} \)  
equivalent mass flow rate due to solidification, per unit height and thickness of the part solid region, gm/sec

\( x, y, z \)  
coordinates, cm

**Greek Symbols**

\( \gamma \)  
proportionality constant, cm

\( \Delta p \)  
pressure change per unit length of packed column, gm/cm\(^2\) sec\(^2\)

\( \mu \)  
viscosity, poise

\( \rho, \rho_l, \rho_s \)  
density, liquid density, solid density, gm/cm\(^3\)

\( \Sigma \)  
specific surface, l/cm

\( \Sigma_c \)  
surface area of liquid channels per unit volume of the part solid region, l/cm

\( \Sigma_{d',d,f} \)  
specific surface of dendrite arms in a dendritic area during solidification, after solidification is complete, l/cm

\( \tau \)  
time constant for flow in a tube, sec

\( \theta_f \)  
local solidification time, sec
GLOSSARY OF SOLIDIFICATION TERMS

A number of terms are presented here which have a particular usage in the field of solidification. The definitions given are those which are used in this work. They may not be entirely accurate in other contexts.

bulk liquid - The liquid at the center of an ingot into which the solidification front proceeds.

casting - Metal which is freezing or has frozen into a specific shape in a mold.

chill - The surface of a mold at which heat is removed most rapidly, to cause directional solidification.

columnar zone - The region of an ingot in which freezing has occurred in a directional manner. It is characterized by long primary dendrite arms.

coring - Variation of composition across a dendrite arm. It is caused by the buildup of rejected solute at the freezing surface of the dendrite arm.

dendrite - A branched, tree-like solid structure which forms during the rapid freezing of an alloy. Except where the elements (arms) of the structure join, they are surrounded by unfrozen liquid.

dendrite arm - A distinct element, or "branch" of a dendrite.
equiaxed zone - The region of an ingot in which the solidification structure does not exhibit any directionality. It is usually the central portion of the ingot.

freezing range - The range of temperature over which an alloy freezes.

ingot - Metal which is freezing or has frozen into a simple shape in a mold.

interdendritic liquid - Unfrozen liquid between the solid dendrite elements.

macrosegregation - Changes from one location to another within an ingot of the average composition of an area which is large compared with the dendrite arm spacing.

melt - A liquid alloy in the mold.

microsegregation - Variations of composition across and between dendrite arms.

mold - A shaped container in which liquid metal is frozen.

mushy zone - The part solid region of a freezing alloy. The presence of both a solid dendrite structure and unfrozen liquid gives the region a characteristic "mushy" consistency.

primary dendrite arms - A major "branch" of a dendrite which grows in a direction which is generally opposite to the direction of heat flow.
**secondary dendrite arm** - A minor "branch" of a dendrite which grows from a primary dendrite arm.

**superheat** - The heat added to a melt to raise its temperature above the equilibrium liquidus temperature. This heat must be removed before any solidification can occur.

**tertiary dendrite arm** - A minor "branch" of a dendrite which grows from a secondary arm.
APPENDIX A
MATERIALS ANALYSIS AND PREPARATION

A.1 Composition

Aluminum - The aluminum used in this study contained less than 0.01 wt pct of impurity elements.

Copper - Qualitative spectroscopic analysis of the OFHC copper rod material which was used to make the aluminum-4.5 wt pct copper and iron-50 wt pct copper alloys showed it to contain less than 0.06 wt pct of impurities. The microprobe standards were made with Baker reagent grade copper foil, 99.9 wt pct.

Graphite - Union Carbide graphite was used throughout the work. The blocks for the aluminum-copper ingot mold were grade AUC graphite. The graphite paper was 12 mils thick Grafoil. All other graphite used, both for the iron-carbon alloy and for susceptors, was grade CS graphite.

Iron - Armco iron rod was used to make the iron alloys.

Nickel - Baker Chemical nickel shot, 99.5 wt pct was used to make the iron-nickel alloy.

A.2 Preparation of alloys

Aluminum-4.5 wt pct copper - There were three separate melting steps in the preparation of the aluminum-4.5 wt pct copper alloy. First, an aluminum-50 wt pct copper master alloy was prepared by melting 99.9 wt pct OFHC copper in a clay-graphite crucible. The 99.99 wt pct aluminum alloy was then added and the melt was degassed with chlorine. The alloy was then cast into ingots and drillings were taken from the ingots for wet chemical analysis of the copper content.

Second, one complete ingot was remelted and the 99.99 wt pct
aluminum was added to dilute the master alloy to 4.5 wt pct copper, the melt was degassed with chlorine, and the alloy was then cast into graphite crucibles. Plugs for wet chemical analysis were dipped out every third ingot.

Finally, one ingot of the aluminum-4.5 wt pct copper alloy at a time was remelted, stirred, and poured into three ingot molds with a 70-90°C superheat for the slow freeze-transverse quench experiment. Three-tenths gram samples for wet chemical analysis were drawn from the melt in the crucible into a four-hole mullite tube after each ingot was poured. The compositions of samples taken before and after the pouring of a number of ingots are shown in Table A.1.

Microprobe standards - Two gram standards were made by levitation melting pieces of 99.99 wt pct aluminum and 99.9 wt pct Baker reagent grade copper foil. Each standard was prepared to correspond exactly to a specific area of the sample.

To match the dendrite arms which are α aluminum containing up to 5.65 copper, samples of 1 to 5 wt pct copper were melted and then quenched from about 700°C into copper cups. They were then homogenized for two days at 535°C to dissolve the nonequilibrium eutectic. To match the interdendritic eutectic, 33.2 wt pct copper samples were melted and quenched from about 600°C into copper cups. To keep the CuAl₂ phase dispersed, these samples were not homogenized.

The CuAl₂ phase was also prepared by melting, freezing, and homogenizing 53.5 wt pct copper samples.

These samples, as well as pieces of pure aluminum and copper, were then divided: one part for chemical analysis, and the other to be mounted, polished, and etched in the same manner as the ingot sections.
Table A.1
Compositions of samples removed from the crucible before and after pouring a number of aluminum-copper ingots

<table>
<thead>
<tr>
<th>Ingot Number</th>
<th>Composition wt pct Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-14</td>
<td>4.40</td>
</tr>
<tr>
<td>A-15</td>
<td>4.56</td>
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<td>A-16</td>
<td>4.74</td>
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<td>A-49</td>
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<td>A-57</td>
<td>4.57</td>
</tr>
<tr>
<td>A-64</td>
<td>4.42</td>
</tr>
<tr>
<td>A-66</td>
<td>4.67</td>
</tr>
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</table>
Iron-50 wt pct copper - Armco iron rods and OFHC copper rods were placed in the fused silica crucible. An addition of 0.2 wt pct silicon was made to prevent dissolution of the crucible, and 0.1 gm of aluminum was added to limit undercooling. The solid rods and the additions were melted in the induction coil at the start of the experiment.

Iron-2 wt pct carbon, vertical solidification - Armco iron rod was melted in a graphite crucible placed in an induction coil. The melt was cooled slowly from 1500°C to 1175°C to allow the carbon in excess of the eutectic composition to precipitate. The resulting ingot, together with additional iron rod, 0.2 wt pct silicon and about 0.2 gm of aluminum were then placed in the silica crucible.

Iron-2 wt pct carbon, horizontal solidification - As the silica crucible for horizontal solidification had a restricted shape, the carbon-saturated iron ingot was remelted with additional iron, 0.2 wt pct silicon and about 0.2 gm of aluminum in a magnesia crucible, and poured into a machined graphite block. The resulting ingot then fit into the fused silica crucible, and no additions were required for the experiment. Although the aim composition was 2.0 wt pct carbon, a piece of one ingot was analyzed as 2.24 wt pct carbon.

Iron-20 wt pct nickel - Armco iron rod and nickel shot were placed in the fused silica crucible, together with an addition of 0.2 wt pct silicon and 0.1 gm of aluminum.
APPENDIX B
TEMPERATURE MEASUREMENTS

B.1 Apparatus

Several pieces of equipment for connecting the thermocouples to the chart recorder were designed and built.

Voltage suppression box - An electrical circuit was built which reduced the voltage of the thermocouple to the zero to ten millivolt range of the chart recorder by adding a negative voltage to the thermal emf. This is a better method than simply dividing the thermocouple voltage, since the latter method divides the entire thermal scale, whereas the voltage suppression method only eliminates the lower portion of the temperature scale by removing a specified voltage, and draws no current from the thermocouple.

As shown in Fig. B.1, the current through a standard resistance, $R_1$, is adjusted to produce a fixed potential drop. This potential directly opposes part of the voltage from the thermocouple. Since the chart recorder functions by opposing the remaining voltage, no current is drawn from the thermocouple during the measurement.

The complete circuit of the voltage suppression box is shown in Fig. B.2. It was operated by turning on the battery switch, and placing switch $S_1$ in the calibration position. The output of the suppression box was directed to a calibrated potentiometer by switch $S_2$. The variable resistor, $R_3$, was adjusted to make the voltage, $V_2$, across one step of the 100 ohm per step precision resistor, $R_1$, exactly 5.00 millivolts, as measured by the potentiometer. The switch $S_2$ was then moved to the chart recorder position and the recorder was adjusted to read
Fig. B.1 Electrical circuit for removing part of the voltage produced by a thermocouple.
Fig. B.2 Schematic diagram of the voltage suppression box.
5.00 millivolts.

Then switch $S_1$ was moved to the measurement position, and voltage $V_3$ could then be set to suppress from 0 - 50 millivolts in 5-millivolt steps. No change in calibration was ever measured when the calibration voltage, $V_2$, was checked with the potentiometer at the end of an experiment. The values and tolerances of the components are listed in Table B.1.

Table B.1

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Tolerance</th>
<th>Thermal Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_1$</td>
<td>1.356 v</td>
<td>$\pm 0.025%$</td>
<td>$&lt; \pm 20$ ppm/°C</td>
</tr>
<tr>
<td>$R_1$</td>
<td>100 Ω/step</td>
<td>$\pm 0.025%$</td>
<td>$\pm 100$ ppm/°C</td>
</tr>
<tr>
<td>$R_2$</td>
<td>25.5 KΩ</td>
<td>$\pm 0.025%$</td>
<td>$\pm 70$ ppm/°C</td>
</tr>
<tr>
<td>$R_3$</td>
<td>0 - 1 KΩ</td>
<td>$\pm 0.025%$</td>
<td>$\pm 70$ ppm/°C</td>
</tr>
</tbody>
</table>

Rotating switch - A rotating switch which could place the potential of from one to four thermocouples sequentially across the recorder input was designed and built by Jeryl Wright. This allowed direct comparison of the thermocouple readings through one measuring system. The switch was normally used with two thermocouples and a rotation of two cycles per minute.

B.2 Vertical solidification

The treatment of the thermal data is identical for both the vertical and horizontal experiments. Therefore the calculations will be explained in detail in this section for vertical solidification and repeated only briefly in section B.3 for horizontal solidification.
Location of the dendrite tips - The location of the tips of the dendrites at the top of the columnar zone can be found in two ways. First, the distance from the chill at the time of the transverse quench can be measured directly on the etched ingot. Second, for experiments in which solidification proceeded past one or both thermocouples, the location of a thermocouple and the time when its temperature fell below the liquidus temperature (see Fig. 5.7) are known. Both types of data are plotted in Fig. B.3. Since each experiment began from a different superheat, the data are quite scattered.

Effect of superheat - It is possible to correct all of the data to the same starting temperature using the cooling rate of the ingot while the superheat is being lost. From Fig. 5.7, the cooling rate is taken as ten degrees per minute. Thus to correct a point on Fig. B.3 by adding ten degrees to the actual starting temperature of that experiment, the point is moved one minute to the right. Figures 5.8 and 5.9 were obtained by correcting all of their data points to a starting temperature of 710°C. The data in Fig. 5.8 show considerably less scatter than in Fig. B.3.

Thermal gradients - The vertical thermal gradients in an ingot which is freezing because of a nitrogen gas flow of 12 liters/min can be derived from the temperature curves shown in Fig. 5.7. If the thermal conditions in the melt and the rate of advance of the dendrite tips were constant, the temperature curves from thermocouples 1 and 2 would have identical shapes, translated in time, to compensate for the distance between the two thermocouples. A series of such translated curves could be constructed to represent other thermocouples at different locations. A vertical line on the graph at some time, t, would intersect
Fig. B.3 Position of the solidification front as a function of time after the start of nitrogen gas cooling at 12 liters/min, as measured on etched ingots and from thermocouple measurements.
all of these thermocouple curves at the temperatures which would correspond to the locations of the thermocouples. These points could be plotted to show the vertical thermal gradient at time t.

Since the thermal gradient in the liquid ahead of the dendrite tips changed drastically during solidification because the superheat was removed quickly (and because the ingot was not "semi-infinite"), the shape of the temperature curve changed from that shown by thermocouple 2 to that shown by thermocouple 1. Although a simple linear translation of the curves may therefore not be performed, it is possible to interpolate between the curves. Using the rate of advance of the solidification front, 0.9 cm/min, curves are interpolated for thermocouples 3.0 and 5.9 cm from the chill. These are the dashed lines on Fig. 5.7.

The points plotted in Fig. 5.10 are the interceptions of vertical lines placed two minutes apart with the temperature curves of Fig. 5.7.

B. 3 Horizontal solidification

The derivations of section B. 2 may be repeated for the horizontal solidification of the aluminum-4.5 wt pct copper alloy to determine the effect of superheat on the progress of the solidification front and the thermal gradients in the ingot during solidification.

Location of the dendrite tips - Measurements of the location of the solidification front vs time, from the quenched ingots, and from thermocouple data, are plotted in Fig. B.4. The scatter of the data is the result of using a different superheat for each experiment.

