INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
ROEHRIG, Frederick Karl, 1942-
EFFECT OF FIELD-FREEZING ON SOME TIN-
BISMUTH AND TIN-ANTIMONY ALLOYS UNDER
VARIOUS DEGREES OF LIQUID CONVECTION.

The Ohio State University, Ph.D., 1976
Engineering, metallurgy

Xerox University Microfilms, Ann Arbor, Michigan 48106
EFFECT OF FIELD-FREEZING ON SOME TIN-BISMUTH AND TIN-ANTIMONY ALLOYS UNDER VARIOUS DEGREES OF LIQUID CONVECTION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Frederick Karl Roehrig, B.S., M.S., P.E.

* * * * *

The Ohio State University
1976

Reading Committee:
J. P. Hirth
G. Meyrick
D. A. Rigney

Approved By

D. A. Rigney

Adviser
Department of Metallurgical Engineering
ACKNOWLEDGEMENTS

The author wishes to extend his appreciation to Professors J.P. Hirth, G. Meyrick, and D.A. Rigney for sitting as the reading committee and for their willingness to serve on the final oral examination committee. The author is indebted to Professor Meyrick for helping to overcome some of the experimental problems that plagued the project in the beginning, his suggestions are greatly appreciated. To Professor D.A. Rigney, the author's adviser, special thanks are extended for his patience, faith, numerous helpful discussions and suggestions and his friendship. Recognition is due to the Machine Shop personnel of the Metallurgy Department for constructing the mechanical equipment used in this project. Also thanks are due to Mr. George Strabel of Battelle-Columbus Laboratories for assistance in the electron microprobe analysis.

Finally the author wishes to acknowledge the contribution made to this project by his wife, Karla, who lent support and encouragement throughout its duration. On more than one occasion, she assisted in performing some of the experiments and did an excellent job of typing the manuscript. The author's association with her has been very enriching.

This project was supported by a grant from the National Science Foundation which is gratefully acknowledged.
VITA

June 25, 1942 ......................... Born - Peoria, Illinois

1965 ................................. B.S., Mechanical Engineering, Bradley
University, Peoria, Illinois

1965-1966 ......................... Graduate Research Associate, Department
of Metallurgical Engineering, University
of Illinois

1967 ................................. M.Sc., Metallurgical Engineering, University
of Illinois

1966-1972 ......................... Research Metallurgist, Battelle Memorial
Institute, Columbus, Ohio

1972-1976 ......................... Graduate Research Associate, Department
of Metallurgical Engineering, The Ohio
State University, Columbus, Ohio

1976-present ....................... Senior Scientist, Owens Corning Fiberglas, Granville, Ohio

PUBLICATIONS

Roehrig, F. K. and Wright, T. R., Journ. Vacuum Sci. and Tech., 9, 1368,
1972.
Las Vegas, Nevada
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>II. Background</td>
<td>5</td>
</tr>
<tr>
<td>III. Experimental Equipment and Procedures</td>
<td>38</td>
</tr>
<tr>
<td>IV. Experimental Results and Discussion</td>
<td>71</td>
</tr>
<tr>
<td>V. Conclusions and Recommendations</td>
<td>120</td>
</tr>
<tr>
<td>APPENDIX</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>122</td>
</tr>
<tr>
<td>B</td>
<td>136</td>
</tr>
<tr>
<td>C</td>
<td>141</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>150</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table I. List of "characteristic distances" and their degree of convective liquid mixing. ...................... 14
Table II. "Characteristic distances" $\delta_{\text{int}}$ and $\delta_{\text{sol}}$ ...................... 74
Table III. "Characteristic distances", $\delta_{\text{int}}$ and $\delta_{\text{sol}}$ for AC FF experiments .......................... 108
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Advancing interface and solute profile.</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Element outlined by $x'$ and $x' + dx'$ and regions of mass balance.</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Verhoeven's variation of the critical Rayleigh number</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>Effective distribution coefficient as a function of the relative field flux</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>The Mullins and Sekerka $\frac{\delta}{\delta}$ function plotted against $\omega$.</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>The capillary filling apparatus</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>The field-freezing apparatus</td>
<td>49</td>
</tr>
<tr>
<td>8</td>
<td>The primary and auxiliary furnaces</td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td>Details of the cooling chamber</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>The gas train</td>
<td>58</td>
</tr>
<tr>
<td>11</td>
<td>The longitudinal magnetic flux density.</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
<td>Transverse magnetic flux density.</td>
<td>61</td>
</tr>
<tr>
<td>13</td>
<td>Arrangement of Lucalox specimen capillary and extension capillaries.</td>
<td>63</td>
</tr>
<tr>
<td>14</td>
<td>The swage-lock &quot;T&quot; fitting and top extension capillary</td>
<td>65</td>
</tr>
<tr>
<td>15</td>
<td>The general as-cast dendritic microstructure</td>
<td>72</td>
</tr>
<tr>
<td>16</td>
<td>Sn-Bi, $H = 0$, $CD = 0$ A/cm², $\bar{R} \equiv 1.4 \mu m/sec.$</td>
<td>73</td>
</tr>
</tbody>
</table>
Figure 17. Sn-Sb, \( H = 0 \), \( CD = 0 \) A/cm\(^2\), \( R \approx 1.0 \) \( \mu \)m/sec. .... 76
Figure 18. Sn-Bi, \( H \approx 300 \) Gauss, \( CD = 0 \) A/cm\(^2\), \( R \approx 1.3 \) \( \mu \)m/sec. 78
Figure 19. General longitudinal microstructure of an Sn-Bi alloy. ... 80
Figure 20. Twinned longitudinal microstructure of a directionally solidified Sn-Bi alloy ....... 81
Figure 21. Twinned longitudinal microstructure of directionally solidified Sn-Bi alloy showing a stable grain boundary. ... 82
Figure 22. Interfacial breakdown ... 83
Figure 23. General longitudinal microstructure indicating CS breakdown in an Sn-Bi alloy. .... 84
Figure 24. Transverse microstructure of Sn-Bi alloy that exhibited streaks .... 85
Figure 25. Transverse microstructure of Sn-Bi alloy that exhibited no streaks. .... 87
Figure 26. The CS criterion of Tiller et al. as a function of composition for an Sn-Bi alloy. .... 88
Figure 27. The instability parameter of Mullins and Sekerka plotted against spatial frequency .... 90
Figure 28. Transverse microstructure of Sn-Bi alloy showing nodes .... 91
Figure 29. Sn-Bi, \( H = 0 \), \( CD \approx 485 \) A/cm\(^2\), \( +VE \), \( R \approx 1.3 \) \( \mu \)m/sec. 94
Figure 30. Sn-Bi, \( H = 0 \), \( CD \approx 485 \) A/cm\(^2\), \( +VE \), \( R \approx 1.1 \) \( \mu \)m/sec 96
Figure 31. Sn-Bi, \( H \approx 300 \) Gauss, \( CD \approx 485 \) A/cm\(^2\), \( +VE \), \( R \approx 1.7 \) \( \mu \)m/sec 97
Figure 32. Sn-Bi, $H = 300$ Gauss, $CD \approx 485$ A/cm$^2$, +VE; $R \approx 1.3$ um/sec. .................................................. 98

Figure 33. Sn-Bi, $H = 0$ Gauss, $CD \approx 485$ A/cm$^2$, +VE; $R \approx 0.93$ um/sec ................................................................. 100

Figure 34. The effective distribution coefficient plotted against solidification speed for an Sn-Bi alloy. .................................................. 102

Figure 35. Sn-Sb, $H = 0$ Gauss, $CD \approx 485$ A/cm$^2$, +VE; $R \approx 1.1$ um/sec ......................................... 104

Figure 36. Typical longitudinal microstructure of Sn-2 atom% Sb .............................................. 106

Figure 37. Sn-Sb, $H = 0$ Gauss, $CD \approx 485$ A/cm$^2$, +VE; $R \approx 1.0$ um/sec......................................... 107

Figure 38. Sn-Bi, $H = 0$ Gauss, $CD \approx 485$ A/cm$^2$, AC, $R \approx 1.3$ um/sec. .................................................. 109

Figure 39. Sn-Bi, $H \approx 300$ Gauss, $CD \approx 485$ A/cm$^2$, AC, $R \approx 1.2$ um/sec. .................................................. 111

Figure 40. Sn-Bi, $H \approx 300$ Gauss, $CD \approx 485$ A/cm$^2$, +VE; $R = 0$ um/sec. .................................................. 113

Figure 41. Sn-Bi, $H \approx 300$ Gauss, $CD \approx 485$ A/cm$^2$, +VE; $R = 0$ um/sec. .................................................. 114

Figure 42. The microstructure of the quenched solid/liquid interface for the ET of an Sn-2 atom% Bi alloy. .................................................. 116

Figure 43. The microstructure of the quenched solid/liquid interface for the ET of an Sn-2 atom% Bi alloy with Bi driven toward the solid. .......... 117

Figure 44. The static equilibrium position (a), displacement of the mass (b), free-body diagram (c), and resultant motions upon release of the mass (d) .......... 125

Figure 45. The effect of viscous damping upon the motion of the spring/mass system. .......... 126

Figure 46. The transmissibility ratio, TR as a function of the frequency ratio .......... 130

Figure 47. The relative displacements for a mass excited by a sinusoidal displacement .......... 132

Figure 48. Position of SR-4 strain gage on cantilever beam. .......... 134
Figure 49. Log of normalized critical Rayleigh number under magnetic field conditions plotted against log of Q parameter. ............................ 139

Figure 50. The spatial arrangement of the magnet coil, furnace cooling chamber and heat pipe "ears". ......................... 143

Figure 51. Arrangement of magnet wire, copper girdle, mullite tube, asbestos retainer rings and wooden jig fixtures 144

Figure 52. The coil and the BH-206 Hall probe used to characterize magnetic flux .................................................. 147

Figure 53. The calibration curve of Hall voltage with flux density for a Hall current of 200 mA ..................... 148
CHAPTER I. INTRODUCTION

Atomic species in an alloy can be spatially arranged in various configurations by the imposition of various "driving forces" or potential gradients placed on the system. Such "driving forces" as chemical potential gradients, pressure gradients, temperature gradients, or electrical potential gradients can induce atomic rearrangement in the solid or liquid state. Electrical potential gradients can cause spatial rearrangement of atomic species in solid or liquid alloys from the effects of the interaction of the migrating charge species (e.g., electrons) with the screened ions of the alloy. This phenomenon is called electromigration, electrodiffusion, or electrotransport.

When an electric field is applied to an alloy at constant temperature, the constituent ions experience a direct force, $F_{\text{ion}}$, due to the applied field, and an indirect force, $F_{\text{ele}}$, due to the "electron wind" effect. It is now believed (1) that the latter force is the dominant one for electrotransport in most metallic systems. For the case of a liquid binary alloy, the two atomic species will respond differently to the imposed electric field during an electrotransport (ET) experiment; thus, the end result of an ET experiment is that one species will migrate with the electrons toward the positive electrode and, by volume conservation, the other species will be displaced toward the negative
electrode. Such spatial separation suggests the potential for obtaining purification of an alloy by using ET; in fact, Drakin (2) was the first to suggest this application of electrotransport. While purification by ET could also be done in the solid state, the mobilities of most species are too low to allow for separations in reasonable time periods (3). However, the application of ET for the removal of rapidly diffusing interstitial contaminants in solids has been demonstrated by various investigators (3,4,5).

Aside from the potentially beneficial effects of ET, severe detrimental effects attributed to electrotransport have been encountered in thin film integrated circuit devices (6). Recently, extensive research has led to improved understanding and control of these phenomena (7-9).