Effect of superheat - From cooling curves such as Fig. 6.3 it is possible to estimate the cooling rate during the time when the superheat was being removed. For a gas flow of 96 liters/min the cooling rate was 35°C/min, for the usual gas flow of 12 liters/min it was 12°C/min,
Fig. B.4 Position of the solidification front as a function of time after the start of nitrogen gas cooling, as measured on etched ingots and from thermocouple measurements.
and for the slowest gas flow rate of 2.4 liters/min it was 10°C/min. These rates can be applied to the corresponding data points to correct for the effect of starting temperature on the location of the dendrite tips. The result of correcting all of the data to an effective starting temperature of 710°C is shown in Fig. 6.4.

**Thermal gradients** - The horizontal temperature gradient in an ingot which is freezing because of a gas flow of 12 liters/min is obtained by combining the thermocouple data, Fig. 6.3, with the solidification rate just obtained. As in section B.2, it is imagined that two additional thermocouples are located between the two real thermocouples, and that their thermal history is intermediate in form between the curves given by the real thermocouples, Fig. 6.3. Thus the thermal gradient at any time is found by plotting the temperature of each thermocouple at that time vs its distance from the chill and, in addition, plotting the liquidus temperature vs the distance solid at that time. The thermal gradients that are found by this procedure are shown in Fig. 6.5.

B.4 **Tables of temperature as a function of distance**

The tables of x vs T which are used by subroutines PTABL1, PTABL2, XVTABL, and XHTABL were obtained by a series of calculations. First, the thermocouple data and distance solidified at eight minutes after the start of gas cooling were plotted, and a smooth curve was drawn by hand through the points. (cf. the curves at eight minutes in Fig. 5.10 and Fig. 6.5.) The temperature on this curve was then read at a series of distances. For horizontal solidification, these temperatures were corrected to the assumed liquidus temperature of 647°C by subtracting 3.5°C from each value. A computer program, written by Alan Campagna, was used to smooth the data and produce a
table of 50 pairs of values of temperature and distance.
Table B.2

Pairs of temperature and distance values for an aluminum-4.5 wt pct copper ingot freezing vertically due to a gas flow of 12 liters/min.

<table>
<thead>
<tr>
<th>T(II)</th>
<th>X(II)</th>
<th>FOR VERTICAL INGOTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>633.01830</td>
<td>0.00000</td>
<td>633.41300</td>
</tr>
<tr>
<td>634.61320</td>
<td>0.34286</td>
<td>635.01580</td>
</tr>
<tr>
<td>636.22360</td>
<td>0.68571</td>
<td>636.62400</td>
</tr>
<tr>
<td>637.81000</td>
<td>1.02857</td>
<td>638.19870</td>
</tr>
<tr>
<td>639.33710</td>
<td>1.37143</td>
<td>639.70620</td>
</tr>
<tr>
<td>640.77510</td>
<td>1.71428</td>
<td>641.11790</td>
</tr>
<tr>
<td>642.09960</td>
<td>2.05714</td>
<td>642.41060</td>
</tr>
<tr>
<td>643.29050</td>
<td>2.40000</td>
<td>643.56560</td>
</tr>
<tr>
<td>644.33370</td>
<td>2.74286</td>
<td>644.57050</td>
</tr>
<tr>
<td>645.22020</td>
<td>3.08571</td>
<td>645.41650</td>
</tr>
<tr>
<td>645.94530</td>
<td>3.42857</td>
<td>646.10150</td>
</tr>
<tr>
<td>646.51040</td>
<td>3.77143</td>
<td>646.62790</td>
</tr>
<tr>
<td>646.92230</td>
<td>4.11429</td>
<td>647.00210</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T(II)</th>
<th>X(II)</th>
<th>FOR VERTICAL INGOTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>633.81070</td>
<td>0.08571</td>
<td>633.81070</td>
</tr>
<tr>
<td>635.48257</td>
<td>0.42857</td>
<td>635.48257</td>
</tr>
<tr>
<td>637.02220</td>
<td>0.77143</td>
<td>637.02220</td>
</tr>
<tr>
<td>638.58340</td>
<td>1.11429</td>
<td>638.58340</td>
</tr>
<tr>
<td>640.06930</td>
<td>1.45714</td>
<td>640.06930</td>
</tr>
<tr>
<td>641.55330</td>
<td>1.80000</td>
<td>641.55330</td>
</tr>
<tr>
<td>642.13100</td>
<td>2.14286</td>
<td>642.13100</td>
</tr>
<tr>
<td>643.15120</td>
<td>2.48571</td>
<td>643.15120</td>
</tr>
<tr>
<td>644.32857</td>
<td>2.82857</td>
<td>644.32857</td>
</tr>
<tr>
<td>645.16320</td>
<td>3.17143</td>
<td>645.16320</td>
</tr>
<tr>
<td>646.24800</td>
<td>3.51429</td>
<td>646.24800</td>
</tr>
<tr>
<td>646.63840</td>
<td>3.85714</td>
<td>646.63840</td>
</tr>
<tr>
<td>647.00000</td>
<td>4.20000</td>
<td>647.00000</td>
</tr>
</tbody>
</table>
Fortran function for calculating temperature as a function of distance by a linear interpolation in Table B.2.

REAL FUNCTION PTABL1(XF)
C HOWARD PIELET 10-18-70 PTABL1 VERSION 1
C THIS IS A FUNCTION SUBROUTINE. IT READS ARGUMENTS IN TABLE
C FORM, THEN SUPPLIES INTERMEDIATE VALUES BY LINEAR INTERPOLATION.
C CAUTION--X VALUES MUST BE IN ASCENDING POSITIVE ORDER.
C IN THE INPUT DATA DECK TO BE READ FOLLOWING THE FIRST USE OF THE
C FUNCTION.
   LOGICAL FIRST
   DATA FIRST/.TRUE./
   DIMENSION X(100),Y(100)
   IF(.NOT.FIRST) GO TO 1
   READ(5,501) NVALS,(Y(I),X(I),I=1,NVALS)
   ***
   FORMAT(I2 /(8F10.7))
   FIRST=.FALSE.
   DO 1000 I=2,NVALS
      IF(XF.LE.X(I)) K=I
      IF(XF.LE.X(I)) GO TO 2
   1000 CONTINUE
   K=NVALS
   ***
   2 DYDX=(Y(K)-Y(K-1))/(X(K)-X(K-1))
   PTABL1=Y(K-1)+DYDX*(XF-X(K-1))
   RETURN
END
Fortran function for calculating distance as a function of temperature by a linear interpolation in Table B.2.

```
REAL FUNCTION XVTAB(XF)
C HOWARD PIELET 11-17-70 XHTAB(TF) VERSION 1
C THIS IS A FUNCTION SUBROUTINE. IT READS ARGUMENTS IN TABLE
C FORM, THEN SUPPLIES INTERMEDIATE VALUES BY LINEAR INTERPOLATION.
C CAUTION--X VALUES MUST BE IN ASCENDING POSITIVE ORDER.
C IN THE INPUT DATA DECK TO BE READ FOLLOWING THE FIRST USE OF THE
C FUNCTION.
   LOGICAL FIRST
   DATA FIRST/=TRUE/=/
   DIMENSION X(100),Y(100)
   IF(.NOT.FIRST) GO TO 1
   READ(5,501) NVALS,(X(I),Y(I),I=1,NVALS)
   501 FORMAT(I2,/(8F10.7))
   FIRST=.=FALSE.,
   1 DO 1000 I=2,NVALS
   IF(XF.LE.X(I)) K=I
   IF(XF.LE.X(I)) GO TO 2
   1000 CONTINUE
   K=NVALS
   2 DYNX=(Y(K)-Y(K-1))/(X(K)-X(K-1))
       XVTAB=Y(K-1)+DYNX*(XF-X(K-1))
   RETURN
END
```
Table B.3
Pairs of temperature and distance values for an aluminum-4.5 wt pct copper ingot freezing due to a gas flow of 12 liters/min.

<table>
<thead>
<tr>
<th>T(1), X(1) FOR HORIZONTAL INGOTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>634.49790 0.00000 634.78290</td>
</tr>
<tr>
<td>635.64080 0.37551 635.92450</td>
</tr>
<tr>
<td>636.77120 0.75102 637.05240</td>
</tr>
<tr>
<td>637.89690 1.12653 638.17890</td>
</tr>
<tr>
<td>639.02560 1.50204 639.30830</td>
</tr>
<tr>
<td>640.15740 1.87755 640.44060</td>
</tr>
<tr>
<td>641.28610 2.25306 641.56640</td>
</tr>
<tr>
<td>642.39660 2.62857 642.67300</td>
</tr>
<tr>
<td>643.47820 3.00408 643.73990</td>
</tr>
<tr>
<td>645.42400 3.75510 645.63640</td>
</tr>
<tr>
<td>646.21990 4.13061 646.39330</td>
</tr>
<tr>
<td>646.84050 4.50612 646.96210</td>
</tr>
</tbody>
</table>
Fortran function for calculating temperature as a function of distance by a linear interpolation in Table B.3.

REAL FUNCTION PTABL2(XF)
C HOWARD PIELET 10-18-70 PTABL1 VERSION 1
C THIS IS A FUNCTION SUBROUTINE. IT READS ARGUMENTS IN TABLE
C FORM, THEN SUPPLIES INTERMEDIATE VALUES BY LINEAR INTERPOLATION.
C CAUTION--X VALUES MUST BE IN ASCENDING POSITIVE ORDER.
C IN THE INPUT DATA DECK TO BE READ FOLLOWING THE FIRST USE OF THE
C FUNCTION.
   LOGICAL FIRST
   DATA FIRST/.TRUE./
   DIMENSION X(100),Y(100)
   IF (.NOT. FIRST) GO TO 1
   READ(5,501) NVALS,(Y(I),X(I),I=1,NVALS)
501  FORMAT(12/(8F10.7))
   FIRST=.FALSE.
1  DO 1000 I=2,NVALS
   IF (XF.LE.X(I)) K=I
   IF (XF.LE.X(I)) GO TO 2
1000  CONTINUE
   K=NVALS
2  DYDX=(Y(K)-Y(K-1))/(X(K)-X(K-1))
   PTABL2=Y(K-1)+DYDX*(XF-X(K-1))
   RETURN
END
Fortran function for calculating distance as a function of temperature by a linear interpolation of Table B. 3.

```
REAL FUNCTION XHTAB(XF)
C HOWARD PIELET 11-17-70 XHTAB(TF) VERSION 1
C THIS IS A FUNCTION SUBROUTINE. IT READS ARGUMENTS IN TABLE
C FORM, THEN SUPPLIES INTERMEDIATE VALUES BY LINEAR INTERPOLATION.
C CAUTION--X VALUES MUST BE IN ASCENDING POSITIVE ORDER.
C IN THE INPUT DATA DECK TO BE READ FOLLOWING THE FIRST USE OF THE
C FUNCTION.
LOGICAL FIRST
DATA FIRST/.TRUE./
DIMENSION X(100),Y(100)
IF(.NOT.FIRST) GO TO 1
READ(5,501) NVALS,(X(I),Y(I),I=1,NVALS)
501 FORMAT(I2,/(8F10.7))
FIRST=.FALSE.
1 DO 1000 I=2,NVALS
IF(XF.LE.X(I)) K=I
IF(XF.LE.X(I)) GO TO 2
1000 CONTINUE
K=NVALS
2 DYDX=(Y(K)-Y(K-1))/(X(K)-X(K-1))
   XHTAB=Y(K-1)+DYDX*(XF-X(K-1))
RETURN
END
```
APPENDIX C
METALLOGRAPHY

C.1 Aluminum-copper ingots

Rough grinding and macroetching - The aluminum-4.5 wt pct copper ingots were ground flat on one or both sides on a 60 grit silicon carbide wheel. This removed up to one millimeter from the surface of the ingot. The ingots were then ground on 240, 320, and 400 grit silicon carbide papers.

The etchant was a solution of 13 ml H₂O, 37 ml HCl, 45 ml HNO₃, and 50 ml HF. This etchant was developed by Uhlman, Seward, and Chalmers. It was found to give the maximum differentiation between coarse and fine dendritic regions when used hot and swabbed across the ingot for 30 to 50 seconds.

The photographs of the macrostructures were taken with a Polaroid MP-3 copy camera. The ingot was immersed in a pan of propylene glycol* and one or two floodlights were placed as nearly as possible directly above the ingot. Polaroid type 55 positive/negative film was used for the negatives and Agfa number 6 high contrast paper was used for printing.

Fine polishing and etching for electron microprobe studies - Sections were cut from the ingots and then set into one inch Bakelite mounts. To prepare them for microprobe work, they were first ground on 400 and 600 grit silicon carbide papers, and then rough polished with

* Air bubbles which rose from the ingot through the propylene glycol are visible on some of the photographs. They are artifacts only. Actual porosity appears as black spots on the ingot, while the bubbles are shadowed.
six micron diamond paste on a nylon cloth. Magnesium oxide powder, mixed with water to a pasty consistency, was used for the final polish on a soft napped cloth.

The etchant described above was diluted with ten parts of cold water and swabbed on the sample for three seconds, making the structure just slightly visible. The end points of the probe traces were marked with diamond hardness indentations.

After the probe data was taken, the samples were again etched in the diluted etchant for about five seconds. They were photographed at 10X in a Leitz metallograph which used a glass slide set at a 45 degree angle between the sample and the objective to obtain direct overhead lighting.

C.2 Iron ingots

The iron ingots were sectioned and rough polished in the same manner as the aluminum-copper ingots. They were then fine polished with 0.3 micron alumina and etched in nital, 3 percent nitric acid in alcohol.