For liquid alloys, purification by electrotransport alone has not been very successful, primarily because convective mixing destroys the compositional profile developed by ET (unless precautions are taken to prevent convection) (10). Also the process is inherently inefficient. For example, it has been estimated that the ratio of mobile electrons to mobile ions in liquid alkali alloys undergoing ET is of the order of $10^4$ which implies a low efficiency (11). However, the coupling of ET with either unidirectional solidification or zone refining (collectively called field-freezing) has shown promise as a purification tool. Angus, et al. (12) were the first to suggest field-freezing (FF) as a purification technique, and numerous articles have since appeared in the literature concerning various aspects of field-freezing (13-20). The objective of most of the theoretical analyses performed in relation to
FF has been to relate the compositional profile obtained in the solidified solid to the ET phenomena occurring in the liquid under various physical conditions (freezing speed and mode, electric field strength and polarity, and stirring or lack thereof). Usually, a relationship between these physical conditions and the effective distribution coefficient ($k_{\text{eff}} = C_s/C_1$ (bulk)) is reported (13, 16) with local equilibrium at the solid/liquid interface being assumed. Potential applications of FF would be in removing contaminants where $k_0 = 1$, leveling out trace elements where $k_0 \geq 1$, removing a contaminant without disturbing a dopant, and possibly altering eutectic morphology for composites.

Since the occurrence of liquid convection (21) during FF has been a problem, and since the main effect of ET in purification may be in the quiescent boundary layer adjacent to the solid/liquid interface, then if convection could be controlled in the melt during a FF experiment, the full potential of ET could be realized in its effect on solute distribution during solidification. This goal of performing field-freezing under controlled convection was one of the objectives of this project. Specifically, the project was concerned with 1) investigating the effect of convection control upon the solute compositional profile in a unidirectionally solidified alloy undergoing electrotransport (alloys with $k_0 < 1$ and $k_0 > 1$ where $k_0 = C_s/C_1$ (interface) were investigated), 2) attempting to obtain quantitative verification of the Pfann-Wagner (13) relationship for the effective distribution coefficient (if their boundary conditions pertained), and 3) examining the relative contributions of ET scattering parameters of the
two solutes in the same solvent undergoing separate FF experiments.
CHAPTER II. BACKGROUND

A. Electrotransport

While the application of an electric field (E) of a given polarity and strength to a binary liquid alloy will result in spatial separation of the constituent ions, in order to use this phenomenon one must know which ion will be migrating toward the positive or negative electrode. The following paragraphs will briefly discuss some of the highlights of the more recent electrotransport (ET) models used to explain the migration directions of ions undergoing ET. For further details the reader is referred to the literature (1,3,24).

Early work on ET models placed emphasis on the direct field effect (24) with experimental results being given as the net force on the ith ion, \( F_i = eEZ_i^* \), where \( Z_i^* \) is an "effective valence" of the migrating ion, and \( e = |e| \) the magnitude of electronic charge. These "effective valence" values were reported to vary from fractions to several hundred (3). However, later ET work had shifted the emphasis from the direct field effect to the "electron wind" effect (1) since electronic screening would effectively decrease the former (25, 26).

In pursuing studies of the "electron wind" effect, Epstein and Paskin (26) considered electrotransport in liquid alloys as being a scattering problem involving a competitive momentum transfer between the
conduction electrons and the constituent ions. Effectively, the ionic component with the larger scattering cross-section would migrate with the electrons to the anode while the other component (for a binary) would be displaced to the cathode. Epstein and Paskin proposed that the strength of the scattering cross-section be taken as proportional to the resistivity of each pure liquid metal component, and used this approach to predict migrational directions. This simple rule worked for several systems but has failed for others and it could not explain the reversals in migrational direction at specific compositions occurring in some liquid alloy systems (27).

Subsequent work on ET scattering by Epstein and Dickey (27) has treated the scattering with quantum mechanics by considering the scattering center to be a spherically symmetrical potential with the total wave function in the asymptotic limit expressed in the form

$$\psi \approx e^{i \mathbf{k} \cdot \mathbf{r}} + f(\theta)/r \left( e^{i kr} \right),$$

where the first term is the incident plane wave and the second is a spherical wave modulated by the scattering amplitude $f(\theta)$, where $f(\theta) = (1/2i\lambda_k) \sum_{l=0}^{\infty} (2l+1)(e^{2i\lambda_k} - 1) P_l(\cos \theta)$. The scattering angle is $\theta$ (is twice the value of the Bragg angle, $\theta_B$), $\lambda_k$ is the partial wave phase shift evaluated at the Fermi surface, $k$ is the wave vector, and $P_l(\cos \theta)$ is the Legendre polynomial. The differential scattering cross-section is related to the scattering amplitude by $S = |f(\theta)|^2$. The relative magnitude of $S$ for the constituents in an alloy dictates which specie will drift to the anode, i.e., the specie with the larger $S$ goes with the electrons.

Using the differential scattering cross-section for the case of
back-scattering (\( \Theta = \pi \)) where one would expect most of the momentum exchange to occur, Olsen, et al. (11) have successfully predicted the compositional dependence of S and obtained fairly good cross-over compositional positions for the liquid Na-K system.

Recently, Stroud (30) has extended this work using pseudopotential theory to obtain the resistivity of an ionic specie in a liquid metal alloy for both monovalent and polyvalent components. The results are generally good, except that reversals in migration direction are not accurately predicted.

The significance of these approaches to ET theory is that using the compositional dependence of S, the relative migrational response to ET (or field-freezing) of various solutes in a given solvent can be estimated (31), and a computer simulation of an ET compositional profile can be calculated as was done by Olsen, et al. (32).

For the systems chosen for this project, both Bi and Sb were predicted (31) to have the same approximate resistivity in liquid Sn over the compositional range selected. Therefore, it could be possible to make a qualitative assessment of the relative contributions between ET (through the differential scattering cross-section parameter S) and \( k_0 \) in a field-freezing experiment under controlled liquid convection since for a dilute Sn-Bi alloy, \( k_0 < 1 \), and for a dilute Sn-Sb alloy, \( k_0 > 1 \).

B. Unidirectional Solidification and Convection Control

1. Unidirectional Solidification. The following discussion reviews some concepts in unidirectional solidification of alloys under various degrees of convection as it pertains to this project.
Nucleation will not be discussed since the field-freezing (FF) experiments performed in this program always started with an established solid/liquid interface. The solid compositional profile will be obtained for the cases of 1) no liquid convective mixing, resulting in an initial transient and steady-state solute boundary layer profile, and 2) complete liquid convective mixing. These two extreme cases will be pertinent to the evaluation of the field-freezing experiments encountered in this work. For a more complete treatment, the reader should consult the literature (33-37).

Case 1: Convective Mixing. For an alloy system where the solute lowers the liquidus, the equilibrium distribution coefficient is

\[ k_0 = \frac{C_S}{C_L^i} < 1, \quad (C_L^i = \text{solute composition in the liquid at the interface}), \quad \text{and} \quad C_S = \text{solute composition in the solid at the interface}), \]

unidirectional solidification results in the freezing solid rejecting the solute at the interface. In order to obtain a quantitative relationship between the solute composition in the freezing solid and the fraction solidified, the following assumptions are made: 1) local equilibrium pertains at the solid/liquid interface, 2) a planar interface exists resulting in no transverse solute migration, 3) convective mixing as well as diffusion occurs in the liquid, 4) no solid state diffusion occurs, and 5) negligible change in density on going from the liquid to the solid occurs.

Consider the composition profile shown in Figure 1 (a). When the interface advances a distance \( dx \), solute is rejected at the interface and is uniformly mixed in the remainder of the liquid. A mass
Figure 1. In (a), an advancing interface is shown with solute mass balance; in (b), the solute profile in the solid and in the quenched liquid is shown.
balance yields $dx A_S(C_L - C_S) = A_L(C - x) dC_L$. Assuming a uniform cross-sectional area, $A_S = A_L$, and rearranging after substituting for $C_S$ and $dC_S$, one obtains 

$$\frac{CL}{C_0} \int \frac{dC_L}{C_L(1 - k_0)} = \frac{x}{L} \int dx/(L-x).$$

Solving for $C_L(g)$ where $g$ is the fraction solidified = $x/L$, $C_L(g) = C_0(1 - g)^{k_0 - 1}$, where $C_0$ is the initial alloy composition. The solid composition profile is given by substituting for $C_L(g) = k_0^{-1}C_S(g)$. $C_S(g)$ is equal to $C_0k_0(1 - g)^{k_0-1}$ and is schematically shown in Figure 1 (b). Thus, for $k_0 < 1$, and extensive portion of the unidirectionally frozen alloy is lowered in solute content. For the case of $k_0 > 1$, just the opposite type of profile would be obtained.

**Case 2: No Convective Mixing.** For an alloy unidirectionally solidified with no convective mixing in the liquid and $k_0 < 1$, the rejected solute at the solid/liquid interface builds up until a steady-state is reached when the build-up is balanced by solute diffusion into the liquid. Thus, a solid compositional profile for this case would contain an initial transient which transforms into a steady-state profile where the composition of the solidifying solid is the same as the "bulk" liquid.

In obtaining a quantitative relationship between the freezing solid and the fraction solidified for the initial transient, nearly the same assumptions are prevalent as before, except that diffusion of the solute into the liquid is the mass transport mechanism operative. The following derivation for the initial transient and the steady-state profile follows the approach of Tiller, et al. (38); a more detailed treatment of the initial transient was done by Smith, et al. (39), but it differs little from Tiller's results. However, before continuing, an
expression relating the compositional profile of the solute in the steady-state solute boundary layer is needed.

From Tiller, a steady-state is assumed in the solute boundary layer adjacent to the solid/liquid interface and Fick's second law on an elemental section can be written as \( \frac{\delta C_L}{\delta t} = 0 = -\frac{\delta}{\delta x'}(\sum J_i) \), where \( J_i \) refers to the separate fluxes occurring at the boundaries of the section. In Figure 2 part (a) the flux of solute going into the element at position \( x \) is \(-D(dC_L/dx')x\), and that flux going out at \( x' + dx' \) is \(-D(dC_L/dx')(x' + dx')\). Therefore, the net flow into the section is \( D(d^2C_L/dx'^2) \) per unit volume. With the origin remaining at the interface, as freezing progresses, the liquid distribution essentially moves past the interface at \( R \) (cm/sec) and therefore the net flow of solute out of the same volume element is \( R(dC_L/dx') \). At steady-state, \( D(d^2C_L/dx'^2) + R(dC_L/dx') = 0 \) where \( x' \) is zero at the interface and is positive into the liquid. The relevant boundary conditions are: 1) \( C_L = C_0 \) at \( x' = 0 \), and 2) \( C_L = C_0/k_0 \) at \( x' = 0 \), that is, local equilibrium is assumed. The equation can be written as

\[
\int \frac{d(dx')}{(dC/dx')} = -\frac{R}{D}\int dx', \text{ integrating implicitly,}
\]

\[
\ln(dC/dx') = -(R/D)x' + I_1, \text{ or } (dC/dx') = I_1 e^{-Rx'/D}.
\]

Integrating implicitly a second time, \( C_L(x') = I'_1(-D/R)e^{-Rx'/D} + I_2 \).

Applying boundary condition 1), \( C_L(\infty) = C_0 \), this gives \( I_2 = C_0 \). Then, \( C_L(x') = C_0 - I'_1(D/R)e^{-Rx'/D} \), and applying boundary condition 2), \( C_L(0) = C_0/k_0 \), this gives \( C_0/k_0 = C_0 - I'_1(D/R) \), or \( I'_1 = (R/D)C_0(k_0-1/k_0) \), thus \( C_L(x') = C_0(1 + ((1 - k_0)/k_0) e^{-Rx'/D}) \). This expression for the
Figure 2. In (a), the element outlined by $x'$ and $x' + dx'$ is shown; in (b), the regions of mass balance during the development of the initial transient is shown.
solute compositional profile in the solute boundary layer gives a "characteristic distance", $\delta_{\text{sol}} = D/R$ where the liquid composition drops to 57% of its original value. Thus, based on this model, measurement of the "characteristic distance", $\delta_{\text{sol}}$, for the experimentally obtained compositional profile can give information on the degree of convective mixing in the liquid. In this expression $D$ is the solute diffusion coefficient.