Photography was the same as for the aluminum-copper ingots.
APPENDIX D

COORDINATE SYSTEM FOR ALUMINUM-COPPER INGOTS

The coordinate system used for vertically and horizontally solidified aluminum-4.5 wt pct copper alloys is shown in Fig. D.1. The origin is placed in the center of the ingot thickness at the lower left corner.

Sections of the ingot are identified by the sign and axis direction of the outward drawn normal to the visible surface. Thus the large, flat surface nearest the viewer in the figure is labelled the -z face.
Fig. D.1  Coordinate system and terminology used to describe locations and faces in the aluminum-4.5 wt pct copper ingots.
APPENDIX E

DISTRIBUTION OF LIQUID IN THE PART SOLID REGION

Some additional material concerning the distribution of liquid in the part solid region is collected here.

The derivation of the location of the inflection in the curve of fraction liquid as a function of distance is presented.

Horizontal sections of ingots A-57, A-52, and A-46, and data from the sections of ingots A-57 and A-52 are shown.

The computer program and the data used to calculate the volume fraction and specific surface of channels are given.

E.1 Inflection in the curve of fraction liquid vs distance

Assuming a constant equilibrium partition ratio, $k$, the curve of weight fraction solid, $f_s$, vs temperature, as calculated from the Scheil equation, is monotonic. Figure E.1 illustrates this curve for several alloy compositions in the aluminum copper system. When the temperature in the part solid region is a linear function of distance,

$$T = Ax + B,$$

the curve of $f_s$ vs distance is also monotonic. If $dT/dx$ decreases with distance, the curve of $f_s$ vs distance may have an inflection, as shown in Fig. 5.31 and Fig. 6.28.

These considerations may be expressed algebraically. The Scheil equation for the weight fraction liquid, $f_L$, in terms of the melting temperature of the pure element, $T_m$, and the liquidus temperature of the alloy, $T_{L,0}$, is

$$f_L = \left(\frac{T_m - T}{T_{m} - T_{L,0}}\right)^{\frac{1}{1-k}}.$$
Fig. E.1 Weight fraction solid as calculated from the Scheil equation for a number of aluminum-copper alloys.
The second derivative of $f$ with respect to distance is

$$\frac{d^2 f}{dx^2} = \left( T_m - T_f, 0 \right) \frac{1}{1-k} \left[ \frac{2-k}{(1-k)^2} \left( T_m - T \right) \left( \frac{dT}{dx} \right)^2 - \frac{2+k}{1-k} \left( \frac{dT}{dx} \right) \left( \frac{d^2 T}{dx^2} \right) \right].$$

To determine the location of an inflection, this derivative is set equal to zero, which gives

$$\frac{2-k}{1-k} \left( \frac{dT}{dx} \right)^2 = \left( T - T_m \right) \frac{d^2 T}{dx^2}.$$  \hspace{1cm} (E.1)

For the case of a linear temperature gradient, the first and second derivatives of temperature with distance are

$$\frac{dT}{dx} = A$$

and

$$\frac{d^2 D}{dx^2} = 0.$$

This gives

$$\frac{2-k}{1-k} A^2 = (Ax + B) \cdot 0,$$

which has no real solution. For other temperature distributions, Eq. E.1 may have a real solution.

E.2 Additional photographs and data

Ingots A-57, A-52, and A-46 from series HA, Table 6.1, were sectioned as shown in Fig. 6.24. Photographs of the top surfaces of
these sections are shown in Figs. E. 2 - E. 4. Data on the distribution of liquid channels on the sections shown for ingots A-57 and A-52 are given in Fig. E. 5 and Fig. E. 6.
Fig. E.2  Horizontal sections of Ingot A.57, 3X.
Fig E.3  Horizontal sections of Ingot A.52, 3X.
Fig. E.4  Horizontal sections of Ingot A.46, 3X.
Fig. E.5 Distribution of liquid as a function of distance from the chill for four horizontal sections in ingot A.57, series HA. (a) Section B. (b) Section C. (c) Section D. (d) Section E.
Fig. E.5, continued.
Fig. E.6 Distribution of liquid as a function of distance from the chill for four horizontal sections in ingot A. 57, series HA.  (a) Section B.  (b) Section C.  (c) Section D.  (d) Section E.
Fig. E.6, continued.
E.3 Computer program

Program FCHAN converts the data obtained from linear traces across an ingot to values of volume fraction channel and surface area per cm$^3$.

```
C HOWARD PIELET 11-11-70 FCHAN VERSION 5
C MAIN PROGRAM TO CONVERT COUNTS ON SAMPLES TO FRACTION CHANNEL.
C CARDS FOR GRDOMET PLOTTING ARE PUNCHED.

DIMENSION BCD(15)
DIMENSION BCD1(40), BCD2(320), BCD3(201), BCD4(240)
REAL NCCM, NCCM3
READ(5,701) BCD1, BCD2, BCD3, BCD4

READ(5,500) N, BCD, XTIPS
WRITE(6,600) N, BCD, XTIPS
WRITE(7,701) BCD1
WRITE(7,702) BCD
  XCOR=4.5-XTIPS
WRITE(7,701) BCD2
  NVALS=N*8
WRITE(7,703) NVALS
WRITE(7,703) BCD3
DO 1000 I=1,N
READ(5,101) X, NCHAN, CCHAN, CTOT
  T=PTABL1(X+XCOR)
IF(NCHAN.EQ.0) GO TO 4
  GCHAN=CCHAN/CTOT
  NCCM=NCHAN*1440./CTOT
  DCHAN=CCHAN/(1440.*NCHAN)
  NCCM3=(3.14159/4.*GCHAN/(DCHAN*DCHAN))
  SIGMA=NCCM*4.*
  IF((NCHAN.EQ.1).AND.(GCHAN.GT.0.5)) SIGMA=NCCM*2.0
```

$\text{AK} = 0.24 \times \text{GCHAN} \times \text{GCHAN} \times \text{GCHAN} / (\text{SIGMA} \times \text{SIGMA})$

3
\begin{verbatim}
WRITE(6,601) X,T,GCHAN,SIGMA,AK,NCCM,DCHAN,NCCM3
WRITE(7,704) X,T,GCHAN,SIGMA,AK,NCCM,DCHAN,NCCM3
\end{verbatim}

GO TO 1000

4
\begin{verbatim}
CCHAN=0.0
NCCM=0.0
DCHAN=0.0
NCCM3=0.0
SIGMA=0.0
AK=1.0E-20
\end{verbatim}

GO TO 3

1000 CONTINUE
\begin{verbatim}
WRITE(7,701) BCD4
GO TO 1
\end{verbatim}

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11X,5X,T,GCHAN,SIGMA,AK,NCCM,DCHAN,NCCM3*)

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702 FORMAT(20X,15A4)

703 FORMAT(14,12X,"d")

704 FORMAT(4F10.3,E15.3/3F10.3)

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  2 2
  2 8
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POINTS ARRAYS
   3 8 8
PLOT SPECIFICATIONS
  5
DATA ARRAYS
   4 8 8
PLOT SPECIFICATIONS
  4
NEXT

DISTANCE, CM

5 FRACTION CHANNEL
4 CHANNEL, 100/CM
Data for the determination of volume fraction channel and surface area per cm$^3$. Distance from the chill, number of channels encountered by the trace, length of channels, length of the trace.

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APPENDIX F

ELECTRON MICROPROBE ANALYSIS

Since most of the liquid channels represented by the fine quenched structure are less than one millimeter in diameter, their composition was analyzed with an electron microprobe. The diameter of the analyzing spot of the microprobe is about four microns, while the size of the dendrite arms frozen during the quench is about 15 microns. Since the dendrite arms are highly segregated, the average composition cannot be determined by a single stationary measurement. A method is presented here for taking data in a highly segregated dendritic structure and for converting these data to average composition, local composition, and composition as a function of fraction solidified. This method has been described by Pielet, Saffir, and Elliott, and is amplified here.

F.1 Trace method of taking data

The sample was translated at a constant velocity within the microprobe chamber, causing the analyzing spot to move across the fine dendrite arms which constitute a liquid channel, Fig. F.1. The velocity, \( V \), was 96 microns per minute. Thus it took about ten minutes to complete the one millimeter long trace shown in the figure. The intensity of the CuK\( \alpha \) radiation received by the detector was integrated for a time, \( t_c \), as the sample moved, Fig. F.2. The value in the counter after \( t_c \) was printed during an interval of time, \( t_p \), as the sample continued to move and the counters reset. Thus a "dead space" was created and only a fraction, \( t_c / (t_p + t_c) \), of the trace length was actually used for the analysis. For the most part, \( t_c \) was five seconds
Fig. F.1 Microprobe data was taken by translating the sample at a constant velocity beneath the analyzing spot. Ingot A.43, area B, 50X.
Fraction Analyzed = \frac{t_c}{(t_p + t_c)}

Distance Represented = V(t_c + t_p)

Fig. F.2 The intensity of radiation received by the detector was integrated by the counters for a time, $t_c$, and printed during time, $t_p$. The sample moved at a constant velocity, $V$. 
and tp was one second. Therefore 5/6 of the trace length was analyzed, and each data point represents the composition of a region 9.6 microns long and about four microns wide. The probe analyzes the sample to a depth of about three microns. The result of the trace, then, is a set of data points which represent the average compositions of small volumes along the trace.

F.2 Presentation of the data

The data points obtained from the trace procedure are converted from integrated intensity to weight percent copper by the calculations given in section F.3. The resultant data is then presented in three different ways. First, all of the data from the liquid or solid portion of the trace are averaged to determine the average composition of a liquid channel or the solid regions adjacent to it. Second, a running average over two dendrite arms at a time is computed, to examine the structure for local composition gradients. Third, the data points from the liquid or solid portions of the trace are reordered to obtain the curve of composition in the solid as a function of fraction solid.

Average concentration - All of the data from a given portion of the trace are taken together to calculate the average concentration of copper in that area. The data points represent the composition of equal linear distances on the sample, but the density at each location, and thus the weight of each point, is a function of composition. Therefore a correction for density must be made when the data are averaged.

Taking the density, \( \rho \), from Eq. G.6, the average concentration is

\[
\bar{C} = \frac{\sum \rho_i C_i}{\sum \rho_i}.
\]

(F.1)

The same volume is represented by each data point and therefore the
volume need not appear explicitly in the equation.

**Moving average concentration** - The dendrite arms across which the probe trace moved are highly segregated, from one percent copper at the center of the dendrite arms to thirty-three percent copper in the interdendritic eutectic. This segregation is reflected by the data points, Fig. F.3. Thus in order to investigate local gradients of composition within the liquid channel it is necessary to calculate the moving average of several adjacent data points at a time.

Because the dendrite arms are not evenly spaced and especially because the average dendrite arm size is much larger in the solid portion of the trace than in the liquid portion of the trace, a constant averaging distance cannot be used. For this reason, the averaging distance is constantly adjusted to correspond to the dendrite arm spacing. The peaks of concentration which occur at the interdendritic eutectic are taken as limits, and a moving average is computed for two adjacent dendrite arms at a time. The averaging distance is therefore related consistently to the microstructure.

To do this directly on the computer, an algorithm was defined to locate the interdendritic eutectic maxima. Some intermediate test composition was chosen (e.g., the line at 6 pct, Fig. F.3), and a maximum was defined as the largest value of a group of adjacent data points all of which are higher than the test composition. All maxima must thus be greater than the test composition.

As shown in Fig. F.4, the moving average composition of two adjacent dendrite arms changes abruptly at the interface between the liquid channel and the part solid region. No distinct concentration gradient is evident, however, in either the liquid channel or the adjacent
Fig. F.4 Moving average concentration of copper.
part solid region. The smoothing of the data from F. 3 is quite good.

**Composition as a function of fraction solidified** - The data may also be analyzed to determine the concentration of the solidifying dendrite arms at the interface of the arms and the surrounding interdendritic liquid.

Each data point in a given region represents, with a density correction, a certain weight fraction of the total region. The lowest concentrations are from the cores of dendrite arms, which were the first areas to solidify. The highest concentrations are from the interdendritic eutectic, which solidified last. By reordering the data and plotting them against the cumulative weight fraction solid, the concentration in the solid at the solid liquid interface as a function of the fraction solidified is obtained, Fig. F. 5.

There are two factors which can distort the form of this curve from its true form. First, the length along the trace represented by each data point is a finite proportion of the dendrite arm spacing. This must affect the curve form. Second, areas with different average compositions may occur along the trace either because of actual fluctuations in the local average, or because of the variations in the location at which the trace cuts across each dendrite. This also must change the form of the curve.

For example, consider data from a region whose true relation between composition and fraction solid is shown in Fig. F. 6(a). First, if each data point represents a length along the trace which is three-tenths of the size of the dendrite arms, the curve is distorted as shown (b). Second, if data from another region, (c), equal in size to the first but with a different true curve of composition as a function of fraction solid,
Fig. F.5 Composition in the solid at the solid-liquid interface as a function of the fraction solidified. Obtained by reordering the data shown in Fig. F.3.
Fig. F.6 Distortion of the true curve of composition vs fraction solid. (a) true curve of one region; (b) distortion of the true curve of (a) when the data points represent areas 1/3 as large as the dendrite arms; (c) true curve of a second region; (d) curve which results from combining regions (a) and (c).
is included with the data from the first region, a distorted curve results, (d). Thus the finite size of the area represented by each data point causes expansion and rounding of the eutectic portion of the curve at high concentration and high fraction solid. Inclusion of data from areas with different average compositions causes distortions in the curve at low concentrations and low fraction solid.