For the initial transient compositional profile without liquid convective stirring, Tiller assumed that the "rate of approach to steady-state is proportional to the deviation from steady-state", i.e., for the initial transient developing as shown in Figure 2 part (a)

$$\frac{d}{dx}(C_0 - C_S) = -\gamma(C_0 - C_S),$$

integrating and using the boundary conditions that as $x \to \infty$, $(C_0 - C_S) \to 0$, or $C_S = C_0 - Ae^{-\gamma x}$. Also, when $x = 0$ (at the solid/liquid interface), local equilibrium is assumed and $C_S = C_0k_0$, then $A = C_0(1 - k_0)$; therefore, $C_S = C_0(1 - (1 - k_0)e^{-\gamma x})$.

The proportionality constant $\gamma$ was obtained by considering a mass balance as shown in Figure 2 part (b), i.e., the solute rejected (proportional to area $A_1$) by the solid/liquid interface as it advances into the liquid must go into building up the solute boundary layer (proportional to area $A_2$). The mass balance is

$$A_2 = \int_0^\infty [C_L(x') - C_0] \, dx' = A_1 = \int_0^\infty [C_0 - C_S(x)] \, dx,$$

but

$$C_L(x') = C_0 \left[1 - \frac{(k_0 - 1)/k_0}{e^{-Rx'/D}}\right]$$

and

$$C_S(x) = C_0 \left[1 - (k_0 - 1)e^{-\gamma x}\right].$$

Then

$$\left(C_0/D/R\right)\left(\frac{(k_0 - 1)/k_0}e^{-Rx'/D}\right) = \left(C_0/\gamma\right)(k_0 - 1)e^{-\gamma x} \left|_0^\infty\right.,$$

or
\( y = \frac{Rk_0}{D} \), then the initial transient compositional profile becomes

\[ C_S(x) = C_0 \left( 1 - (1 - k_0)e^{-\frac{Rk_0x}{D}} \right), \]

and a "characteristic distance" \( \delta_{\text{int}} = \frac{D}{Rk_0} \), defines where the freezing solid has reached 63% of its terminal value. Thus, again a comparison can be made with an experimentally determined \( \delta_{\text{int}} \) to ascertain the degree of liquid convection that had occurred during the experiment.

Table I summarizes the various "characteristic distances" encountered in unidirectional solidification experiments under different degrees of convective liquid mixing. By taking an appropriate value for the diffusion coefficient and the appropriate \( k_0 \) and \( R \), one can compute the desired "characteristic distance" and compare it to experimentally determined ones to ascertain the degree of liquid convective mixing occurring during the experiment.

<table>
<thead>
<tr>
<th>Stirring Conditions</th>
<th>&quot;Characteristic Distance&quot;</th>
<th>( \delta_{\text{int}} )</th>
<th>( \delta_{\text{sol}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Stirring</td>
<td>D/Rk_0</td>
<td>D/R</td>
<td>Negligible^a</td>
</tr>
<tr>
<td>Stirring</td>
<td></td>
<td>Negligible^a</td>
<td>Negligible^a</td>
</tr>
</tbody>
</table>

^a It is expected that some finite solute boundary layer would exist even for a case of vigorous stirring.

2. Convection Control. Discussions on the inhibition of convection in liquids with vertical, adverse temperature gradients usually
start with Rayleigh's original work (40) on explaining Bénard convection cells or Chandrasekhar's very comprehensive text (41).

The condition for occurrence of a quiescent fluid (no convection) is that the temperature and concentration gradients must be such that no buoyant forces tending to turn-over the fluid be stronger than viscous forces tending to oppose such motion. Rayleigh treated this instability problem for a thin fluid of infinite horizontal extent and found that convective motion did not begin until a dimensionless number called the Rayleigh number (Ra) involving the density gradient exceeded a critical value.

Verhoeven (42) has extended these concepts to liquid metals in capillary containers. He analyzed separately the cases for the onset of convection by an adverse temperature gradient and by an adverse solute concentration gradient for the boundary conditions prevalent with capillary-type experiments. In order to extend these calculations to capillary geometries, the aspect ratio (container height to radius ratio) was changed from essentially zero for Rayleigh's case to essentially infinity for Verhoeven's. Figure 3 schematically shows his results (43). These results apply for either an adverse temperature gradient or an adverse solute concentration gradient and can be used as discussed by Verhoeven to predict the critical gradients (for either case) for the onset of convection.

Using the following expression for the Rayleigh number,
\[ R_t = -(\alpha \nabla T^4 / \nu K) \], and a value of 68 for the critical Rayleigh number computed for the case of antisymmetric flow in a capillary of
Figure 3. Verhoeven's variation of the critical Rayleigh number for a vertical tube is schematically shown as a function of tube aspect ratio. When $H/R = 0$, the value of $(Ra)_{crit}$ approaches $10^9$.4.
essentially infinite aspect ratio (43), Verhoeven estimated that for a pure tin melt in a 1mm or 2mm diameter capillary a critical temperature gradient of -32,800 °C/cm and -2,040 °C/cm, respectively would be needed (42). In the expression, $\nabla T$ is the vertical temperature gradient, $r$ is the capillary radius, $K$ is the thermal diffusivity, $\nu$ is the kinematic viscosity, $g$ is the gravitational acceleration, and $\alpha$ is the thermal expansion coefficient ($\alpha = -1/\rho_0(d\rho/dT)$). Clearly, in experiments using a positive thermal gradient, it is unlikely that thermal induced convection would occur.

The case for alloys may not be so favorable, since during solidification in a vertical mode, solute induced convection could occur resulting from the density differences between the solute and the solvent. Verhoeven (42) also treated this case using the following form of the Rayleigh number: $R_s = -(g \alpha' \nabla C r^4 / \nu D)$, where $\alpha'$ is the solute expansion coefficient ($\alpha' = -1/\rho_0(d\rho/dC)$) with the solute selected so that $\alpha' > 0$. $D$ is the solute diffusion coefficient and the other terms are as given above. Verhoeven then estimated the critical solute concentration gradient needed for the onset of convection in the Sn-Bi system, where $\alpha' = 0.22$ per atom fraction Bi at 500 °C. For the capillary sizes of 1mm and 2mm, the critical concentration gradients over a one centimeter length were estimated to be approximately -3900ppm and -253 ppm, respectively. Obviously, in considering the factors that contribute to convective mixing, one must be aware of the potential for solute induced convection whenever a density difference exists between the solute and the solvent.
Various experimental techniques have been tried to control convection in solidification experiments (36), and among those reported to be successful is the use of a magnetic field. An early application of a DC magnetic field to solidification experiments was that of Pfann and Dorsi (44) who tried to increase stirring in the molten zone of a horizontal zone refiner. Their work used the Lorentz force to achieve stirring by passing a direct current through the specimen with a transverse magnetic field parallel to the gravitational potential vector. Similar results were obtained by Cole and Bolling (45) who applied a transverse DC magnetic field of ~1,000 Gauss across a horizontal boat of Sn(1) and passed a direct current of ~140 amps through the specimen; the enhanced convection was attributed to the Lorentz force.

Uhlmann, Seward, and Chalmers (46) attempted to inhibit convection during casting of Al-Cu alloys. Their experiments consisted of impressing a transverse 2,000 Gauss DC magnetic field onto a vertical crucible and observing the resultant grain morphology. The observed columnar grain structure indicated that convective mixing was inhibited by the magnetic field.

Utech and Flemings (47) reported inhibition of convection in an InSb melt by the application of a vertical DC magnetic field across the horizontal boat. They observed an inhibiting effect at a field strength of 1,300 Gauss. In another paper by the same authors (48) they reported on the elimination of solute banding upon the application of a vertical DC magnetic field across a horizontal Al-Cu melt undergoing unidirectional solidification. In this work, an effect was
observed at a flux density of 250 Gauss. Convection was followed by observing the presence or absence of temperature oscillations in the melt as well as observing solute banding (or lack thereof) in the solidified ingot.

From the above brief review of the literature, it appears that convection can, under certain conditions, be inhibited by a DC magnetic field. However, in the work reported above, the geometry has been such that the field was always transverse to the direction of solidification, and for the cases of an additional complication involving an applied direct current, the Lorentz force gave stirring.

A very thorough treatment of the inhibition of the onset of convection in an electrical conductor caused by an adverse temperature gradient in a vertical DC magnetic field was done by Chandrasekhar (41,49). A brief review of Chandrasekhar's paper is given in Appendix B along with its application to this project. Essentially, Chandrasekhar obtained the critical Rayleigh number for the onset of convection in an electrically conducting medium for various boundary conditions and relative alignments of the DC magnetic field vector with the gravitational potential vector. For liquid mercury at room temperature, he estimated that the application of a magnetic field of 1,000 Gauss would give a critical Rayleigh number of 4,018 for the boundary condition of one bounding surface closed and the other open.

The application of a vertical magnetic field to a capillary containing a liquid conductor for the prevention of the onset of convection has not been reported in the literature. The closest arrangement
reported in the literature was work done by Nakagawa and Goroff (50) who reported the inhibition of convection in Hg(l) in a container with an aspect ratio of .12. The fluid was heated from below and an impressed vertical DC magnetic field of \(-1,200\) Gauss was used. They did not report the threshold field.

C. Field-Freezing

Angus, Ragone, and Hucke (12) were the first to suggest the application of a direct current to a specimen undergoing unidirectional solidification for the purpose of enhanced purification. In their paper, they suggested that an additional electrotransport flux superposed on the ordinary diffusion flux could lead to enhanced segregation and could relieve interface stability problems caused by constitutional supercooling. They obtained a relationship between the effective distribution coefficient, \(k_e\), and the applied electric field, \(E\), and the other standard parameters by assuming a steady-state condition at the moving solid/liquid interface. However, their final equation is in error and therefore, their conclusion of not being able to reduce \(k_e\) below \(k_0\) is suspect.

In a paper on field-freezing (a word coined by the authors), Pfann and Wagner (13) obtained a valid relationship between the effective distribution coefficient and the electric field for a dilute solution. In their derivation, they took the superposed solute speed due to electrotransport as given by \(f' = \Delta \mu E\) where \(\Delta \mu\) is the differential electric mobility between the solute and the solvent. By setting up a flux balance at the moving solid/liquid interface, and assuming steady-state
with the two boundary conditions of (1) \( C_L(x) = C_0 \) at \( x = \delta \) (which presupposes some convection) and (2) \( C_L(x) = C(0) \), at \( x = 0 \) (the solid/liquid interface), Pfann and Wagner obtained the following expression for the effective distribution coefficient:

\[
 k_e = \frac{k_0(1 + f'/f)}{k_0 + (1 + f'/f - k_0)\exp (1 + f'/f)(-f\delta/D)}
\]

where \( f \) is the solidification rate (cm/sec), \( k_0 \) is the equilibrium distribution coefficient, \( D \) is the solute diffusion coefficient (cm²/sec), and \( \delta \) is the solute boundary layer thickness (cm). For an alloy system with \( k_0 < 1 \), driving the solute into the liquid changes the sign on the \( f'/f \) term and consequently \( k_e \) is lowered, thereby resulting in "field-aiding". The "field-opposing" case has a positive \( f'/f \) for a solute that goes to the anode, i.e., the solid end of the specimen.

Pfann and Wagner's equation is schematically shown in Figure 4, where for a given electric field strength and polarity, the effective distribution coefficient can theoretically be made to be smaller than \( k_0 \) if the factor \( f\delta/D \) is increased. Increasing \( f\delta/D \) essentially means either increasing \( f \) and/or \( \delta \) within limits of the avoidance of constitutional supercooling. The authors did not report any experimental verification of the equation.

A more detailed analysis of field-freezing was done by Verhoeven (16) who treated the more general case of a concentrated solution. His derivation starts out by assuming a superposition of solute speed due to electrotransport upon the normal diffusion and bulk flow speeds at the interface and initially takes the differential mobility as the
Figure 4. The effective distribution coefficient is shown as a function of the relative field flux for two values of \( f\delta/D \) based on the Pfann-Wagner relationship. Negative values of \( f'/f \) denote "field-aiding".
speed difference between the solute and solvent at an arbitrary frame of reference per unit electric-field intensity. However, he then assumes ideal solution behavior which makes his results reduce to the Pfann-Wagner relationship. Also, Verhoeven's equation (V-12) is as follows:

\[
ke = \frac{k_0(1 + \alpha/R)}{k_0 + \left[1 + \alpha/R - k_0\right]\exp - \left[(1 + \alpha/R)\delta/\beta\right]}
\]

where \( \alpha = C_2\overline{V}_2U_1^2E \) and \( \beta = C_0\overline{V}_2D \). Here \( C_2 \) is the solvent concentration, \( \overline{V}_2 \) is the solvent partial molar volume, \( U_1^2 \) is the differential mobility, \( C_0 \) is the molar density, and \( D \) is the mutual diffusion coefficient. This expression does not follow directly from his prior equations, the sign of the \( \alpha/R \) term should be negative. Again his model assumes a finite amount of convection beyond the solid/liquid interface as was verified from his compositional profiles. Verhoeven's rather extensive convection in his FF work with an Sn-5 atom % Bi alloy was attributed to the Lorentz force induced stirring from his convex solid/liquid interface and was reported for both DC and AC cases. Since his capillary size was 5mm internal diameter, it is not surprising that he had extensive convection. Verhoeven obtained a qualitative verification of the Pfann-Wagner relationship which is rather interesting since the equation was derived for a planar interface, and his interfaces were not planar. Nevertheless, his results did suggest some control over \( k_e \) could be obtained with ET and that further improvement would probably come from extending the solute boundary layer by decreasing stirring. In another
paper by Verhoeven (51), he had observed that increasing the current
density resulted in increased convection with a levelling off of $k_e$.
This suggests again that FF may be more effective at lower current
density with controlled convection than at large current density with
increased convection.

Experimental work in FF was reported by Tougas and Hone (14) who
investigated a Sn-2 weight % Pb alloy. These authors used a horizontal
boat and a current density of 225 A/cm$^2$; the effective distribution
coefficient was obtained from the normal unidirectional solidification
expression for the complete mixing case. Their FF experiments were com-
pared to solidification with induction stirring and the resultant in-
crease in stirring for the FF case was attributed to the current density.
Although a better assessment of the effect of FF on purification should
have used an AC mode for a baseline instead of induction stirring, it is
well-known that extensive convection generally occurs in horizontal sol-
idification experiments (42) unless certain precautions are taken (52)
which the authors apparently ignored. Therefore, their results did not
indicate the effect of FF for purification in the Sn-Pb system.

Field-freezing experiments in the Sn-Bi and Au-Ge systems were
reported by Wagner, Miller, and Brown (17). Of particular interest are
their experiments with Sn-0.5 atom % Bi alloys which were field-frozen
in a vertical mode under a current density of 1360 A/cm$^2$. Their re-
sults showed negligible convective mixing in the bulk liquid even for
the case of "field-aiding" where the Bi was being driven up, conditions
underwhich an adverse solute concentration gradient would develop.
Apparently, their small capillary size (0.7 mm diameter) was instrumental in helping to prevent the onset of convection by an adverse solute concentration gradient. This may be observed to be valid if a comparison is made of their solute concentration gradient for a straight ET run in the "field-aiding" mode (Bi driven up) with the critical solute concentration gradient for this alloy computed from Verhoeven's analysis (42). The ET solute gradient is \(-4000\) appm/cm while the critical solute gradient is estimated to be \(-6000\) appm/cm for this size capillary. Clearly, the resultant convectionless condition obtained by the authors resulted from the very small capillary size used in their FF experiments. While the experiments did qualitatively indicate an effect of the relative ratio of local interface speeds and ET speeds, quantitative analysis was not done and would be rather difficult since the bulk liquid composition would be a function of both time and position. It should be noted that the Pfann-Wagner equation is invalid under these experimental conditions. Also, since the authors reported no metallography as to interface stability, the question of constitutional supercooling leading to interface breakdown is open to debate.

Since their FF experiments were carried out along the entire length of the capillaries, no solute compositions at the quenched solid/liquid interface were reported. For completeness, the authors should have run a straight unidirectional solidification experiment with complete mixing in the liquid for comparison with their FF runs. Nevertheless, this work demonstrated the potential of FF for purification in the presence of limited liquid convection.
In a later paper, Verhoeven (53) reported on some vertical mode FF experiments done on a Sn-5 atom % Bi alloy. His results for these series of experiments were that ET was a significant factor only in the solute boundary layer since bulk convection limited its application to that region. Use of a smaller diameter capillary appeared to inhibit convection (as was observed by Wagner, et al.), and the convection that occurred in the bulk was probably the result of horizontal temperature gradients which seems credible since his solid/liquid interface was curved. For a capillary size of 1.9 mm diameter and a current density of ~2,000 A/cm², Verhoeven estimated that the solute boundary layer was 0.05 mm. No attempt was made to verify this estimate by actual measurements. Also, he stated that the same degree of convection was prevalent for both the AC and DC modes and that the Pfann-Wagner equation was qualitatively verified by his results.

Work reported by Murphy, Morrice and Henrie (18) on the field-freezing of Ce-Fe alloys in a horizontal boat indicated that extensive convection in the liquid allowed for the resultant solute concentration profile in the solid to be described by the normal unidirectional solidification equation for the complete mixing case. Again, complete mixing in a horizontal system is not surprising. These experiments used a current density of ~240 A/cm² to drive iron to the anode. The conditions for the greatest redistribution of solute were reported to be the existence of vertical thermal gradients and low solidification speeds.

Warner and Verhoeven (20) continued work in the Sn-Bi system by
studying the effect of ET on the solidification of a Sn-2 weight \% Bi alloy. Specifically, their investigation was concerned with examining the effect of ET on the stability of a planar interface. They observed that the sign of the applied field altered slightly the constitutional supercooling criterion but not as extensively as predicted. Their evaluation of stability was based on a criterion that involved the formation of macroscopic grooves in the interface. A better basis would have been to use "nodes", where nodes are local solute-rich regions on the interface for alloys with $k_0 < 1$ (58). Using a node criterion, their observed "instability line" can be shifted to coincide with that for zero electric field, since it is known that nodal breakdown occurs prior to cellular breakdown (55).

The preceding work was all done with ET combined with normal freezing. The application of ET to zone-refining was investigated by Hay and Scala (56) using tungsten. Although their work did not involve any quantitative analysis, it was observed that an increase in the resistivity ratio ($\rho_{300k}/\rho_{4.2k}$) was obtained for "field-aiding" during zone-refining. The major impurity was molybdenum ($k_0 = 1$ in tungsten) and was found by chemical analysis to go to the anode under the influence of ET. Although they no doubt had extensive stirring in the molten zone, it appears that FF was somewhat effective in that upon reversal of the electric field, the resistivity ratio decreased.

Thus, it can be seen that the research reported in the literature indicates that FF can be effective in aiding purification of alloys, provided that convective mixing in the liquid can be controlled and
provided that solute migration is longitudinal and not transverse (as it is during interface breakdown due to constitutional supercooling).

D. Interface Stability

Since available analyses of the effects of potential gradients on solute redistribution for enhanced purification rely on the assumption of a planar interface, the conditions under which this assumption becomes invalid should be examined. In particular, the interface stability should be examined to insure that lateral mass transport is minimized.

The necessity of treating the lateral distribution of solute at a moving interface under unidirectional steady-state solidification conditions was recognized by Rutter and Chalmers (57) in their discussion of cell formation. In this paper, they coined the phrase "constitutional supercooling" (CS) to account for the morphological breakdown of a planar interface into a hexagonal cellular microstructure. While their discussion on CS was qualitative, a later paper by Tiller, Jackson, Rutter and Chalmers (58) derived the well-known quantitative CS criterion, i.e., \( G/R = \left( \frac{mC_0/k_0D}{1-k_0} \right) \) where \( G \) is the actual thermal gradient in the liquid ahead of the interface moving at speed \( R \), \( m \) is the slope of the liquidus, \( C_0 \) is the initial solute concentration, \( D \) is the solute diffusion coefficient in the liquid and \( k_0 \) is the equilibrium distribution coefficient (assumed \(<1\) although similar behavior is expected for \( k_0 > 1 \)). The condition for interface stability is that the left-hand side of the equation must be greater than the right-hand side. Otherwise, the interface becomes unstable to projections in the
liquid, with subsequent transverse solute mass transport.

Experimental verification of the CS criterion was obtained by Walton, et al. (59) where the breakdown of a dilute Pb in Sn alloy was investigated for the transition from a planar interface to a cellular interface. This work was further extended by Morris et al. (60) for the transition of a cellular interface to a dendritic interface. Working with small amounts of Sn, Ag, or Au in Pb, Tiller and Rutter (61) observed the breakdown sequence during CS and concluded that the beginning started with the appearance of "pox" on the surface of the solid/liquid interface. The "pox", revealed by a decanting technique, were observed to be projections pointing into the liquid.

In an investigation of interface breakdown of aluminum containing trace impurities (of the order of 70 wppm Fe and Cu), Biloni, Bolling, and Domain (62) observed that although no cellular morphology was present, local solute-rich regions (which they called "nodes") were observed at the solid/liquid interface. They were able to obtain an approximate size of the nodes and found a distribution of diameters which led them to postulate that the nodes may be prolate spheroidal segregation regions in three dimensions (long axis parallel to growth direction). The authors did not examine longitudinal sections to see if the nodes were continuous rods or prolate spheroids as suggested. Biloni et al. (63) continued investigations of nodes in a low Pb containing Sn alloy and concluded that the nodes persisted into the bulk solid after the pox had disappeared from the decanted interface following polishing. They also observed that the nodes, under more severe
CS breakdown conditions, formed the walls of the resultant cellular morphology.

Biloni et al. (64) firmly established that pox were not necessarily related to planar instability but that nodes were. They also indicated that nodes were the first manifestation of CS breakdown. Working with an Sn-30 wppm Pb or Sb alloy, these authors postulated that the near-hexagonal array that nodes form is probably the result of a dislocation nucleated event with a diffusion controlled growth step. They envisaged each node to act as a local well or depression in the solid/liquid interface drawing solute into itself.

Nodal breakdown of an unstable planar interface during CS in non-metallic systems was observed by James (65) in his investigation of the $\text{H}_2\text{O}-\text{NH}_4\text{F}$ and $\text{H}_2\text{O}$-air systems. Using a stereomicroscope and oblique polarized light, James was able to observe that the initial breakdown was the formation of local nodes or depressions on the solid/liquid interface.

Further analysis of nodes was done by Davis (66) who examined dilute alloys of either Tl or Ag in Sn. Davis measured nodal spacing and obtained nodal concentration (using an electron microprobe X-ray analyzer) for several initial compositions. His conclusions were that node spacing at low initial solute content was independent of concentration but increased with concentration at higher solute levels, and that nodal concentration was independent of initial alloy composition. Davis believed that nodal concentration was governed by the amount of supercooling that the second phase could attain in the presence of the
primary phase.

An examination of the general mode of morphological breakdown during unidirectional solidification of a dilute binary alloy of Sb in Pb was done by Morris and Winegard (67). These authors also examined the effects of crystal orientation on the breakdown sequence and observed that crystals oriented with $\langle 100 \rangle$ parallel to the heat transfer direction (longitudinal direction) had nodes at the initial stage of instability while crystals oriented with $\langle 110 \rangle$ parallel to the heat transfer direction experienced initial breakdown in the form of elongated cells. Contrary to Biloni et al.'s (64) conclusions, Morris and Winegard suggested that since nodal geometry was in the form of a regularly spaced array, their location was probably governed by solute diffusion in the liquid rather than by the location of the dislocations. Although no quantitative relationship was obtained, they observed a decrease of nodal spacing with an increase in solidification speed holding other variables constant. It was found that the transition from a planar morphology to a nodal (or cellular) morphology was reversible in that decreasing the speed of solidification during an experiment to a region below the critical conditions resulted in the planar interface becoming stable once more. However, once a nodal morphology was obtained, increasing the speed (causing the interface to become more unstable) resulted in the nodes connecting to form a regular hexagonal cellular network.