F. 3 Conversion of data from intensity to composition

The probe measurements were made with a high voltage of 30 kV at a take-off angle of 52.5°. The intensities of CuKα and AlKα radiation from the alloy were measured. These intensities must be divided by the intensity measured on pure copper or pure aluminum to convert them to concentrations. Corrections must be made to the data for background radiation, for instrument drift, and for the interactions between aluminum and copper atoms, according to equations presented by Ziebold.93

Correction for background radiation - Let Ni be defined as the measured intensity of the CuKα radiation on a sample composed of material i, and let i be the intensity which has been corrected by subtracting the background radiation of the continuous spectrum. For example, the measured intensity of CuKα radiation from a sample of pure aluminum is denoted as NAl.

The corrected intensity from a pure copper standard is

\[ I_{Cu} = N_{Cu} - N_{Ni} \]  (F. 2)

where the background is measured on a nickel standard NNi, and subtracted from the measured copper intensity.
For the alloy, A, the corrected intensity is

$$I^A = N^A - N^{Al}(1 - C) - N^{Ni} C$$

(F. 3)

where C is the weight fraction of copper*, and the background correction is the sum of the background due to aluminum times the weight fraction of aluminum, and the background due to copper (measured on nickel) times the weight fraction of copper.

The relative intensity, K, is the ratio of the corrected intensity from the alloy to the corrected intensity from pure copper.

$$K = \frac{I^A}{I^{Cu}}.$$

(F. 4)

Combining this equation with Eqs. F. 2 and F. 3 gives

$$K = \frac{N^A - N^{Al}}{N^{Cu} - (C/K) N^{Al} - (K-C/K) N^{Ni}}.$$  

(F. 5)

The true weight fraction, C, is not the same as the relative intensity, K, but is related to it by the empirical formula:

$$C/(1-C) = a K/(1-K),$$

(F. 6)

where a is determined from measurements of K on a series of standards of compositions, C, as shown below. Assuming either that C = K or $N^{Al} = N^{Ni}$, Eq. F. 5 reduces to

$$K = (N^A - N^{Al})/(N^{Cu} - N^{Al}).$$

(F. 7)

*Note that C in this section only is taken as weight fraction. In the rest of the thesis, it represents weight percent.
The fractional error in K introduced by this simplification is less than 0.2 percent for aluminum-copper alloys. Thus Eq. F.7 was used to convert the measured values of $N^A$ to relative intensities K. The corresponding equation for the relative intensity of AlKα radiation is obtained by interchanging the superscripts Al and Cu in Eq. F.7.

**Correction for instrument drift** - The electronics of the electron probe are somewhat unstable, so that a correction must be made for drift of the instrument. To do this, the measurements on pure copper and pure aluminum, $N^{Cu}$ and $N^{Al}$, are repeated every few hours during the operation of the probe. Any changes in the values of these measurements are assumed to occur as a linear function of the time between the two measurements. The values of $N^{Cu}$ and $N^{Al}$ which were used for each trace were calculated for the time at which the analyzing spot was at the center of the trace. Thus constant values of $N^{Cu}$ and $N^{Al}$ were used to calculate all of the values of K for any one trace. The relative change in K from the start to the end of a one-millimeter long trace was less than 0.2 percent.

**Correction for interaction between the atoms** - The effect of the interaction of the copper and aluminum atoms on the relative intensity is shown by the constant $a$ in Eq. F.6. In effect, $a$ is an indication of the degree to which K and C are different.

To determine the value of $a$, a series of standards was prepared to correspond to the different areas found on the ingot samples, Appendix A. Compositions from one to five wt pct copper were homogenized to correspond to the dendrite arms. A 33.2 wt pct copper standard was prepared to correspond to the interdendritic eutectic, and was not homogenized. A 53.5 wt pct copper standard was prepared to
correspond to the CuAl₂ phase within the interdendritic eutectic. The measured values of Kₜₕ and Kₐₜ are plotted against the true compositions of Cₜₕ and Cₜₐ in Figs. F.7 and F.8. The data were fit to Eq. F.6, rearranged to the from

$$\frac{C}{K} = a + (1-a)C.$$  \hspace{1cm} (F.8)

This is a linear equation with one constant, a. The value of a which minimizes the sum of the squares of the deviations of the data from Eq. F.8 is

$$a = \frac{\sum C(1/K-1)(C-1)/\sum(C-1)^2}{\sum(C-1)^2}.$$  \hspace{1cm} (F.9)

The results are aₜₕ = 1.056 and aₜₐ = 4.91, as shown in Figs. F.7 and F.8. To convert the data from relative intensity to true composition, Eq. F.6 is rearranged to give

$$C = \frac{a K}{1 + K(a - 1)}.$$  \hspace{1cm} (F.10)

**Effect of averaging** - Plotting K as a function of C illustrates the extent of the difference between them, Fig. F.9. The difference is greater for AlKα radiation than from CuKα radiation. Now because all of the original data are integrated intensities, taken from areas of a finite length, a certain degree of averaging is inherent in each point. As an example, consider the result of a data point whose integrated intensity was derived from equal lengths over a dendrite arm low in copper, and interdendritic eutectic high in copper, compositions 1 and 2 on Fig. F.9. The average integrated intensity of AlKα radiation will yield point 3 which, since it is assumed to lie on the curve, is taken as point 4, a decrease in the apparent copper content of several percent.
Fig. F.7 Electron microprobe measurements of CuKα radiation on a series of aluminum-copper standards. The straight line is the function $C/K = a + (1 - a)C$, where $a$ is 1.056.
Fig. F.8 Electron microprobe measurements of AlKα radiation on a series of aluminum-copper standards. The straight line is the function $C/K = a + (1 - a)C$, where $a$ is 4.91.
Fig. F.9 Difference between the measured relative intensity, $K$, and the actual composition, $C$, for CuKα and AlKα radiation.
The corresponding point for copper, 5, produces a very slight increase in the apparent copper content. In fact, the concentrations of copper calculated from the AlKα data were invariably about 20 percent lower than that obtained from the corresponding CuKα data. Therefore, only the CuKα data is presented in the body of the thesis.

The arithmetic average composition of two areas, equal in size, but with different concentrations of copper also is in error because the area with the higher concentration of copper is more dense than the other area. The correction used when data points are averaged together is given in Eq. F.1. Some averaging, however, is involved in the very taking of the data. A data point which averages a dendrite arm and interdendritic eutectic, as above, might thus be too low by ten percent of its value. The actual data, however, do not show this discrepancy, so no correction was attempted.
4.4 Computer Programs

All of the data points were keypunched for further processing on an IBM 360 computer. After preliminary analysis of the measured data points, the data were plotted as moving average concentration and concentration in the solid as a function of the fraction solidified. These curves were plotted with a Stromberg-Carlson SC4020 cathode ray tube display.

Programs and subprograms listed here are:

PROBE. A. 0

PROBE. A. 1 (PRSCL, PLT1, PRNVRT, PINVRT)

PROBE. A. 2 (MAXMIN, VWAV2, VWAV1)

PROBE. A. 3 (PLOHI)

LSA
F. 4 Computer Programs

The integrated intensities were keypunched onto cards. Subsequent calculations were all done on the computer. The GRMDET plotting system was used to plot the results. Program PROBE.A,0 was used to calculate the correction for instrument drift.

C HOWARD PIELET 8-30-70 PROBE.A,0 VERSION 1
C THIS PROGRAM INTERPOLATES TO FIND THE CORRECT COUNTS FROM THE
C PROBE STANDARDS AT THE TIME OF EACH TRACE.
DIMENSION X1(4),X2(4),XT(4),DUM(7)
DATA TCU/5.0/,TA/5.0/
1 READ(5,101) T1,X1,T2,X2
101 FORMAT(5F10.7)
102 FORMAT(12)
DO 1000 I=1,N
103 FORMAT(F10.7,4X,7A4)
DO 1010 J=1,4
1010 XT(J)=X1(J)+(X2(J)-X1(J))*((T-T1)/(T2-T1))
WRITE(7,204) XT(1),XT(2),TCU,DUM,XT(3),XT(4),TA,DUM
204 FORMAT(3F10.2,22X,7A4)
1000 CONTINUE
GO TO 1
END
Program PROBE.A.1 was used to convert the integrated intensities to wt pct copper. Subroutines PRSCL and PLT were written by Roberts. They were used to plot the data for preliminary analysis.

C HOWARD PIELET 8-16-70 PROBE.A.1 VERSION 2
C HOWARD PIELET 12-27-70 INVERSION OF DATA ARRAY ADDED.
C THIS IS A MAIN PROGRAM FOR CONVERTING PROBE COUNTS TO WEIGHT PERCENT.
C RESULTS ARE PRINTED, PLOTTED, AND PUNCHED FOR FURTHER PROCESSING.
C COMPONENT 1 IS AL, COMPONENT 2 IS COPPER.
REAL IACU,IAAU,IZCU,IZAU,IBAC,IBCA,K2
REAL K1
LOGICAL INVERT
DIMENSION SUM(1000)
DIMENSION IACU(1000),IAAU(1000),K2(1000),K1(1000),NPT(1000),X(1000)
DUM(10),VAR(10),LVAR(10),SU(10),SL(10)
DATA BCOK2/*C2 '",
1 SU/10*50./*SL/10*0.0/*LVAR(1)/'C '/.NN/10/,NVAR/2/,
2 LVAR(2)/*A */
DATA A2/1.056 /*A1/ 4.91 /
DA2=(A2-1.0)/100.0
DA1=(A1-1.0)/100.0
C THIS SECTION READS COUNTS AND CONVERTS THEM TO WEIGHT PERCENT.
1 READ(5,100)
100 FORMAT(1H1,78H THIS SPACE WILL BE FILLED AT PROGRAM EXECUTION
1 TIME /1X,78H
2 /1X,78H
3
4 )
READ(5,101)IZCU,IBAC,TCU,IBCA,IZAU,TA
101  FORMAT(3F10.1, 49H
1  /,3F10.1, 49H
2  /,79H
3  /,79H
4
5)
102  IZCU=IZCU/TCU
103  IBCA=IBCA/TA
104  DC=IZCU-IBCA
105  IZAU=IZAU/TA
106  IBAC=IBAC/TCU
107  DA=IZAU-IBAC
108  READ(5,102) INVERT,NDATA,TCOUNT,TRESFT,VPROBE,DUM
109  FORMAT(L1, I9, 2F5.0,F10.0,20X,6A4)
110  DELOPS=(TCOUNT+TRESFT)*VPROBE
111  WRITE(6,100)
112  DO 1000 J=1,NDATA
113  READ(5,103) IACU(J),IAAU(J),NPT(J)
114  FORMAT(2F10.5,25X,I5)
115  K2(J)=((IACU(J)/TCOUNT)-IBCA)*160./DC
116  K2(J)=A2*K2(J)/(1.0+K2(J)*QA2)
117  K1(J)=((IAAU(J)/TCOUNT)-IBAC)*100./DA
118  K1(J)=A1*K1(J)/(1.0+K1(J)*QA1)
119  SUM(J)=K1(J)+K2(J)
120  IF((K2(J).LT.0.0).OR.(K2(J).GT.50.0).OR.(K1(J).LT.50.0)
121     .OR.(K1(J).GT.100.0).OR.(SUM(J).LT.96.0).OR.(SUM(J).GT.110.0))
122     WRITE(6,302) NPT(J)
123  FORMAT(* CHECK POINT NUMBER *.*13,** FOR KEYPUNCH ERRORS*)
124  X(J)=DELOPS*(J-1)
125  1000 CONTINUE
126  IF(.NOT.INVERT) GO TO 2
127     CALL PRNVRT(K1,NDATA)
128     CALL PRNVRT(K2,NDATA)
129     CALL PRNVRT(SUM,NDATA)
130     CALL PINVRT(NPT,NDATA)
131  2 NOUT=NDATA+1
K1(NOUT)=0.0
K2(NOUT)=0.0
SUM(NOUT)=100.0
X(NOUT)=DELP**NDATA

C***********************************************************************
C THIS SECTION PRINTS AND PUNCHES RELATIVE INTENSITIES VS. DISTANCES.
   DUM(1)=RCDK2
   WRITE(6,303)DUM,(K2(I),K1(I),SUM(I),X(I),NPT(I),I=1,NOUT)
303 FORMAT(2X,6A4/(1X,4(E14.6,3F5.1,F7.4,I4)))
   WRITE(7,308)NOUT,DUM
308 FORMAT(I10,6A4)
   NEND=(NOUT+3)/4
   DO 1001 J=1,NEND
      K=4*J-3
      M=K+3
      IF(J*FQ,NEND)M=NOUT
      WRITE(7,704)J,DUM,(K2(I),X(I),I=K,M)
1001 CONTINUE
704 FORMAT(I6,6A4,2X,4(F6.3,F6.4))
C***********************************************************************
C THIS SECTION PLOTS RELATIVE INTENSITIES VS. POINT NUMBER.
   LCT=0
   WRITE(6,100)
   CALL PRSCL(NVAR,LVAR,SU,SL)
   DO 1060 J=1,NDATA
      VAR(1)=K2(J)
      VAR(2)=100.0-K1(J)
      RNPT=NPT(J)
      CALL PLT1(NVAR,RNPT,VAR,LVAR,SU,SL,NN,LCT)
1060 CONTINUE
   CALL PRSCL(NVAR,LVAR,SU,SL)
   GO TO 1
END
SUBROUTINE PRSCL(NVAR,LVAR,SU,SL) PRSCL010
   PRSCL020
   PRSCL030

C 11-16-68
C PRINT SCALES WITH ASSOCIATED LETTERS AT LEFT (TCP) OF

400
C GRAPH BEFORE PLOTTING
C WHERE NVAR IS THE NUMBER OF VARIABLES TO BE PLOTTED (LEQ 10).
C LVAR IS A VECTOR CONTAINING THE CORRESPONDING LETTERS.
C (A FORMAT)
C SU IS A VECTOR CONTAINING THE CORRESPONDING UPPER LIMIT
C OF THE DEPENDENT SCALES.
C SL IS A VECTOR CONTAINING THE CORRESPONDING LOWER LIMIT
DIMENSION LVAR(10),SU(10),SL(10),S(5),L(10)
WRITE(6,9)
9 FORMAT(1H1)
I = 1
7 SI = (SU(I)-SL(I))/4.
DO 1 J=1,5
XJ = J-1
1 S(J) = SL(I)+XJ*SI
DO 2 J=1,10
L(J) = LVAR(I)
I = I+1
IF (I-NVAR) 5,5,4
5 IF (SU(I)-SU(I-1)) 4,3,4
3 IF (SU(I)-SU(I-1)) 4,2,4
2 CONTINUE
4 WRITE (6,6) S,L,(L(K),K=1,J)
6 FORMAT(1X,5(9X,E15.6),1X,10A1)
IF (I-NVAR) 7,7,8
8 RETURN
END
SUBROUTINE PLT1(NVAR,TIME,VAR,LVAR,SU,SL,N,LCT)
C 11-16-68
C PLOT ONE LINE
7/18/66
C FORM AND PRINT ONE LINE OF PLOT
C WHERE NVAR IS THE NUMBER OF VARIABLES TO BE PLOTTED (LEQ 10).
C TIME IS THE VALUE OF THE INDEPENDENT VARIABLE. (IT IS
C CONVERTED TO INTEGER BEFORE PRINTING.)
C VAR IS A VECTOR CONTAINING THE VALUES TO BE PLOTTED.
C LVAR IS A VECTOR CONTAINING THE CORRESPONDING LETTERS.
(A1 FORMAT)

SU IS A VECTOR CONTAINING THE CORRESPONDING UPPER LIMIT
OF THE DEPENDENT SCALES.

SL IS A VECTOR CONTAINING THE CORRESPONDING LOWER LIMIT
NN IS THE NUMBER OF LINES BETWEEN PRINTING VALUE OF TIME.
LCT IS LINE COUNT. IT SHOULD BE SET TO ZERO BEFORE EACH

DIMENSION VAR(10), LVAR(10), SU(10), SL(10), LINE(101), LSP(5,10),
INLS(5), LNS(14)
DATA LCM/'+', '/LPL/*', '/.LBK/*', '/.LMN/*', '/'
NSP=0
DO 1 I=1,101
1 LINE(I)=LBK
DO 2 N=1,NVAR
   I=((VAR(N)-SL(N))/(SU(N)-SL(N)))*100.+1.5
   IF(I-101) 25,25,2
25 IF(I12,2,26
26 IF(LINE(I)=LBK)3,4,3
3 IF(NSP)5,6,5
5 DO 7 M=1,NSP
   IF(LSP(M,1)=LINE(I))7,8,7
7 CONTINUE
6 NSP=NSP+1
   LSP(NSP,1)=LINE(I)
   LSP(NSP,2)=LVAR(N)
   NLS(NSP)=2
   GO TO 2
8 J=NLS(M)+1
   LSP(M,J)=LVAR(N)
   NLS(M)=J
   GO TO 2
4 LINE(I)=LVAR(N)
2 CONTINUE
K=1
IF(NSP)11,12,11
11 DO 15 L=1,NSP
15 CONTINUE
IF(K-1)13,14,13
13  LNS(K)=LCM
   K=K+1
14  J=NLS(L)
   DO 16 I=1,J
   LNS(K)=LSPIL,I
16  K=K+1
15  CONTINUE
12  DO 17 I=K,14
17  LNS(T)=LBK
   DO 9 I=1,101,25
   IF(LINF(I)-LBK)9,10,9
10  LINE(I)=LPL
9  CONTINUE
   ITIME=TIME
   LCT=LCT-1
   IF(LCT)19,19,18
18  WRITE(6,90) LINF,LNS
   RETURN
19  DO 22 I=3,99,2
   IF(LINE(I)-LBK)22,23,22
23  LINE(I)=LMN
22  CONTINUE
   LCT=NN
20  WRITE(6,24) ITIME,LINE,LNS
24  FORMAT(14,101A1,1X,14A1)
90  FORMAT(4X101A1,1X,14A1)
21  RETURN
END
SUBROUTINE PRNVRT(X,NPTS)
C HOWARD PIELET 12-27-70  PRNVRT VERSION 1
C THIS SUBROUTINE INVERTS A LINEAR ARRAY
DIMENSION X(1),Y(1000)
   NEND=NPTS+1
   DO 1000 I=1,NPTS
   Y(I)=X(NEND-I)
1000  CONTINUE
Program PROBE A.2 was used to calculate and plot the moving average compositions, the average compositions in solid and liquid regions, and the average compositions along short portions of a trace. Subroutine MAXMIN finds the maxima and minima of copper concentration along the trace. Vwav2 computes the moving average concentrations and Vwav1 averages separate regions. Input cards for the GRDMET plots are also listed.

C HOWARD PIELET 9-6-70 PROBE A.2 VERSION 2
C THIS IS A MAIN PROGRAM FOR FINDING THE RUNNING AVERAGE OF COPPER
C FOR TWO DENDRITE ARMS AT A TIME, AND PRODUCING DATA CARDS FOR USE
C BY THE GRDMET PLOTTING SYSTEM.
C SOLID AND LIQUID REGIONS AND SUB-REGIONS ARE ALSO AVERAGED.
REAL K2,K2MAX,K2MIN,K2AV
DIMENSION K2(1000),NPT(1000),DUM(6),X(1000),
IIMAXAR(300),K2MAX(300), MINAR(300),K2MIN(300),NPTMAX(300),NPTMIN(3
200), IDELMX(300), IDELMN(300),XMAX(300),XMIN(300),
BCD1(40),BCD2(20),BCD3(20),BCD4(60),BCD5(40),BCD6(40),
K2AV(300),XAV(300),ISTOP(25),REGION(25),BCD2P(40),BCD4P(40)
DATA B/3.372/,C/-0.0026/,BC2AV/'C2AV'/
DO 1000 I=1,1000

1000 NPT(I)=1
READ(5,101) BCD1,BCD2,BCD2P,BCD3,BCD4,BCD4P,BCD5,BCD6

101 FORMAT(20A4)
1 READ(5,308) NOUT,DUM,HIST
308 FORMAT(I10,6A4,1X,F10.7)
READ(5,703)(K2(I),X(I),I=1,NOUT)
703 FORMAT((32X,4(OPF6.3,1PF6.4)))
NDATA=NOUT-1
WRITE(7,101) BCD1
DUM(1)=BC2AV
WRITE(7,401) DUM

401 FORMAT(20X,6A4)
WRITE(7,101) BCD2
C THIS SECTION FINDS AND PRINTS MAXIMA AND MINIMA.
CALL MAXMIN(K2, NDATA, HITST, IMAXAR, K2MAX, NMAX, IMINAR, K2MIN, NMIN)
IF(INMAX.LE.3) GO TO 2
WRITE(7,101) 8CO2P
DO 1010 I=1,NMAX
XMAX(I)=X(IMAXAR(I))
NPTMAX(I)= NPT(IMAXAR(I))
1010 CONTINUE
IDELMX(I)=0
DO 1011 I=2,NMAX
IDELMX(I)=NPTMAX(I)-NPTMAX(I-1)
1011 CONTINUE
WRITE(6,100) DUM
100 FORMAT(1H1,6A4)
WRITE(6,305)(K2MAX(I),XMAX(I),NPTMAX(I),IDELMX(I),I=1,NMAX)
305 FORMAT(1HO,*MAXIMA IN RELATIVE INTENSITY, LOCATION OF MAXIMA,*/
1 1X,*POINT NUMBER OF MAXIMA, AND NUMBER OF POINTS BETWEEN MAXIMA.
2/(1X,F10.3,F10.5,2I10))
DO 1020 I=1,NMIN
XMIN(I)=X(IMINAR(I))
NPTMIN(I)=NPT(IMINAR(I))
1020 CONTINUE
IDELMN(I)=0
DO 1021 I=2,NMIN
IDELMN(I)=NPTMIN(I)-NPTMIN(I-1)
1021 CONTINUE
WRITE(6,306)(K2MIN(I),XMIN(I),NPTMIN(I),IDELMN(I),I=1,NMIN)
306 FORMAT(1HO,*MINIMA IN RELATIVE INTENSITY, LOCATION OF MINIMA,*/
1 1X,*POINT NUMBER OF MINIMA, AND NUMBER OF POINTS BETWEEN MINIMA.
2/(1X,F10.3,F10.4,2I10))
C THIS SECTION FINDS, PRINTS, AND PUNCHES RUNNING AVERAGES.
CALL VMAV2(K2, X,B,C, IMAXAR,NMAX, K2AV, XAV, NOUT)
WRITE(6,307) NOUT, DUM, (K2AV(I),XAV(I),I=1,NOUT)
307 FORMAT(1HC,*AVERAGE VALUES OF RELATIVE INTENSITIES AND LOCATIONS.*)
1  /1X,'THESE ARE RUNNING AVERAGES FOR TWO ARMS.'/1X,I11,6A4/
2  (1X,5(F7.3,F8.5)))
   NVALS=NOUT*2
   WRITE(7,402) NVALS
402  FORMAT(I4)
   WRITE(7,101) BCD3
   NEND=(NOUT+3)/4
   DO 1030 J=1,NEND
   K=4*J-3
   M=K+3
   IF(J.EQ.NEND) M=NOUT
   WRITE(7,704) J,DUM,(K2AV(I),XAV(I),I=K,M)
704  FORMAT(I6,6A4,7X,4(0PF6.3,1PF6.4))
1030  CONTINUE
   WRITE(7,101) BCD4
C*****************************************************************************
C THIS SECTION AVERAGES SOLID AND LIQUID REGIONS.
2  WRITE(7,101) BCD4P
   READ(5,102) NSTOPS,(ISTOP(I),REGION(I),I=1,NSTOPS)
102  FORMAT(I2,8X,14(I4,A1)/(16(I4,A1)))
   IF(NSTOPS.LT.2) GO TO 3
   DO 1040 I=1,NSTOPS
   XSTOP=X(ISTOP(I))
   WRITE(7,301) XSTOP,XSTOP
301  FORMAT(5X,F10.2,'22.',10X,F10.2,'28.',1X)
1040  CONTINUE
   CALL VAV1(K2,X,B,C,ISTOP,NSTOPS,K2AV,XAV,NOUT)
   WRITE(6,201) DUM,(REGION(I),ISTOP(I),K2AV(I),XAV(I),I=1,NOUT)
201  FORMAT(1H0,6A4/1X,'TYPE OF REGION, START, AVERAGE, AND LOCATION OF
1 AVERAGE'/1X,A1,15,F10.3,F10.5))
   WRITE(7,101) BCD5
   WRITE(7,302) (XAV(I),REGION(I),K2AV(I),I=1,NOUT)
302  FORMAT(14X,'2 2 2 2 *.90',2X,F10.5,'22.',10X,A1,'.',1X)
   1  F4.1)
   WRITE(7,101) BCD6
C*****************************************************************************
C THIS SECTION FINDS AVERAGES OF SUB-REGIONS.
3 READ(5,102) NSTOPS,(ISTOP(I),REGION(I),I=1,NSTOPS)
   IF(NSTOPS.LT.2) GO TO 1
   CALL VVAV1(K2,X,R,C,ISTOP,NSTOPS,K2AV,XAV,NOUT)
   WRITE(6,201) DUM,(REGION(I),ISTOP(I),K2AV(I),XAV(I),I=1,NOUT)
   GO TO 1
   END
   SUBROUTINE MAXMIN(Y,NPTS,HITST,IMAXAR,YMAXAR,NMAX,IMINAR,YMINAR,
   1 NMIN)
C CHANGED TO ENSURE THAT FIRST MAXIMUM IS TRUE MAXIMUM.
C HOWARD PIELEFT 11-11-69 MAXMIN VERSION 2
C HOWARD PIELEFT 11-17-69 CORRECTED TO ACCOUNT FOR A MAXIMUM
C AT NPTS-3.
C Y IS THE INPUT DATA ARRAY.
C NPTS IS THE SIZE OF THE Y ARRAY.
C HITST IS THE CUTOFF PT.--MAXIMA ARE THE LARGEST VALUES BETWEEN TWO
C CONSECUTIVE DIPS OF THE Y ARRAY VALUES BELOW HITST, AND MINIMA ARE
C THE MINIMUM VALUES BETWEEN SUCCESSIVE RISES ABOVE HITST.
C IMAXAR IS AN ARRAY CONTAINING THE INDICES OF THE Y ARRAY AT WHICH
C MAXIMA OCCUR.
C YMAXAR IS THE ARRAY OF MAXIMUM VALUES RETURNED.
C NMAX IS THE NUMBER OF MAXIMA RETURNED.
C IMINAR, YMINAR, AND NMIN ARE CORRESPONDING VARIABLES FOR MINIMUM VALUES.
   DIMENSION Y(1),IMAXAR(1),YMAXAR(1),IMINAR(1),YMINAR(1)
C THIS SECTION FINDS MAXIMUM VALUES
   NMAX=0
   NMIN=0
   DO 1001 I=1,NPTS
      IF(Y(I).LE.HITST) GO TO 1
   1001 CONTINUE
   RETURN
   1 ISTRT=I+1
   DO 1000 I=ISTRT,NPTS
      IF(Y(I).GE.HITST) GO TO 2
   1000 CONTINUE
   GO TO 3
IMAX=1
ISTRT=1
YMAX=Y(I)
DO 1010 I=ISTRT,NPTS
  IF(Y(I).LT.YMAX) IMAX=I
  IF(Y(I).GT.YMAX) YMAX=Y(I)
  IF(Y(I).GE.HITST) GO TO 1010
NMAX=NMAX+1
YMAXAR(NMAX)=YMAX
IMAXAR(NMAX)=IMAX
IF(I.LE.(NPTS-2)) GO TO 1
IF(I.GT.(NPTS-2)) GO TO 3
1010 CONTINUE
3 IF(NMAX.LT.2) RETURN
C THIS SECTION FINDS MINIMA.
NFND=NMAX-1
DO 1030 J=1,NFND
  IMIN=IMAXAR(J)
  YMIN=Y(IMIN)
  NFIN=IMAXAR(J+1)
  ISTRT=IMIN+1
  DO 1020 I=ISTRT,NFIN
    IF(Y(I).LT.YMIN) IMIN=I
    IF(Y(I).LT.YMIN) YMIN=Y(I)
 1020 CONTINUE
NMIN=NMN+1
YMINAR(NMIN)=YMIN
IMINAR(NMIN)=IMIN
1030 CONTINUE
RETURN
END