In a recent paper investigating the development of cells during unidirectional solidification of a dilute Zn containing Sn alloy,
Audero and Biloni \((68)\) observed a strong crystallographic orientation effect on node morphology. Specifically, for crystals oriented with the basal plane perpendicular to the solid/liquid interface, disordered nodes formed first then aligned nodes developed as the instability increased. For crystals with the basal plane parallel to the solid/liquid interface, instability set in with disordered nodes earlier than for the case just mentioned and eventually transformed to an ordered hexagonal array of nodes. In both cases, eventually a fully-developed hexagonal cell pattern was generated as the degree of CS increased. The authors speculated that the crystallographic orientation effect was the result of a competition between the various planes in the solid having different values of interfacial free energy and that highly anisotropic materials would probably have their breakdown morphology strongly related to the growth or heat transfer direction.

While the CS criterion has been successful in predicting the breakdown of a planar interface at a critical G/R for a given \(C_0\), the theory can not account for the subsequent microstructure existing at the unstable solid/liquid interface or that which exists in the solid. Also, the CS criterion was obtained from a macroscopic point of view applying equilibrium arguments that gave the slope of the equilibrium liquidus temperature, \(T_E = T_0 - mC_0(1 + ((1 - k_0)/k_0)\exp(-RX/D))\) \((35)\) equal to the local actual thermal gradient, \(G\), in the liquid at the onset of instability. In this expression, \(T_0\) is the equilibrium melting temperature for the pure solvent and \(x\) is the longitudinal distance measured positive into the liquid from the solid/liquid interface.
An instability theory examining the details of heat and solute transport at a perturbation on an interface was developed by Mullins and Sekerka (69). They developed a stability theory based on the time dependent growth of the amplitude of a sinusoidal perturbation of infinitesimal initial amplitude growing on an initially planar solid/liquid interface. As the instability of the interface increased, those perturbations of specific wavelengths would grow at the maximum rate and would dictate the inter-perturbation or inter-node separation. Mullins and Sekerka assumed no convective mixing in the liquid in their calculations and predicted a maximum growth rate at a critical wavelength. Their assumptions of the use of steady-state thermal and diffusion fields means that their analysis is only valid for wavelengths near the critical one so that the perturbations are changing shape slowly. Also, they assumed isotropy of bulk and surface parameters as well as local equilibrium at the solid/liquid interface. Their final expression for the growth of a perturbation amplitude $\delta$ and spatial frequency $\omega$ is

$$\frac{\delta}{\delta t} = V \omega \left[ -2TM \Gamma \omega^2 \left[ \omega^*(V/D)P \right] -(G'-G) \left[ \omega^*(V/D)P \right] +2\omega G_c \left[ \omega^*(V/D) \right] \right] \left[ \omega^*(V/D) P \right] + 2 \omega \Gamma G_c$$

The definitions of the terms are as follows:

$V$ = solidification speed (cm/sec)

$\omega = 2\pi / \lambda$, $\lambda$ = wavelength of a perturbation (internodal separation)

$T_M$ = melting temperature of a flat interface (K)

$\Gamma = \gamma / L$, $\gamma$ = specific solid/liquid interfacial free energy (erg/cm$^2$)

$L$ = latent heat of solvent (erg/cm$^3$)

$D$ = solute diffusion coefficient in liquid phase (cm$^2$/sec)
m = slope of liquidus line on phase diagram for solvent side (C/w/o)

$G_C$ = concentration gradient of solute in boundary layer (w/o/cm)

$G' = (k_S/k)G'$

$G = (k_L/k)G$

$k_S, k_L, k = thermal conductivities of solid, liquid and their average, respectively$

$G' = thermal gradient at flat interface in the solid (C/cm)$

$G = thermal gradient at flat interface in the liquid (C/cm)$

$P = (1 - k_o); k_0 is the equilibrium distribution coefficient$

$\omega^* = (V/2D) + ((V/2D)^2 + \omega^2)^{1/2}$

Figure 5 schematically shows the Mullins and Sekerka $\delta/\delta$ parameter as a function of the spatial frequency $\omega$ for two cases, one for an unstable condition (Curve 1) and the other for a stable condition (Curve 2). For the unstable case, the region between $\omega_L$ and $\omega_H$ corresponds to conditions for which the perturbation can grow. At the maximum $(\delta/\delta)_{max}$, the dominant spatial frequency should be growing faster than any of the others. Thus, the Mullins-Sekerka $\delta/\delta$ expression could be used to obtain the $\omega$-value at a maximum $\delta/\delta(\omega_{max})$ and this $\lambda$ would be the wavelength of the perturbation most likely to be observed. The sign of $\delta/\delta$ is determined by the sign of the terms in the numerator of their expression which varies for different systems and experimental conditions. It should be noted that the Mullins-Sekerka analysis was time-independent (time independence of the diffusion and thermal fields in the frame of reference in which the interface is at rest, that is at steady-state) and is more valid for a slowly changing perturbation than for a rapidly changing perturbation, i.e., for $\omega$'s for which $\delta/\delta$
Figure 5. The Mullins and Sekerka $\dot{\delta}/\delta$ function is schematically shown plotted against $\omega$ for two cases as discussed in the text.
Sekerka (70) re-examined the interface stability problem by assuming an explicit time-dependent analysis of the thermal and diffusion fields. However, to make the mathematics tractable, he assumed a "thermal steady-state" based on the fact that the thermal diffusion coefficients (for the solid and the liquid) are much larger than the respective solute diffusion coefficients. After an extensive mathematical discourse, Sekerka demonstrated that in the "thermal steady-state" approximation, the time-dependent stability theory reduces to the time-independent stability theory given by Mullins and Sekerka (69). In a review article on stability theory, Sekerka (71) stated that while numerous stability calculations had been recently published, few experimental comparisons had been reported in the literature. Those few usually reported cellular spacing as a function of speed, obtaining a relationship between \( \lambda \) and speed as \( \lambda \sim (V)^{-1/2} \).

The above perturbation analysis assumed no convective mixing in the liquid. In a paper by Hurle (72), an attempt was made to incorporate the effect of stirring into stability theory by considering the effect of the solute boundary layer, \( \delta_{\text{sol}} \), upon the stability equations. As was later pointed out by Coriell et al. (73), Hurle had made a mistake in his computations, and the conclusions were erroneous. Coriell, et al. predicted that \( \lambda \) was related to speed as \( \lambda \sim (V)^{-1/3} \). Again there appears to be a dearth of experimental work on this subject. Even in a comparison between the CS criterion and the interface stability theory no definitive conclusions can be made, as was observed by Davis and
Fryzuk (74). Nevertheless, of the current literature, it appears that nodal breakdown of a planar interface is the first manifestation of instability and of the two leading theories for describing morphological breakdown, the Mullins and Sekerka (69) stability theory approach seems to be able to describe the microstructure better than the constitutional supercooling approach of Tiller et al. (58).
Chapter III. EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. Overall Design Philosophy. Since the project was concerned with solute diffusive transport, the equipment for performing the experiments had to be designed so as to be isolated as best as possible from any external effects that could cause bulk transport of solute during an experiment. Bulk transport of solute caused either by external vibrations from other equipment in the building or by internal vibrations from power drive equipment had to be avoided. Also, any variations in local translational speed of the solid/liquid interface had to be minimized since such effects would manifest themselves as banding in a longitudinal compositional profile. Of course, one well-known source of bulk transport involves convection in the liquid caused by an unstable density gradient resulting from adverse solute and/or temperature gradients, as discussed in Chapter II.

Along with the above guidelines for major equipment design, the ancillary equipment needed for filling the capillaries had to be designed such that the filled capillaries had a uniform compositional profile and a structure free of shrinkage porosity that could cause local flux variations and overheating during field-freezing. The capillaries 1) had to be made from a material that was chemically inert with respect to the liquid metal alloys, 2) had to have close geometric tolerances, primarily on the internal diameter, and 3) had to have
good thermal shock resistance. The capillaries used in this project were made from Lucalox, a fine-grained, high-purity, recrystallized alumina with close tolerances on the diameter and good straightness.

B. Alloy Preparation. As mentioned in Chapter I, the material systems chosen for this project were Sn-based alloys. The tin was purchased as 99.999% pure tin as quoted by the vendor\(^a\) and was in the form of an ingot nominally 2.54-cm (1 inch) square. The alloying elements of bismuth\(^b\) and antimony\(^c\) were of the same purity level and were in the form of splatters and chunks, respectively.

Alloy preparation consisted of the following steps: 1) generating a master alloy of given composition by melting the constituents under argon and casting this heat into a water-cooled Pyrex crucible, 2) inverting this first casting and melting it under a static hydrogen atmosphere, and 3) melting the ingot of step 2 (under a static hydrogen atmosphere) in an induction furnace with vigorous stirring followed by a rapid chilled water quench. The quenched master alloy was then ready for vacuum outgassing, after which it was used for capillary filling. These procedures were necessary to insure that the filled capillary would have a high probability of being free of gas bubbles which could adversely affect the field-freezing experiments.

The details of these procedures are described in the following paragraphs.

---

\(^a\) The vendor was United Mineral and Chemical Co., New York, N. Y.
\(^b\) The vendor was American Smelting and Refining Co., S. Plainfield, N.J.
\(^c\) The vendor was United Mineral and Chemical Co., New York, N. Y.
The master alloy ingots were generally 200 gm which allowed for most of the capillaries to be filled from the same initial melting. The tin was carefully cut into nominally 50-100 gm sections and deburred using 120-grit SiC abrasive paper. Following deburring, the tin was given a chemical polish (52) by dipping it into a solution consisting 48 v/o H₂O, 48 v/o HNO₃, 2 v/o HCl, and 2 v/o H₃PO₄ for several seconds then quickly dipping it into a solution of 50:50, H₂O/HCl. Afterwards, the tin pieces were rinsed in distilled water, then rinsed in methyl alcohol and air dried. Following the chemical polish, the tin pieces were stored in a desiccator until needed. The bismuth and antimony were already in a convenient form for weighing and consequently they did not need any further treatments.

The first melt of the master alloy was done in a new 400 ml Pyrex beaker that had been previously cleaned in an Alconox solution, thoroughly rinsed in distilled water and then rinsed in methyl alcohol and air dried. The alloy constituents were carefully weighed out on a an Ainsworth balance to an accuracy of ± 0.5 mg with care taken to minimize contamination of the alloying elements. Before placing the alloy constituents in the beaker, it was purged with argon gas for a sufficient time to have at least 10 volume changes, whereupon a Bunsen burner was ignited under the beaker. When the tin started to melt, the alloying element (bismuth or antimony, depending upon which master alloy was being cast) was dropped in and upon complete melting of the tin, a clean Pyrex stirring rod was used to mix the melt. After several minutes of stirring, the melt was quickly swirled then poured into a 16 mm
ID by 21 cm length Pyrex tube (which had been previously cleaned in the same way as the melt beaker). The 16 mm ID tube was contained inside a 25 mm ID by 19 cm length Pyrex safety tube which was inside a large container holding cold water. As soon as the melt was poured, the assembly was transferred under flowing cold water to facilitate further cooling. Each master alloy was melted and cast into its separate Pyrex ware.

The cast master alloy was removed from the Pyrex tube by gently breaking the glass away. The casting was then rinsed with methyl alcohol, air dried and visually inspected for defects and general appearances. The casting was then sectioned with a jeweler's saw into several pieces, deburred with clean 120-grit SiC abrasive paper then rinsed in methyl alcohol and air dried. A previously cleaned Vycor tube (26 mm ID by 17 cm length) with a constriction of nominally 2-4 mm was loaded with the master alloy ingot in such a manner that the ingot was inverted with respect to the position in which it was cast. In this configuration the alloy pieces were above the constriction. The constriction was included in the design so that upon melting, the master alloy would flow through the reduced section and most of the oxide would adhere to the walls of the reduced region while the alloy would fall to the bottom and solidify.