SUBROUTINE VWAV2(Y,X,B,C,ISTOP,NSTOPS,YAV,XOFYAV,NOUT)
C HOWARD PIELET 11-10-69 VWAV2 VERSION 1
C THIS SUBROUTINE CALCULATES WEIGHTED AVERAGES OF CONCENTRATION.
C FOR VARIABLE AVERAGING DISTANCES.
C Y IS THE INPUT DATA ARRAY.
C X IS THE CORRESPONDING X ARRAY,
C A AND C ARE CONSTANTS FOR THE CALCULATION OF DENSITY,
C ISTOP IS THE ARRAY OF STOP POINTS FOR AVERAGING Y,
C NSTOPS IS THE NUMBER OF STOP POINTS,
C YAV IS AN OUTPUT ARRAY CONTAINING THE AVERAGE VALUES OF Y,
C OVER TWO INTERVALS AT A TIME,
C XOFYAV IS AN ARRAY CONTAINING THE X VALUES CORRESPONDING TO YAV,
C NOUT IS THE NUMBER OF OUTPUT VALUES=NSTOPS-1
C OUTPUT IS SPECIFICALLY DESIGNED FOR PLOTTING WITH HISTOGRAM IN
C THE GRMET PLOTTING SYSTEM.

DIMENSION Y(1),X(1),ISTOP(1),YAV(1),XOFYAV(1)
NOUT=NSTOPS-1
DO 1010 N=1,NOUT
ISTRT=ISTOP(N)
INEXT=ISTOP(N+1)
XSTRT=X(ISTRT)
XNEXT=X(INEXT)
XOFYAV(N)=(XSTRT+XNEXT)/2.0
IF(N.GE.NOUT) GO TO 1010

TOT=0.0
DENOM=0.0
IFDN=ISTOP(N+2)-1
DO 1000 I=ISTRT,IFDN
R=1.0/(B+C*Y(I))
W=Y(I)*R
TOT=TOT+W
DENOM=DENOM+R

1000 CONTINUE
YAV(N)=TOT/DENOM

1010 CONTINUE
YAV(NOUT)=0.0
RETURN
END

SUBROUTINE VWAV1(Y,X,B,C,ISTOP,NSTOPS,YAV,XOFYAV,NOUT)
C HOWARD PIELFT  9-6-70  VWAV1 VERSION 1
C THIS SUBROUTINE CALCULATES WEIGHTED AVERAGES OF CONCENTRATIO,
FOR VARIABLE AVERAGING DISTANCES.
Y IS THE INPUT DATA ARRAY,
X IS THE CORRESPONDING X ARRAY,
B AND C ARE CONSTANTS FOR THE CALCULATION OF DENSITY,
ISTOP IS THE ARRAY OF STOP POINTS FOR AVERAGING Y,
NSTOPS IS THE NUMBER OF STOP POINTS,
YAV IS AN OUTPUT ARRAY CONTAINING THE AVERAGE VALUES OF Y,
XOFYAV IS AN ARRAY CONTAINING THE X VALUES CORRESPONDING TO YAV,
 NOUT IS THE NUMBER OF OUTPUT VALUES=NSTOPS-1

DIMENSION Y(1), X(1), ISTOP(1), YAV(1), XOFYAV(1)
NOUT=NSTOPS-1
DO 1010 N=1, NOUT
ISTR=ISTOP(N)
INEXT=ISTOP(N+1)
XSTR=X(ISTR)
XNEXT=X(INEXT)
XOFYAV(N)=(XSTR+XNEXT)/2.0
TOT=0.0
DENOM=0.0
IEND=ISTOP(N+1)-1
DO 1000 I=ISTR, IEND
R=1.0/(B+C*X(1))
W=Y(I)*R
TOT=TOT+W
DENOM=DENOM+R
1000 CONTINUE
YAV(N)=TOT/DENOM
1010 CONTINUE
RETURN
END
Program PROBE.A.3 was used to take data from the liquid or solid portions of a number of microprobe traces, average them, and plot the curve of composition vs weight fraction solid. Subroutine FLOHI reorders the data from lowest to highest. Input cards for the GRDMET plots are shown.

C HOWARD PIELET  9-10-70  PROBE.A.3  VERSION 1
C THIS IS A MAIN PROGRAM FOR AVERAGING RELATIVE PROBE INTENSITIES
C BETWEEN GIVEN POINTS ALONG A TRACE, AND FOR REORDERING THE POINTS
C IN EACH GROUP TO GIVE K2 VS. FS.
C RESULTS ARE PUNCHED FOR PLOTTING BY THE GRDMET SYSTEM.
C COMPONENT ONE IS AL.
C COMPONENT 2 IS COPPER.
REAL K2,K2NEW,K2ORD,K2AV,K2AV1
DIMENSION K2(1000),K2NEW(1000),K2ORD(1000),FS(1000),DUM(6),
1 ISTART, IEND, R(1000), W(1000)
DIMENSION DUM(6), K2AV(50)
DIMENSION BCD1(40), BCD2(240), BCD3(20), BCD4(40), BCD5(60), BCD6(20),
1 BCD7(80), BCD8(40)
DATA R/2.372/, C/-0.0026/, RDIFF/'C2FS'/
READ(5,701) BCD1, BCD2, BCD3, BCD4, BCD5, BCD6, BCD7, BCD8
701 FORMAT(20A4)
C*****************************************************************************
C THIS SECTION READS THE FIRST DATASET.
1 JSTART=1
WRITE(6,100)
100 FORMAT(1H1)
C*****************************************************************************
C THIS SECTION READS ADDITIONAL DATASETS.
2 READ(5,101) NDATA, DUM
101 FORMAT(I10,6A4)
WRITE(6,203) DUM
203 FORMAT(1X,6A4,' INCLUDED ')
JSTOP=JSTART+NDATA-1
READ(5,111) (K2(I),I=JSTART,JSTOP)
111 FORMAT ((32X,4(F6.3,6X)))
JSTART=JSTART+NDATA
READ(5,103) NEXT
103 FORMAT(I1)
GO TO (1,2,3,4,5),NEXT
C*****************************************************************
C THIS SECTION BEGINS A GROUP. FOR EXAMPLE, ALL DATA POINTS IN A LIQUID
C REGION FROM SEVERAL TRACES WOULD FORM ONE GROUP.
3 K=0
   READ(5,102) DUM1,CODE
102 FORMAT(6A4,6X,A4)
   DUM1(I)=R@OFS
   WRITE(6,204) DUM1,CODE
204 FORMAT(1OH0,'THIS IS GROUP ',6A4,4X,A4)
C*****************************************************************
C THIS SECTION ADDS SETS OF POINTS FROM ONE TRACE TO THE GROUP.
4 READ(5,104) DUM,IADD,NSETS,(ISTART(I),IEND(I),I=1,NSETS)
104 FORMAT(6A4,6X,2I5/(10I5))
   DO 1000 I=1,NSETS
      TOT=0.0
      DENOM=0.0
      NSTART=ISTART(I)+IADD
      NEND=IEND(I)+IADD
      DO 1010 J=NSTART,NEND
         K=K+1
         K2NEW(K)=K2(J)
         R1=1.0/(R+C*K2(J))
         W1=R1*K2(J)
         TOT=TOT+W1
      ENDDO
      DENOM=DENOM+R1
   1010 CONTINUE
   K2AV1(I)=TOT/DENOM
1000 CONTINUE
   WRITE(6,205) DUM,(ISTART(I),IEND(I),K2AV1(I),I=1,NSETS)
205  FORMAT(1HO.,'FROM ',6A4/(1X,2(I,10),', ',T),',I5,',' C2AVERAGE= ',
1 F7.2))
   READ(5,103) NEXT
   GO TO (1,2,3,4,5),NEXT
C******************************************************************************
C THIS SECTION REORDERS ALL OF THE POINTS IN THE GROUP AND FINDS THE
C CORRESPONDING CUMULATIVE FRACTION SOLID.
5   NPTS=K
    CALL PLOHI(K2NEW,K2ORD,NPTS,1)
    TOT=0.0
    DENOM=0.0
    DO 1020 I=1,NPTS
       R(I)=1.0/(B+C*K2ORD(I))
       W(I)=K2ORD(I)*R(I)
       TOT=TOT+W(I)
       DENOM=DENOM+R(I)
    1020  CONTINUE
    K2AV=TOT/DENOM
    FS(1)=0.0
    FSTOT=0.0
    DO 1030 I=1,NPTS
       FSI=R(I)/DENOM
       FSTOT=FSTOT+FSI
       FS(I+1)=FSTOT
    1030  CONTINUE
    NOUT=NPTS+1
    K2ORD(NOUT)=0.0
    WRITE(6,301) K2AV,NOUT,(K2ORD(I),FS(I),I=1,NOUT)
301  FORMAT(1HO.,'CONCENTRATION AS A FUNCTION OF CUMULATIVE WEIGHT FRACTION ',
1 1X,.CONCENTRATION AS A FUNCTION OF CUMULATIVE WEIGHT FRACTION ',
2 'SOLID'/
3 1X,I10/ (1X,5(1X,F7.3,F7.3)))
   READ(5,103) NEXT
   GO TO (1,2,3,4,5,6,7,8),NEXT
C******************************************************************************
C THIS SECTION PUNCHES GROMET CARDS FOR HISTOGRAM OF THE LIQUID REGION.
6       WRITE(7,701) BCD1
       WRITE(7,702) NUM1
702  FORMAT(20X,6A4)  
       WRITE(7,701) BCD2
       NVALS=NOUT*2
       WRITE(7,703) NVALS
703  FORMAT(14)  
       WRITE(7,701) BCD3
       NEND=(NOUT+3)/4
       DO 1040 J=1,NEND
           K=4*J-3
           M=K+3
           IF(J.EQ.NEND) M=NOUT
           WRITE(7,704)J,DUM1,(K2ORD(I),FS(I),I=K,M)
1040  CONTINUE
704  FORMAT(16,6A4,2X, 4(F6.3,F6.4))
       WRITE(7,701) BCD4
       DO 1050 I=1,NPTS
           IF(FS(I) .GE.0.7) GO TO 21
1050  CONTINUE
21     XAV=FS(I)
           YAV=K2ORD(I)+1.0
           WRITE(7,705) XAV,YAV,K2AV,XAV,YAV
705  FORMAT(5X,*CENT  1*18X,2F16.3,10X,"'L, 'F4.1/11X,'3',18X,2F10.3,
           1 18X,'16')
           READ(5,103) NEXT
           GO TO (1,2,3,4,5,6,7,8), NEXT
C******************************************************************************
C THIS SECTION PUNCHES GRDMET CARDS FOR THE SOLID HISTOGRAM.
   7       WRITE(7,701) BCD5
       NVALS=NOUT*2
       WRITE(7,703) NVALS
       WRITE(7,701) BCD6
       NEND=(NOUT+3)/4
       DO 1070 J=1,NEND
           K=4*J-3

JLOW=1
XLOW=X1(I)
K=I+1
DO 1020 J=K,NPTS
  IF(X1(J)-XLOW) 1,1020,1020
  1 XLOW=X1(J)
  JLOW=J
1020 CONTINUE
  X1(JLOW)=X1(I)
  X1(I)=XLOW
1010 CONTINUE
RETURN
END

ENTRY
TITLE
LINES
LAST
XLABEL
LINES
LAST
YLABEL
LINES
LAST
GRID
DATA
INPUT SPECIFICATIONS
POINTS
HISTOGRAM
LABEL
LAST
DATA
INPUT SPECIFICATIONS
POINTS
HISTOGRAM

WEIGHT FRACTION SOLID

COPPER, PCT
Program LSA was used to calculate the least squares lines shown in Figs. F.8 and F.9.

```
C HOWARD PIELET  8-9-70   MAIN PROGRAM FOR PROBE FACTOR A
C LEAST SQUARES CALCULATION
   DIMENSION C(100), DUM(61)
   REAL K(100)
1 READ(5,1F1)N,DUM,(C(I),K(I),I=1,N)
111 FORMAT(13,6A4/(2F2F10.7))
   WRITE(6,2) N,DUM
   FORMAT(1X, 'LEAST SQUARES CALCULATION OF A FOR ',6A4)
   CALL LSA(N,C,K,A)
   GO TO 1
END
SUBROUTINE LSA(N,C,K,A)
C HOWARD PIELET  8-9-70   LEAST SQUARES CALCULATION OF A, LSA
   DIMENSION C(N)
   REAL K(N)
   TOP=0.0
   ROT=0.0
   DO 1000 I=1,N
      TOP=TOP+C(I)*(1.0/K(I)-1.0)*(C(I)-1.0)
      ROT=ROT+(C(I)-1.0)*(C(I)-1.0)
1000 CONTINUE
   A=-TOP/ROT
   SHH=0.0
   DO 1010 I=1,N
      SHH=SHH+(C(I)/K(I)-A-(1.0-A)*C(I))**2
1010 CONTINUE
```
RN=N
SY=SQR(SHH/(RN-1.0))
WRITE(6,2) A,SY
2 FORMAT(1X,A,'=',F14.5,X,SY,'=',F14.5)
RETURN
END
F. 5 Additional plots

Curves of composition as a function of weight fraction solid which were not presented in the text are placed here. They are shown in order of ingot number, area, and line.