The Vycor tube containing the master alloy pieces was attached to a vacuum system and evacuated to a pressure of $10^{-5}$ torr before gently flame heating the bottom reservoir and walls to effect outgassing. After outgassing, the Vycor tube was isolated from the vacuum system and
liquid nitrogen-trapped hydrogen was backfilled into the tube to a pressure of 1/5 of an atmosphere. After backfilling, the alloy was melted and drip-cast into the lower chamber where it solidified. A beaker of cold water was brought up around the alloy to facilitate cooling. Following complete solidification, the system was evacuated and then backfilled with 1/5 atmosphere of liquid nitrogen-trapped hydrogen and sealed off. At this point, the master alloy was ready for the induction melting operation.

An Inducto induction melting furnace was used to melt the encapsulated master alloys. A Pyrex safety crucible was used to hold the encapsulated alloy during melting. The induction melting operation consisted of slowly heating the ingot until a visual determination was made of melting (convection patterns appeared on the surface of the melt), then the alloy was rocked to facilitate mixing. After rocking the melt for approximately 15 minutes, the power was shut off and the encapsulated alloy was quickly dropped into a bucket of cold water and vigorously agitated to obtain a fast quench rate. Usually the agitation was vigorous enough to result in liquid alloy coating the entire inside of the Vycor tube and freezing in that configuration.

After carefully removing the master alloy from the Vycor tube, it was sectioned into pieces nominally 6-8 gm each using a jeweler's saw and deburred. Enough pieces to make up approximately 30 gm of alloy were loaded into an alumina crucible and placed into a vertical tube furnace contained inside a vacuum bell-jar system described

\[^a\text{Induction Melting furnace was manufactured by Inducto Corp.}\]
elsewhere (75). The master alloy charge was evacuated to $10^{-6}$ torr before being slowly heated to 700 C where it was outgassed for one hour. After holding the charge at 700 C for one hour, power was shut off and the alloy was cooled to room temperature before breaking the vacuum and removing it.

The vacuum outgassed master alloy was then ready for capillary filling and was stored in a desiccator until needed. The same procedures as described above were used throughout the program for the preparation of the master alloys needed for the capillary filling operation to be discussed in the next section.

The rather extensive procedures for alloy preparation given above were necessary to insure that the alloy charge used to fill the capillaries was outgassed, homogeneous, and relatively free of residual oxide.

C. Capillary Filling Operation. The size of the Lucalox capillaries was 1.58 mm (1/16 inch) ID by 3.175 mm (1/8 inch) OD with a 15.24 cm (6 inch) length. The somewhat short length was used since this was an "off-the-shelf" item; however, as discussed in the next section, this required the use of extension capillaries for mounting of the Lucalox in the field-freezing apparatus. The Lucalox capillaries were cleaned prior to filling them with master alloy. The cleaning procedure started by dipping them into an Alconox-distilled water solution and ultrasonically cleaning them for five minutes followed with a distilled water ultrasonic rinse for five minutes. At the end of the water rinse, the capillaries were rinsed in methyl alcohol and oven dried.

Lucalox was ordered from General Electric, Cleveland, Ohio.
dried at approximately 80°C. After oven drying, the capillaries were vacuum outgassed at 700°C for one hour at a pressure of approximately 10^{-4} torr; they were then stored in a desiccator until needed. All handling operations were done with forceps or gloves to minimize contamination.

Alloy filling was done by a manual suction technique in which the molten outgassed alloy was suction lifted into the Lucalox capillary, after which it was quenched by a cool blast of air followed by immersion in a stream of cold water. The necessary equipment for capillary filling and the exact procedures are discussed in the next paragraph. The main criteria for the capillary filling apparatus were 1) the alloy had to be quickly filled into the capillary in a controlled manner, and 2) the capillary once filled, had to be quenched rapidly enough to prevent gross segregation yet had to have enough directional heat transfer so as to allow for a shrinkage pipe at the end.

Figure 6 shows schematically the capillary filling apparatus. The melt was contained in a Pyrex crucible that had a protective lid over it and an inlet tube through which dried argon was passed to help prevent surface oxidation of the melt. The center of the lid had a hole in it to allow the capillary to pass through and contact the melt. The Pyrex crucible was heated by a coil of Chromel furnace wire which was driven by a variable autotransformer. The crucible had a 16 mm ID by 2 cm length and could hold approximately 30 gm of master alloy. The capillary pre-heater consisted of an aluminum tube sheathed inside a Pyrex tube which had 12 turns of Chromel furnace wire coiled about it.
Figure 6. The capillary filling apparatus is schematically shown with a Lucalox specimen capillary partially inserted into the melt environment.
Again the coils were driven by a variable autotransformer.

Several arrangements for obtaining a controlled suction on the capillary were tried, but the one finally selected was to press-fit the end of a capillary into a 3.175 mm (1/8 inch) ID Teflon tube approximately 7.62 cm (3 inches) long with the joint coated with vacuum grease. The other end of the Teflon tube was forced into a Propipet. In this manner a controlled withdrawal of alloy melt into the capillary could be obtained by squeezing the appropriate valve on the Propipet.

The specific details of the filling of a capillary consisted of placing nominally 10-15 gm of vacuum outgassed master alloy chunks in the Pyrex crucible then putting the covering lid over it and purging the crucible with dried argon for a minimum of 50 volume changes. After purging, the powerstat to the crucible was advanced until melting of the alloy occurred. At this point a clean Pyrex rod was used to "sweep" the surface of the melt to help remove any oxide film. Then the capillary-Propipet assembly was positioned over the crucible with the capillary inserted approximately half-way down inside the pre-heater with its tip just above the melt line inside the crucible. The Propipet was activated to purge the capillary with argon. After holding the capillary at this level for approximately thirty seconds, the assembly was lowered until the tip of the capillary was approximately 5 mm beneath the surface of the melt and was held in this position for one minute. After this time period, the Propipet was operated such that liquid alloy was suctioned up inside the capillary and approximately 4 mm inside the Teflon tube. This filling operation took about
1/2 to 3/4 seconds. Immediately upon observing the filling inside the Teflon tube, the capillary was withdrawn from the pre-heater and quenched by blasting a cool stream of compressed air onto it while being withdrawn. As soon as the capillary had cleared the pre-heater (this took 2-3 seconds), it was held under a flowing stream of cold water to facilitate further cooling. At this point, the capillary was disconnected from the Teflon tube.

All filled capillaries were visually inspected for casting defects such as porosity or gaps that might have occurred during filling or solidification. This was accomplished by holding the capillary against a narrow slit of bright light and rotating and translating it to examine for defects that would show up in the transmitted light as local bright regions. When the capillary passed this inspection, it was marked for identification and placed in a desiccator until needed.

D. Field-Freezing Experimental Apparatus. The design criteria for the field-freezing equipment were the following: it had to 1) be designed for unidirectional solidification in a controlled manner free from adverse vibrational effects, 2) have a vertical, positive temperature gradient in the furnace with cylindrical heat transfer symmetry, 3) have a cooling chamber that could maintain a steep thermal gradient at the solid/liquid interface yet not transmit vibration to the specimen or result in thermal convection in the furnace, 4) have a quenching mechanism so that the solid/liquid interface could be preserved for metallographic analysis after each field-freezing experiment, and 5) allow for a solenoidal magnetic field to be generated such that its
magnetic flux density vectors were parallel to the local gravitational potential vector and furnace axis.

Satisfaction of the above criteria was obtained by building the equipment shown in Figure 7. Unidirectional solidification was obtained by using a geared, power-drive unit capable of translating the furnace-magnet coil apparatus in a controlled manner past the specimen capillary. Also, vibration isolation was achieved by using springs to separate the support structure and the field-freezing apparatus from the laboratory floor (details of this are given in Appendix A). The vertical, positive temperature gradient was obtained by using a dual furnace design with the main furnace controlled by a Honeywell Electr-O-Pulse temperature controller and the auxiliary furnace operated in the steady-state. Cooling of the specimen was done by using a chilled gas cooling system which effectively had a "soft" mechanical coupling to the specimen so as to minimize vibrational effects resulting from the cooling operation. The quenching requirement was satisfied by using a gas deflection shutter that could deflect the cold gas up into the hot zone of the specimen capillary and also by increasing the gas flow. Finally, the solenoid magnetic field was obtained by constructing an air core solenoid (details in Appendix C) which contained the furnace/cooling chamber apparatus.

1. Support Structure and Power Drive. At the onset of the project, construction of a support structure that could handle three field-freezing units was planned which suggested a support structure with three-fold symmetry with the power-drive shaft (used for translating the
Figure 7. The field-freezing apparatus is schematically shown. Only one of the three guide rods appears in the figure.
furnace-magnet coil apparatus) centrally located. The three units were reduced to one in the final design with lead bricks replacing the other units. The final design is shown in Figure 7.

The support structure consisted of three 2024 aluminum alloy plates nominally 1.9 cm thick and 40.6 cm in diameter. Two of the plates were designed to be the ends of the structure and were connected by the central power-drive (which had 6.3 threads per cm) and three guide rods. The power drive shaft was threaded into a bronze nut that was fastened to the center of the third plate which also had three holes equally spaced about the center. Teflon bearing sleeves were fastened on the plate so that the guide rods passed through them and minimized frictional drag during the translation of the plate. This third plate which held the furnace-magnet coil apparatus moved up or down as the power-drive shaft was turned by a geared motor drive and was constrained to move in the vertical direction by three guide rods. The ends of the power-drive shaft were set into thrust bearings which were pressed into the end plates. Thus, the weight and thrust in the longitudinal direction gave minimal frictional torques on rotation of the shaft. The support structure was set on the rigid surface of a table constructed from Unistrut members which were bolted together. The isolation springs were bolted to the legs of the table and could be adjusted to facilitate leveling of the overall apparatus.

The requirements of the power drive unit needed to move the translatable plate were 1) sufficient necessary torque to raise the plate with its burden of the furnace-magnet coil apparatus and lead counterweights
2) a sufficient speed range so that speeds encountered in unidirectional solidification experiments from the literature were within its capability, 3) stop/reverse capability, and 4) freedom from vibration.

The torque needed to drive the translatable plate was estimated by assuming 1) approximate values for the weight of the furnace-magnet coil apparatus and measuring the total weight of all the lead counterweights, and 2) a coefficient of friction between the power-screw and its bronze bearing nut which was at the center of the plate (the Teflon sleeves were assumed to have negligible frictional drag). For Acme (76) threads, the torque necessary to raise the translatable plate was estimated to be 1.68 N·m (15 in-lb). However, this value was increased by a safety factor of 50% and, after being multiplied by the "service factor" (another "safety factor", which took into account the running time (up to 20 hours) of the high reduction gear train) of 2.4. The final design torque requirement was 6.16 N·m (55 in-lb). This was the minimum torque needed to operate the equipment and was well within the 35.3 N·m (315 in-lb) torque capability of the drive unit purchased.

Along with an adequate torque output, the drive unit had to have the required speed range which was of the order of 1.3 μm/sec as discussed in Chapter II. A single motor/gear-train unit which met the speed range requirement was purchased. This model had a variable, forward-stop-reverse motor with 1080:1 gear reduction train that had an output torque of 35.3 N·m (315 in-lb). The unit had a rubber "spider" coupler

---

Minarik Electric Co., 232 4th Street, Los Angeles, Calif.
that connected it to the power-drive shaft to dampen out any vibration from the motor.

2. Furnace/Cooling Chamber Apparatus. As outlined in the introduction of this chapter, the furnace was designed to have a cylindrical symmetry with longitudinal heat transfer and low radial heat losses. Also, the cooling chamber had to be contiguous with the furnace and allow for the attainment of a steep thermal gradient at the solid/liquid interface without vibration problems. In addition, a mechanism had to be provided for obtaining a sufficiently rapid quench of the molten alloy such that the solid/liquid interface was preserved for subsequent metallographic analysis after a field-freezing experiment.