Fig. F.10 Reordered data.

(a) Ingot A-15, area A, line C
(b) Ingot A-15, area A, line D
(c) Ingot A-15, area A, line F
(d) Ingot A-15, area A, line G
(e) Ingot A-15, area A, line H
(f) Ingot A-49, area G, line A
(g) Ingot A-49, area H, all lines
(h) Ingot A-49, area I, line A
(i) Ingot A-49, area L, line A
(j) Ingot A-49, area M, line A
(k) Ingot A-49, area N, all lines
(l) Ingot A-49, area P, all lines
(m) Ingot A-49, area Q, line A
(n) Ingot A-57, area F, lines A, B, and C
(o) Ingot A-57, area F, line D
(p) Ingot A-57, area G, line A
(q) Ingot A-57, area G, line B
Fig. F.10, continued.
Fig. F.10, continued.
Fig. F.10, continued.
Fig. F.10, continued.
Fig. F.10, continued.
Fig. F.10, continued.
Fig. F.10, continued.
Fig. F.10, continued.
Fig. F.10, continued.
APPENDIX G

PHYSICAL PROPERTIES OF ALUMINUM-COPPER ALLOYS

A number of physical properties of aluminum-copper alloys have been expressed as simple equations for the purpose of calculation.

Liquidus - The liquidus line of the aluminum-liquid field on the phase diagram was assumed to be a straight line, Fig. G.1, passing through the proper temperatures at 4.5 and 33.2 pct copper:

\[ C_L = C_0 + 0.290 \left( T_L, 0 = -T \right) \]  \hspace{1cm} (G.1)

where \( T_L, 0 = 647 \) for \( C_0 = 4.5 \).

Weight fraction liquid - A form of the Scheil equation which agrees with the calculations of Bower, Brody and Flemings, 8

\[ f_L = \left\{ (660.0 - T_L, 0)/(660.0 - T) \right\}^{1-k} \]  \hspace{1cm} (G.2)

where \( k = 0.171 \) was used to calculate the weight fraction of interdendritic liquid.

Volume fraction liquid - The volume fraction of interdendritic liquid was computed from the weight fraction liquid

\[ g_L = (f_L/\rho_L)/( (f_L/\rho_L) + (f_S/\rho_S) ) \]  \hspace{1cm} (G.3)

where \( \rho_S \) is calculated from Eq. G.5 and the density of the average composition of the solid which is

\[ \bar{C}_S = (C_0 - C_L f_L)/(1.0 - f_L). \]

Both the weight and volume fractions of liquid are shown in Fig G.2.
Fig. G.1  The linear relation assumed for the equilibrium liquidus concentration in the aluminum-copper system.

Fig. G.2  Weight and volume fractions of unfrozen liquid assumed for the aluminum-4.5 wt pct copper alloy.
Density of the liquid - The density of the interdendritic liquid was taken as a linear extrapolation of data by Gebhardt, Becker, and Dorner.\textsuperscript{95}

\[ \rho_\ell = 2.521 - 2.333 \times 10^{-4} \, T + 0.019 \, C_\ell \] \hspace{1cm} (G. 4)

Density of the solid - The density of the solid alloy was taken as a linear interpolation of reported calculated values.\textsuperscript{95}

\[ \rho_s = 2.839 - 4.37 \times 10^{-4} \, T + 0.019 \, C_s \] \hspace{1cm} (G. 5)

The density of liquid at the liquidus line of the phase diagram and of solid at the solidus line are plotted in Fig. G. 3.

Room temperature density - The density of the solid alloy at room temperature was found by taking a linear relation for the specific volume

\[ 1/\rho_s = 0.372 - 0.0026 \cdot C_{Cu} \] \hspace{1cm} (G. 6)

This equation was used by the computer program PROBE A.2, which averaged the concentrations of highly segregated dendrite arms to convert from volume to weight fraction.

Viscosity - The viscosity of the interdendritic liquid was taken as a linear extrapolation of data by Rothwell\textsuperscript{96} and Gebhardt, Becker and Dorner.\textsuperscript{97}

\[ \mu = 0.0309 - 2.58 \times 10^{-5} \, T + 5 \times 10^{-5} \, C_\ell \] \hspace{1cm} (G. 7)

and is plotted in Fig. G. 4.
Fig. G.3 Assumed values for the densities of liquid and solid at the freezing surface of a dendrite arm, for the aluminum-4.5 wt pct copper alloy.

Fig. G.4 Assumed values of the viscosity of the interdendritic liquid for the aluminum-4.5 wt pct copper alloy.
Fortran functions

The equations for $C_L$, $\rho_L$, $\rho_S$, and $\mu$ derived above were expressed as Fortran IV functions.

```
REAL FUNCTION CLACU(T, TLZERO, CZERO)
C HOWARD PIELET 11-8-70 CLACU VERSION 1
C CALCULATION OF THE LIQUIDUS COMPOSITION FOR TEMPERATURE T IN
C AL-CU ALLOYS. A STRAIGHT LIQUIDUS IS ASSUMED, BUT ERROR IS
C DECREASED BY BEGINNING FROM CZERO AND TLZERO.
C I.E. A STRAIGHT LIQUIDUS FROM 4.5,647 TO 33.2,548 IS ASSUMED.
   CLACU=CZERO+0.290*(TLZERO-T)
   RETURN
END

REAL FUNCTION RLACU(T, CCU)
C HOWARD PIELET 11-15-70 RLACU VERSION 1
   RLACU=2.521-2.333E-4*T+0.019*CCU
   RETURN
END

REAL FUNCTION RSLACU(T, CCU)
C HOWARD PIELET 11-16-70 RSLACU VERSION 1
   RSLACU=2.839-4.37E-4*T+0.019*CCU
   RETURN
END

REAL FUNCTION ALCUMU(T, CCU)
C HOWARD PIELET 11-16-70 ALCUMU VERSION 1
   ALCUMU=0.0309-2.58E-5*T+5.0E-5*CCU
   RETURN
END
```
The equations for weight and volume fraction of unfrozen liquid were also expressed as Fortran IV functions.

```
REAL FUNCTION FLALCU(T, TLZERO)
C HOWARD PIELET  11-8-70  FLALCU  VERSION 1
C CALCULATION OF WEIGHT FRACTION LIQUID FOR THE AL-CU SYSTEM.
C ALTHOUGH NOT STRICTLY ACCURATE SINCE A STRAIGHT LIQUIDUS IS ASSUMED,
C THE VALUES GIVEN CORRELATE WELL FOR AL-4.5%CU GIVEN BY FLEMINGS,
C WHO ASSUMED PARTIAL DIFFUSION IN THE SOLID.
   FLALCU=((650.0-TLZERO)/(660.0-T))*1.206
   RETURN
END

REAL FUNCTION GLALCU(T)
C HOWARD PIELET  11-16-70  GLALCU  VERSION 1
   FL=FLALCU(T,647.0)
   CL=CLALCU(T,647.0,4.5)
   RL=RLALCU(T,CL)
   IF(FL.GE.1.0) CSAV=4.5*0.171
   IF(FL.GE.1.0) GO TO 2
   CSAV=(4.5-CL*FL)/(1.0-FL)
   2
   RS=RSLALCU(T,CSAV)
   GLALCU=(FL/RL)/((FL/RL)+(1.0-FL)/RS)
   RETURN
END
```
APPENDIX H
CALCULATIONS FOR THE FLOW MODEL

H.1 Specific surface of a constant number of freezing particles

The surface area per unit volume, \( \Sigma \), of \( n \) particles per cubic centimeter which freeze but do not change their number is directly related to the volume fraction of unfrozen liquid, \( g_\ell \).

Spheres - The surface area and volume fraction of \( n \) spheres are

\[
\Sigma = n \frac{4\pi r^2}{\text{and}} \quad (H.1)
\]

\[
1 - g_\ell = n \frac{4}{3} \pi r^3 \quad (H.2)
\]

where \( r \) is the radius of the sphere. Solving Eq. H.2 for \( r \),

\[
r = \left\{ \frac{3(1 - g_\ell)}{4n\pi} \right\}^\frac{1}{3}, \quad (H.3)
\]

and substituting this for \( r \) in Eq. H.1

\[
\Sigma = \frac{1}{(4n\pi)^\frac{1}{3}} \frac{2}{3} \left[ \frac{2}{3} \left( 1 - g_\ell \right)^\frac{2}{3} \right]. \quad (H.4)
\]

Rods - For rods of infinite length,

\[
\Sigma = n 2\pi r, \quad \text{and} \quad (H.5)
\]

\[
1 - g_\ell = n \pi r^2. \quad (H.6)
\]

Solving Eq. H.6 for \( r \) gives

\[
r = [(1 - g_\ell)/n\pi]^\frac{1}{2}, \quad (H.7)
\]

and substitution of Eq. H.7 into Eq. H.5 gives

\[
\Sigma = 2(n\pi)^\frac{1}{2} \left( 1 - g_\ell \right)^\frac{1}{2}. \quad (H.8)
\]
General shapes - Note that these derivations may be applied to any shape if the variation of surface area and volume with one or more size parameters can be specified. The constant term is a function of the particle shape, and the exponent is dependent on the powers of the size parameter in the equations used to calculate the surface area and volume. The exponent for a shape which is intermediate in form between a sphere and an infinite rod is therefore between \(2/3\) and \(1/2\).

H. 2 Computer model of macrosegregation

The computer model of macrosegregation uses a stepwise integration for both the flow out of the part solid region and for the fluid which is removed from the mixing region as a result of solidification. At time \(t\), material of weight \(w_{PS} \cdot \Delta t\) and \(w_{SOL} \cdot \Delta t\) and composition \(C_{MIX}\) is removed from the mixing region. Then liquid of weight \(w_{PS} \cdot \Delta t\) and composition \(\bar{C}_{PS}\) is added to the mixing region, and a new concentration \(C_{MIX}\) is calculated. A new calculation is made for \(w_{PS}\) at \(t + \Delta t\), and the computational procedure is repeated. A time step, \(\Delta t\), of one second was used for the calculation.
REAL L
DATA L/7.7/,'H/5.0/,'S/0.0/,'CMIX/4.5/,'DELT/1.0/,'WPSI/0.0/,'WCPS/0.0/,
1 'DSDT/0.013/,'T/0.0/,'VPSO/0.0/,
DO 1010 J=1,100
DO 1000 I=1,10
1  S = S + DSDT * DELT
   T = T + DELT
   SC = S - 0.09
   TSC = PTAABL1(4.629 - SC)
   CPS = CCLAU(TSC, 647.0, 4.5)
   RPS = RLALCU(TSC, CPS)
   WPSI = WPSI + PV(I, SC) * DSDT * DELT * RPS
   WCPS = WCPS + PVC(SC) * DSDT * DELT * RPS
   CPSAV = WCPS / WPSI - 4.5
   RMIX = RLALCU(647.0, CMIX)
   VPSO = VPSO + PV(SC) * DSDT * DELT
   WPSO = VPSO * RMIX
   WMIX = H*(L-S)*RMIX
   CMIX = (CMIX*(WMIX - WPSO) + WCPS)/(WMIX - WPSO + WPSI)
   CMIXD = CMIX - 4.5
1000 CONTINUE
   WRITE(6, 601) T, S, WPSI, WCPS, CPSAV, WMIX, CMIXD
   WRITE(7, 701) T, S, WPSI, WCPS, CPSAV, WMIX, CMIXD
   IF(S.GT.7.0) CALL EXIT
1010 CONTINUE
601 FORMAT(1X,OPF5.0,F6.3,1PE11.3,0PF6.2,1PE11.3)
701 FORMAT( OPF5.0,F6.3,1PE11.3,0PF6.2,1PE11.3)
END

REAL FUNCTION PV(S)
C HJWARD PIELET 11-29-70 PV AND PVC VERSION 2
C STATEMENT FUNCTIONS
DK(T,CL)=-980.0*(KLALCU(T,CL)-RLALCU(647.0,4.5))
PKD(T,X)=0.24+GLALCU(T)**3/IGMA2(X,4.629,T)**2
V(T,CL,X)=DK(T,CL)*PKD(T,X)/ALCUM(T,CL)
C
13
RETURN
ENTRY PVC(S)
X=4.629-S
T=PTABL1(X)
CL=CLALCU(T,647.0,4.5)
PV=V(T,CL,X)*(-1.0)
RETURN
END
H.3 Programs for determination of $g_c$ and $\Sigma_c$ as functions of temperature

This program converts the data obtained from linear traces across an ingot to values of volume fraction channel and surface area per cm$^3$, and in addition converts all of the data to superimpose the locations of the tips of the columnar zone. This allows all of the data to be placed on the same graph.