The primary furnace was an alumina grooved-core 1.27 cm (0.5 inch) ID with 3.54 turns/cm (9 turns/inch) grooves that was wrapped with Chromel resistance wire. The core had a length of 15.24 cm (6 inches) and was coated with a layer of Sauereisen No. 8 high-temperature alumina base cement after being wrapped with resistance wire. The assembly was cured for several hours at 300 C and subsequent calibration runs of the furnace assembly further "seasoned" the windings. In order to increase the probability of attaining a fairly steep thermal gradient near the mouth of the cooling chamber, an auxiliary furnace of 2.54 cm (1 inch) ID with 3.54 turns/cm (9 turns/inch) was positioned to fit around the primary furnace and rested on the 304 stainless steel furnace support plate. The alumina core furnace was also wrapped with Chromel resistance wire and had a length of 2.54 cm (1 inch). Figure 8 shows the arrangement of the primary and auxiliary furnaces in
Figure 8. The primary and auxiliary furnaces are schematically shown along with the other components of the field-freezing apparatus.
relationship to the other components of the field-freezing apparatus.

The size of the magnet coil was dictated by the heat transfer from the furnace. Therefore, it was necessary to perform a simple heat transfer calculation to determine the minimum size of the ceramic tube which would contain the furnace and act as a mandrel for the magnet coil. In order to minimize the ceramic tube size, a high quality thermal insulation was needed to insulate the furnace from the tube. The insulation used was Zircar\textsuperscript{a} a zirconia chopped-fiber insulation with an average thermal conductivity of $k = 6 \times 10^{-4}$ watt/M*K (.05BTU/HR-FT\(^2\)(F/FT)) in the temperature range of interest. A steady-state heat transfer balance was set up between the furnace core surface (which was assumed to be $T_H = 1150 \, ^\circ C$ (2100 F)) and the inside temperature of the ceramic tube which was set at $T_W = 38 \, ^\circ C$ (100 F). The wall was releasing its heat burden to the surrounding air at $T_\infty = 21 \, ^\circ C$ (70 F). The heat convective coefficient (or film coefficient) between the outside surface of the ceramic tube and the ambient air was assumed to be of the order of $30.6$ watt/M\(^2\)\(^°\)K (5.4 BTU/HR FT\(^2\) F). The steady-state heat transfer required that the heat loss to the surroundings from the furnace core be equal to the heat transferred through the Zircar insulation; the resistance due to the thickness of the ceramic tube wall was ignored since it was thin relative to the ID of the tube. The above balance can be expressed mathematically as:

\[
q_{\text{cond}} = \frac{2\pi kL}{\ln(OR/IR)} (T_H - T_W) = q_{\text{conv}} = h_c A (T_W - T_\infty), \text{ where}
\]

\textsuperscript{a}Zircar is manufactured by Union Carbide Corp., Tuxedo, N.Y.
L is the length of the ceramic tube, A is the convective heat transfer area given as $2\pi(\text{IR} + \text{W})\text{L}$. The inside radius (IR) and outside radius (OR) are related through the thickness of the thermal insulation $\text{W}$, viz. $\text{OR} = \text{IR} + \text{W}$. After putting in the specific constants, the required thickness of the Zircar insulation was solved graphically by common intersection of $q_{\text{cond}}$ and $q_{\text{conv}}$ plotted against $\text{W}$ and was found to be approximately 7.6 cm (3 inches). Thus, the inside diameter of the ceramic tube was fixed at 15.3 cm (6 inches). Mullite\textsuperscript{a} was selected as the ceramic tube since it could be procurred as an off-the-shelf item at nominal cost for the size needed. The length was set at 20.3 cm (8 inches) since this was felt to be of sufficient length to avoid "end-effects" of the magnetic field of the coil on the field-freezing experiments using the 15.2 cm (6 inch) length Lucalox capillaries. Since the ceramic tube was longer than the Lucalox capillaries, extension capillaries of alumina were used to help support the Lucalox specimen capillary between the end plates and coaxially align it with the furnace and cooling chamber. As an additional protective measure to help minimize heating the magnet coil by the furnace, two heat pipes were attached to a copper girdle that fit snugly between the Mullite tube and the magnet coil. The copper girdle held the heat pipes and helped level out the inside surface temperature of the magnet coil while the heat pipes helped dump any furnace heat burden to the environment.

The cooling chamber was designed to have a minimum size orifice separating it from the furnace so as to obtain as steep a thermal

\textsuperscript{a}Mullite tube was purchased from McDaniel Refractory Prod. Co., Beaver Falls, Pa.
gradient at the solid/liquid interface as possible. Figure 9 shows the arrangement of the cooling chamber. The numerous perforations in the inner tube were designed to distribute the cooling gas as uniformly as possible around the Lucalox specimen capillary. In order to minimize any convection in the furnace hot zone due to the flow of the cooling gas, an anti-convection device was placed at the top of the furnace. This device was a cylinder of fire brick hollowed out in the center where fiberbrax insulation was placed. In operation, the extension capillary was gently contacted by the insulation forming a seal against loss of air through the top of the furnace which would result in thermal convection in the furnace hot zone. For obtaining the fast quench needed in preserving the solid/liquid interface, a shutter mechanism was constructed which deflected the cooling gas up into the furnace hot zone and around the Lucalox.

The cooling gas was obtained by passing compressed air through a gas train shown in Figure 10. A copper/constantan thermocouple was placed in the dry ice/alcohol cooling bath to monitor its temperature and another copper/constantan thermocouple was placed in the heavily insulated hose between the cooling bath and the cooling chamber of the field-freezing apparatus so that the gas temperature could be recorded during an experiment.

3. Magnet Coil. As mentioned in the beginning of this chapter, a DC magnetic field was needed that had a net flux density vector parallel to the vertical centerline. The magnetic field was generated by an air solenoid of nominally 15.3 cm (6 inch) ID by 20.3 cm (8 inch) OD and
Numerous small holes to help distribute cooling gas uniformly

304 Stainless Steel Furnace Plate

Cooling Gas Inlet

Gas Exit

Figure 9. Details of the cooling chamber.
Figure 10. The gas train used to obtain the dry cooling gas is shown.
20.3 cm (8 inch) in length. The design, construction, and characterization technique for the magnet coil are described in Appendix C.

A centerline longitudinal flux density profile of the magnet coil was obtained for a given coil current and appears in Figure 11. It should be noted that the maximum flux density obtained while operating the coil at its maximum current was approximately 300 Gauss, somewhat lower than the design flux density of 500 Gauss. Apparently, the wrapping of the coil did not result in a close-packed magnet wire configuration as required by the theoretical predictions. However, the relatively large flat zone in the coil was satisfactory for the field-freezing experiments.

The numbered zones on the centerline profile shown in Figure 11 were used to obtain transverse profiles as shown in Figure 12. As expected, the coil had a fairly symmetrical transverse flux density, with the field having a constant strength at the centerline and increasing at the perimeter. The magnet coil was driven by a precision regulated SCR DC power supply with a precision DC ammeter in series with the coil to monitor the coil current.

E. Electrotransport Power Supply. Since the current density used on the program was of the order of 500 A/cm², this required a precision regulated DC power supply that could deliver a current of approximately 9.6 A. A Christie Model MH-36 precision DC power supply was used to drive the direct current field-freezing experiments while the alterna-
Figure 11. The longitudinal magnetic flux density is schematically shown along with the relative position of the Lucalox specimen capillary.
Figure 1. Transverse magnetic flux density is schematically shown for the five levels marked in Figure 11.
ting current experiments were driven by an AC autotransformer. In both DC and AC modes, the specimen current was continuously recorded on a strip chart recorder during an experiment by measuring the voltage drop across a precision 1/2 ohm resistor. For the AC case, this required construction of a full-wave diode rectifier (No. 1N1187A diodes) to convert the AC signal to a DC signal for the recorder.

The electrode that contacted the liquid metal alloy inside the Lucalox specimen capillary was made from 1 mm (0.04 inch) diameter tungsten wire which was brazed to a copper wire of the same size. Tungsten was used for this electrode since previous work (16) had reported negligible interaction between it and liquid tin. The bottom electrode was a copper wire 1 mm (0.04 inch) in diameter that made contact with the solid alloy directly.

F. Field-Freezing Experimental Procedures. Since most of the procedures for the field-freezing runs were approximately the same, a typical experimental run will be described. The calibration runs will not be discussed other than to state that they were used to test the equipment and to establish the operational procedures described here.

The Lucalox specimen capillary containing an alloy of a specified composition was cemented to the two extension capillaries as shown in Figure 13. The extension capillaries all had their top and bottom lengths kept constant so that the original solid-liquid interface in the specimen capillary was located at the same relative position in the furnace for all the runs. The ends of the Lucalox capillary fit inside the extension capillaries approximately 6.4 mm (1/4 inch),
Figure 13. Arrangement of Lucalox specimen capillary and extension capillaries are schematically shown.
and these joints were cemented with freshly prepared Sauereisen No. 8 cement. The specimen/extension capillary assembly was held in a fixture for 24 hours until the cement had set up. After this aging period the joints were given a thin coating of Silicone sealant and dried for several hours at room temperature. The lower electrode was passed up inside the bottom extension capillary and forced into contact with the solid alloy, then it was sealed into place with Silicone sealant. After the sealant had cured, the external Chromel/Alumel thermocouple was mechanically fastened against the Lucalox capillary using a fine chromel wire loop about the bead.

The specimen/extension capillary assembly was placed in the field-freezing apparatus by lowering it through the top plate of the support structure taking care to insure that the assembly was not damaged as it passed through the furnace/cooling chamber apparatus. The specimen/extension capillary assembly was held in place by a swage-lock "T" fitting that gripped the top extension capillary as shown in Figure 14. The "T" fitting allowed the top electrode to pass through an opening in the Teflon plug so that it could be connected to one of the electrodes of the power supply. The other branch of the "T" went either to a vacuum or to an inert gas line. Both lines were connected to a manometer.

After the specimen/extension capillary assembly was placed in the field-freezing apparatus, the cooling gas was turned on to establish a flow of approximately 28 liters/minute (60 CFH). The translatable

\(^{a}\text{Manufactured by the General Electric Co.}\)
Figure 14. The swage-lock "T" fitting and top extension capillary are shown.
Plate holding the furnace-magnet coil apparatus was lowered until it contacted the bottom plate where it was stopped and a dial gage was indexed on it to give a displacement for determining the speed of the translatable plate during an experiment.

While the cooling gas was being cooled by the dry ice-alcohol bath, the specimen capillary was evacuated by a fore-pump. Three series of a sequence consisting of evacuation and back-filling with desiccant-dried argon were performed on the specimen capillary before a final back-filling was done. Following this final back-filling operation, the top electrode was lowered until it made contact with the solid alloy in the specimen capillary. At this point, the specimen capillary was connected via the top and bottom electrodes to a multimeter to observe electrical continuity.

When the cooling gas thermocouple indicated -30°C, the magnet coil was activated if the run required its utilization, and the furnace controller was turned on. The output of the Chromel/Alumel thermocouple fastened to the specimen capillary was continuously recorded on a strip chart recorder along with the cooling gas temperature. The controller set-point temperature was reached in approximately 30-45 minutes and was maintained at this temperature within ±5°C. It was observed that no variations in temperature greater than this were recorded by the specimen capillary thermocouple under static conditions, i.e. without the furnace/cooling chamber moving. Of course, during a field-freezing run, the specimen capillary thermocouple would show changes as the furnace/cooling chamber moved past it and thus the solid/liquid interface...
temperature profile was obtained from the strip chart recording.

As soon as the controlled set-point was reached, the top electrode was gently pushed approximately 6 mm (1/4 inch) into the alloy melt to insure electrical contact, then the multimeter was disconnected from the specimen capillary electrodes and the electrotransport power supply was connected to the specimen. The power supply was then activated and the electrotransport current was recorded on a strip-chart recorder as the voltage drop across a 1/2 ohm precision resistor. Following a stabilization period of approximately 5 minutes, the power-drive unit was started at the desired speed level and the field-freezing experiment was underway.

During the course of the field-freezing experiment, the temperature of the copper girdle, and cooling bath were monitored as well as the gas flow while specimen capillary temperature and electrotransport current were continuously recorded. The translation speed of the furnace was intermittently computed from the displacement as indicated by the dial gage and the known elapsed time from the start of the experiment. Periodically, it was necessary to add additional dry ice to the cooling bath to maintain a constant cooling gas inlet temperature.