C HOWARD PIELET 11-11-70 FCHANTOT VERSION 1
C MAIN PROGRAM TO CONVERT COUNTS ON SAMPLES TO FRACTION CHANNEL.
C THIS IS FOR PLOTTING ALL DATA ON ONE GRAPH.
DIMENSION BCD(15)
REAL NCCM,NCCM3
N=0
1
READ(5,500) N,BCD,XTIPS
N=N+1
WRITE(6,600) N,BCD,XTIPS,N
XCOR=4.6-XTIPS

DO 1000 I=1,N
2
READ(5,101) X,NCHAN,CCHAN,CTOT
X=X+5.0-XTIPS
IF(NCHAN.EQ.0) GO TO 4
GCHAN=CCHAN/CTOT
NCCM=NCHAN*1440.0/CTOT
DCHAN=CCHAN/(1440.0*NCHAN)
NCCM3=(3.14159/4.0)*GCHAN/(DCHAN*DCHAN)
SIGMA=NCCM*4.0
IF((NCHAN.EQ.1).AND.(GCHAN.GT.0.5)) SIGMA=NCCM*2.0
AK=0.24*GCHAN*GCHAN*GCHAN/((SIGMA*SIGMA)
WRITE(6,601) X,T,GCHAN,SIGMA,AK,NCCM,DCHAN,NCCM3
3
WRITE(7,704) X,T,GCHAN,SIGMA,AK,NCCM,DCHAN,NCCM3
GO TO 1000
4
GCHAN=0.0
NCCM=0.0
DCHAN=C.0
NCCM3=0.0
SIGMA=C.0
AK=1.0E-20

GO TO 3
1000 CONTINUE
GG TO 1
101 FORMAT(F10.7,I12,8X,2F10.7)
500 FORMAT(I12,2X,15A4,6X,F10.3)
600 FORMAT(1H0,12,15A4,6X,F10.3,14//
1 1X, "X", T,GCHAN, SIGMA, AK, NCCM, DCHAN, NCCM3)
601 FORMAT(4F10.3,E15.3,3F10.3)
704 FORMAT(4F10.3,E15.3/3F10.3)
END

REAL FUNCTION PTABL1(XF)
C HOWARD PIELET 10-18-70  PTABL1  VERSION 1
C THIS IS A FUNCTION SUBROUTINE. IT READS ARGUMENTS IN TABLE
C FORM, THEN SUPPLIES INTERMEDIATE VALUES BY LINEAR INTERPOLATION.
C CAUTION--X VALUES MUST BE IN ASCENDING POSITIVE ORDER.
C NOTE--THE TABLE MUST BE SUPPLIED AS X(I),Y(I) IN 2F10.7 FORMAT
C IN THE INPUT DATA DECK TO BE READ FOLLOWING THE FIRST USE OF THE
C FUNCTION.
C
   LOGICAL FIRST
   DATA FIRST./,TRUE./
   DIMENSION X(100),Y(100)
   IF (.NOT. FIRST) GO TO 1
   READ(5,501) NVALS,(Y(I),X(I),I=1,NVALS)

501 FORMAT(12 /(8F10.7))
1  DO 1000 I=2,NVALS
   IF(XF.LE.X(I)) K=I
   IF(XF.LE.X(I)) GO TO 2
1000 CONTINUE
   K=NVALS
2  DYDX=(Y(K)-Y(K-1))/(X(K)-X(K-1))
   PTABL1=Y(K-1)+DYDX*(XF-X(K-1))
FIRST = FALSE
RETURN
END
This subroutine is used with the GRDMET plotting program to obtain plots of a series of curves which are then compared to the data on $g_c$ and $\Sigma_c$.

```
C HOWARD PIELET 10-24-70 CRVXYQ SPECIAL VERSION FOR PLOTTING
C \((A-T)/(A-C))^{**B}
REAL FUNCTION CRVXYQ(T,NSECT,P)
DIMENSION P(1)
GO TO (1,2),NSECT
1 CRVXYQ=T
RETURN
2 A=P(1)
   B=P(2)
   C=P(3)
   CRVXYQ=\((A-C)/(A-T))^{**B}
RETURN
END
```
These Fortran IV functions were used by subroutine CRVXYQ and the macrosegregation program. GLMEH is the volume fraction liquid assumed by Mehrabian, Keane, and Flemings, $^{44}$ SIGMAD is the surface area per cm$^3$ in the dendritic region in the presence of channels, and SIGMA2 is the same, assuming that no channels are present.

```fortran
REAL FUNCTION GLMEH(T)
C  HOWARD PIELET  11-16-70  GLMEH  VERSION 1
  CL=CLALCU(T,647.0,4.5)
  GLMEH=(CL**(-1.206)-0.00339)/0.1606
RETURN
END

REAL FUNCTION SIGMAD(X,XTIPS,T)
C  HOWARD PIELET  11-22-70  SIGMAD  VERSION 1
REAL NDCM
  GC(T)=0.1/(647.1-T)
  GD(T)=(GLALCU(T)-GC(T))/(1.0-GC(T))
  IF(X.GT.XTIPS) SIGMAD=1.0
  IF(X.GT.XTIPS) RETURN
  NDCM=107.0*(XTIPS-X)**(-0.39)
  SIGMAF=4.0*NDCM
  SIGMAD=((1.0-GD(T)**0.6/0.807)*SIGMAF
G=GD(T)
IF(G.LT.0.3) SIGMAD=SIGMAF
RETURN
END

REAL FUNCTION SIGMA2(X,XTIPS,T)
C  HOWARD PIELET  11-29-70  SIGMA2  VERSION 1
C  VERSION OF SIGMAD WHICH ASSUMES GC=0.0
REAL NDCM
  IF(X.GT.XTIPS) SIGMA2=1.0
  IF(X.GT.XTIPS) RETURN
  NDCM=107.0*(XTIPS-X)**(-0.39)
  SIGMAF=4.0*NDCM
  SIGMA2=((1.0-GLALCU(T)**0.6/0.807)*SIGMAF
G=GLALCU(T)
IF(G.LT.0.3) SIGMA2=SIGMAF
RETURN
END
```
H.4 Program for conversion of data in dendritic regions

This program was used to calculate log (1/d) and log (θ).
SIGD2 = SIGMA * ((1.0 - FL)**EXP) / FLEDIV
KD2 = 0.24 * FL * FL * FL / (SIGD2 * SIGD2)
WRITE(6, 601) X, T, FLD, SIGD1, KD1, FL, SIGD2, KD2, GCHAN, NDCM,
1 LGLST, LGNDCM
WRITE(7, 701) X, T, FLD, SIGD1, KD1, GCHAN, NDCM,
1 LGLST, LGNDCM
1000 CONTINUE
   GO TO 1
500 FORMAT(12, 2X, 15A4/2F10.7)
5C1 FORMAT(F9.7, I3 , 8X, 2F10.7)
600 FORMAT(1HO, I2, 15A4/1X, 2F10.7/)
   1X, 'X, T, FLD, SIGD1, KD1, FL, SIGD2, KD2, GCHAN, NDCM' 
   2 /1X, 'LGLST, LGNDCM' /
601 FORMAT(4F10.3, E15.3, 2F10.3, E15.3, 2F10.3/2F10.3)
700 FORMAT(20X, 15A4)
701 FORMAT(4F10.3, E15.3, 2F10.3/2F10.3)
END
Data for the determination of $\log(1/\bar{d})$ and $\log(\theta)$. Distance from the chill, number of dendrite arms, trace length of channels, trace length of dendritic regions.

<table>
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<tr>
<th>$t$</th>
<th>$\bar{d}$</th>
<th>$\theta$</th>
<th>$1/\bar{d}$</th>
<th>$\theta$</th>
</tr>
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<td>0.0</td>
<td>1.0</td>
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***TABLE T(I),X(I) FOR HORIZONTAL INGOTS GOES HERE***

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<th>$\bar{d}$</th>
<th>$\theta$</th>
<th>$1/\bar{d}$</th>
<th>$\theta$</th>
</tr>
</thead>
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</tbody>
</table>

<table>
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<th>$\bar{d}$</th>
<th>$\theta$</th>
<th>$1/\bar{d}$</th>
<th>$\theta$</th>
</tr>
</thead>
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<tr>
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<td></td>
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<td></td>
</tr>
<tr>
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H. 5 Subroutine for permeability and flow

Most of the functions dealing with permeability and flow in an horizontally solidifying aluminum-4.5 wt pct copper ingot were collected in subroutine CRVXYQ which was used in the GRDMET plotting program to produce the computer plots shown in the text.

```
REAL FUNCTION CRVXYQ(T,NSECT,P)
C HOWARD PIELET 12-6-70 FUNCTIONS 25-26 ADDED, PKTUT CHANGED.
C AND FUNCTION 24 CHANGED.
C HOWARD PIELET 11-22-70 FUNCTIONS 13 AND 16-24 ADDED.
C HOWARD PIELET 11-17-70 CRVXYQ SPECIAL VERSION PINFILE
C DIMENSION P(1)
C STATEMENT FUNCTIONS
  DRF(T,CL)=-930.3*(RLALCU(T,CL)-RLALCU(647.0,4.5))
  GC(T)=0.1/(647.1-T)
  SIGMAC(T)=80.0/(648.6-T)
  GD(T)=(GLALCU(T)-GC(T))/(1.0-GC(T))
  PKC(T)=0.24*GC(T)**3/SIGMAC(T)**2
  PKD(T,X)=0.24*GD(T)**3/SIGMA2(X,4.629,T)**2
  PKTOT(T,X)=0.24*GLALCU(T)**3/SIGMA2(X,4.629,T)**2
  FKT(T)=3.0E-7*GLALCU(T)**2
  V(T,CL,X)=DRF(T,CL)*PKTOT(T,X)/ALCUMU(T,CL)
C
  GO TO (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,
1, 23, 24, 25, 26, NSECT
1 CRVXYQ=T
   RETURN
2 CRVXYQ=PTABL1(T)
   RETURN
3 CRVXYQ=PTABL2(T)
   RETURN
4 CRVXYQ=FLALCU(T,647.0)
```
RETURN
CRVXYQ=GLACU(T)
RETURN
CRVXYQ=GLMEH(T)
RETURN
CRVXYQ=CLACU(T,647.0,4.5)
RETURN
CL=CLACU(T,647.0,4.5)
CRVXYQ=RLACU(T,CL)
RETURN
CL=CLACU(T,647.0,4.5)
CS=0.171*CL
CRVXYQ=RSLACU(T,CS)
RETURN
CL=CLACU(T,647.0,4.5)
CRVXYQ=ALCUMU(T,CL)
RETURN
CL=CLACU(T,647.0,4.5)
CRVXYQ=DRF(T,CL)
RETURN
CL=CLACU(T,647.0,4.5)
DRFMU=DRF(T,CL)/ALCUMU(T,CL)
CRVXYQ=DRFMU
RETURN
CL=CLACU(T,647.0,4.5)
X=XHTAB(T)
CRVXYQ=V(T,CL,X)
RETURN
CRVXYQ=XHTAB(T)
RETURN
CRVXYQ=XVTAB(T)
RETURN
CRVXYQ=GC(T)
RETURN
CRVXYQ=GD(T)
RETURN CRVXYQ = SIGMAC(T)
19    RETURN X = XHTAB(T)
20    RETURN CRVXYQ = SIGMA0(X, 4.629, T)
21    RETURN CRVXYQ = PKC(T)
22    RETURN X = XHTAB(T)
23    RETURN CRVXYQ = PKD(T, X)
24    RETURN X = XHTAB(T)
25    RETURN CRVXYQ = PKTJT(T, X)
26    RETURN CRVXYQ = FKTJT(T)
27    RETURN CL = CLACU(T, 647.0, 4.5)
28    RETURN CRVXYQ = V(T, CL, X) * (CL - 4.5) * RLACU(T, CL) * (-1.0)
29    RETURN X = XHTAB(T)
30    RETURN CRVXYQ = SIGMA2(X, 4.629, T)
31    RETURN A = P(1)
32    RETURN GL = EXP(2.303 * T)
33    RETURN ALOGK = ALOG10(GL * 3 / (1.0 - GL) ** 1.2) + A
34    RETURN CRVXYQ = ALOGK
35    END
BIBLIOGRAPHY


5. Ref. 2, p. 293.


32. Ref. 2, p. 178.


49. ibid, p. 49.


52. Ref. 48, p. 79.


70. B. Gray: J. I. S. I., 1944, No. III, p. 5P.


Ref. 47, p. 27.


Ref. 81, p. 46.

Ref. 81, pp. 126-130.


K. A. Jackson and C. Elbaum: this movie is available on loan from the Gordon McKay Library at Harvard University.

J. Wright: M.I.T., Cambridge, Massachusetts.

A. Campagna: M.I.T., Cambridge, Massachusetts.


E. B. Roberts: M.I.T., Cambridge, Massachusetts.

Ref. 47, p. 4 and pp. 168-169.

Ref. 47, p. 19.

Ref. 47, p. 180.
**BIOGRAPHY**

The author's grandparents came to America from Russia and Lithuania. His grandfather began as a junk dealer with a cart and horse. His father's family was in the building wrecking and scrap iron business by the time the author was born on November 13, 1942, in Chicago, Illinois. His development as a metallurgist is both an extension of his secular tradition and an affirmation of the American experience.

The author graduated from Austin High School in Chicago in 1959. He received a B.S. degree in Metallurgy from M.I.T. in 1963, and an M.S. degree in Metallurgy from Columbia University in 1966.


The author and his wife, Barbara, have two sons, Josh (Yaakov) and Alan (Eliezer).

The author is a member of the Society of Sigma Xi, and a joint student member of the ASM and the AIME.