At the termination of the experiment, the quenching operation was performed. This operation was done by 1) cutting the electrotransport power and simultaneously increasing the cooling gas flow after the anti-convection device was removed from the top of the furnace (the cooling gas temperature usually dropped to -50 C at this stage), 2) turning off the furnace power, and 3) removing the "T" swage-lock from the extension
capillary. After removal of the "T", the specimen/extension capillary assembly containing the frozen alloy was removed from the furnace/cooling chamber apparatus by pulling it out through the top plate of the support structure.

After removing the specimen/extension capillary assembly from the field-freezing apparatus, the specimen capillary was separated from the specimen by tapping with a hammer. The specimen was then ready for metallographic analysis.

G. Metallographic Procedures. As stated in Chapter II, the evaluation of the effect of field-freezing was to be accomplished by determining the solute compositional profile along the specimen using an electron microprobe X-ray (EMX) analyzer. In order to use the EMX, the specimen was sectioned so that the pieces could fit inside a standard metallographic mount and the surface was polished through 1/4 micron diamond paste; the details are given below.

The nominal 1.6 mm (1/16 inch) diameter rod-like alloy specimen was sectioned by using a sharp razor blade to shear the specimen into nine or ten pieces. These were placed in a mounting ring in an ordered fashion so as to preserve the direction of solidification and were mounted in Quick-Mount. Following mounting, the specimen was removed from the ring and ground through 120, 240, and 600-grit SiC abrasive papers. After grinding, the metallographic specimen was rough polished on 1 micron diamond paste then final polished on 1/4 micron diamond paste using standard metallographic procedures (77). After final

---

*Quick-Mount is an acrylic, low-temperature curing resin made by Fulton Metallurgical Products Corp., Pittsburgh, Pa.*
polishing, the specimen was given a light etch by swabbing with a solution of 5 v/0 HCl in methyl alcohol to reveal the morphology of the quenched solid/liquid interface. After taking photomicrographs of the quenched interface, the specimen was repolished with 1/4 micron diamond paste to remove any etchant traces. To facilitate electrical conductivity in the EMX analysis, the specimen was coated with a layer of carbon of the order of several hundred angstroms thick by physical vapor deposition in a vacuum coater. Afterwards, the specimen was stored in a desiccator until needed.

H. Electron Microprobe X-Ray (EMX) Analysis. The EMX analysis was done on an ARL Microprobe\(^a\) operating at an excitation potential of 20 KV using an ADP (ammonium dihydrogen phosphate) analyzing crystal. The specimen current was 0.1 uA and the beam spot size was approximately 5 microns. In order to make the analysis quantitative, alloy standards were prepared for both the Sn-Bi and Sn-Sb alloys used in the program. These standards were made by carefully weighing out the required masses of the constituents on an analytical balance, sealing the weighed pieces in an evacuated Vycor capsule and then melting them. After shaking the melt to facilitate homogenization, the capsules were quickly quenched into cold water. Several standards of various compositions were synthesized so that they would "overlap" any variations in field-freezing experiments. The standards were placed in the same metallographic mount and processed in a similar manner as the experimental alloys. As a check on the preparation technique of the standards, samples from the

\(^a\) Applied Research Laboratory, Dearborn, Mich.
Sn-Bi standards were sent to an analytical lab\(^a\) for chemical analysis. The results verified that the preparation process was faithfully giving standards of the target composition.

The determination of a specimen compositional profile was obtained by establishing a working curve from the standards and then running the specimen and reading the unknown composition from the working curve. For the Sn-Bi alloys, the microprobe spectrometer was set to detect the Bi M line since the signal to noise ratio was approximately 100:1 for this line. The longitudinal profiles were obtained by starting from an index (microhardness mark) and scanning the probe beam across the specimen at a rate of 96 microns per second for a counting period that varied from 300 seconds for a single phase microstructure to 480 seconds for a two phase structure. The scaler usually recorded counts of the order of \(X_{100,000}\). By traversing the specimen at various intervals along its length, a complete profile of the specimen from the index mark to the quenched liquid was obtained. Of course, wherever the compositional profile appeared to rapidly change, the longitudinal intervals were fairly short. After completing the specimen profile, the standards were again checked to see if any electronic drift of the probe had occurred. The Sn-Sb analysis was performed using the same techniques, except the L line for Sb was used in this case. The reproducibility of the analysis was found to be approximately ±.5%/o.

\(^a\) Herron Testing Laboratory, Cleveland, Oh.
CHAPTER IV. EXPERIMENTAL RESULTS AND DISCUSSION

This chapter is divided into six parts consisting of the following items: A. Preliminary Experiments, B. Interface Stability, C. Direct Current Field-Freezing Experiments, D. Alternating Current Field-Freezing Experiments, E. Electrotransport Experiments, and F. Effect of Magnetic Field on Convection.

A. Preliminary Experiments.

An as-filled Sn-2 atom % Bi alloy capillary was examined for general microstructure and compositional profile. An electron microprobe X-ray (EMX) analysis detected no gross macrosegregation resulting from capillary filling. This indicated that the quench following filling of the capillaries was rapid enough to prevent macrosegregation. A general view of the dendritic microstructure of an as-filled capillary containing Sn-2 atom % Bi alloy is shown in Figure 15. A similar microstructure was observed for the Sn-2 atom % Sb alloy.

Furnace calibration experiments using Sn-2 atom % Bi ($k_0 < 1$) and Sn-2 atom % Sb ($k_0 > 1$) alloys were made to ascertain the extent of any convection in the liquid during vertical unidirectional solidification (UDS) experiments and to search for any solute banding effects resulting from local fluctuations in interface speed. Figure 16 shows the resultant compositional profile for the Sn-Bi alloy unidirectionally.
Figure 15. The general as-cast dendritic microstructure present in the quenched as-filled capillary for a Sn-2 atom % Bi alloy is shown.
Figure 16.

$\frac{C_s}{C_0}$ vs. $d$, mm

- $H = 0$ Gauss
- $CD = 0 \text{ A/cm}^2$
- $\bar{R} \approx 1.4 \mu\text{m/sec}$
- Sn-Bi

---

$\frac{C_s}{C_0}$ vs. $d$, mm

$\frac{C_s}{C_0}$ vs. $d$, mm

$\frac{C_s}{C_0}$ vs. $d$, mm

$\frac{C_s}{C_0}$ vs. $d$, mm
frozen at 1.5 \mu m/sec without the magnetic field being activated. The ordinate has been normalized to the original composition, which was nominally 3.6 weight % Bi. The profile appears very similar to Figure 2 (a) of Chapter II for the case of no convective mixing in an alloy with $k_0 < 1$. Several features of Figure 16 are significant. First, the compositional profile shows an initial transient and a solute boundary layer at the quenched interface. Measured values of the respective "characteristic distances" $\delta_{\text{int}}$ and $\delta_{\text{sol}}$, are shown in Table II along with the theoretical values predicted from the appropriate compositional profile equations. For the Sn-Bi alloy with the magnetic field off, the agreement between theory and experiment is fairly good indicating that the positive temperature gradient in the furnace prevented any convective stirring in the melt. Also, the ratio of the composition of the solid to the liquid at the interface ($k_0$) was found to be approximately 0.26 which is in fair agreement with the $k_0$ value of 0.30 reported by Verhoeven and Gibson (78) for an alloy of the same composition.

Table II. "Characteristic Distances" $\delta_{\text{int}}$ and $\delta_{\text{sol}}$ are listed for UDS experiments for Sn-Bi and Sn-Sb alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\delta_{\text{int}}$ (mm)</th>
<th>$\delta_{\text{sol}}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-2 atom % Bi$^a$</td>
<td>5.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Sn-2 atom % Bi$^b$</td>
<td>4.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Sn-2 atom % Sb$^a$</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$^a$ Magnetic field off.
$^b$ Magnetic field on.
Although the error in the experimentally determined $k_0$ in this project is estimated to be $\pm 15\%$, the agreement lies within this limit and does suggest that equilibrium conditions prevail under UDS of these alloys. As expected, the Sn-Sb alloy showed a different compositional profile (again the magnetic field was off) and appears in Figure 17; here the profile is a qualitative mirror image (about the mean composition) to that of the Sn-Bi case. Since $k_0 > 1$ for Sn-Sb, the initial solid to form during UDS is rich in Sb, while, due to solvent-rejection, an Sn-rich boundary layer in the liquid builds up in front of the advancing interface until steady-state is attained. The "characteristic distances" for Sn-Sb are also reported in Table II and again imply a lack of convective mixing in the liquid. At the quenched interface of Figure 17, the $k_0$ value (ratio of solute in the solid to that of the liquid at the interface) is approximately 1.53 which is in fairly good agreement with the value of 1.66 reported by Verhoeven and Gibson (78). This again suggests that local equilibrium appears to be existing at the solid/liquid interface. In both the Sn-Bi and the Sn-Sb alloys, no evidence of solute banding was observed by EMX. This was ascertained by performing a longitudinal probe traverse along the length of the specimen using a beam diameter of $\approx 5\mu m$. Within the sensitivity of the analysis ($\approx .5$ weight $\%$), no spatial variations of the composition was observed in the steady-state portion of the profile. This means that the furnace drive unit was mechanically smooth and external vibration effects, as discussed in Appendix A, were effectively eliminated below the background threshold detection limit of the analytical
Figure 17.

\[ H = 0 \text{ Gauss} \]
\[ CD = 0 \text{ A/cm}^2 \]
\[ \bar{R} \approx 1.0 \mu m/sec \]
Sn-Sb

\( \frac{C_s}{C_0} \) vs. d, mm

\( \frac{C_s}{C_0} \) vs. d, mm
An Sn-2 atom % Bi alloy was unidirectionally solidified at a speed of \(-1.3\) \(\mu\)m/sec in the presence of the magnetic field. The resultant compositional profile is shown in Figure 18 which again indicates a lack of convective mixing in the liquid. Table II lists the \(\delta_{\text{int}}\) and \(\delta_{\text{sol}}\) which are in good agreement with those expected for no mixing. The \(k_0\) value was found to be \(-0.26\), agreeing with that of Figure 16. As expected, the magnetic field did not alter the profile for the no convective mixing case and did not alter the local equilibrium at the solid/liquid interface.

The furnace calibration experiments indicated that for both Sn-Bi and Sn-Sb alloys undergoing UDS, negligible convective mixing had occurred in the melt and local thermodynamic equilibrium had pertained at the solid/liquid interface. The next question remaining to be satisfied was the determination of the upper speed limit that a FF experiment could sustain before the solid/liquid interface became unstable with respect to constitutional supercooling.

B. Interface Stability.

Several preliminary experiments were performed to examine for CS breakdown into cells of the Sn-Bi alloy. These experiments indicated that breakdown first occurred with the formation of nodes and not cells. Viewed on a longitudinal section, the breakdown took on the appearance of "streaks" or "rods" of solute-rich regions (as determined by EMX) which appeared as nodes in a transverse microstructure. However, for an alloy where breakdown was evident as nodes or streaks, the interface
Figure 18. 

- $c_s = 0.01 A/cm^2$
- $H = 300$ Gauss
- $C_D \approx 0 A/cm^2$
- $\bar{R} \approx 1.3 \mu m/sec$
- Sn-Bi

Graphs showing the relationship between $c_s/c_0$ and $d$ (mm) for different values of $d$. The graphs indicate an increase in $c_s/c_0$ as $d$ increases.
retained its flatness similar to that for an alloy where no breakdown was evident.

Figure 19 shows the microstructure of a quenched interface of an Sn-Bi alloy which showed no evidence of nodes or streaks. The interface is reasonably flat and the region behind the interface in the solid is free of streaks. In fact, generally, the directionally solidified region, regardless of whether it was from an ET or FF experiment with or without the magnetic field, was a single crystal usually exhibiting twins as seen in Figure 20. A stable grain boundary was observed in one DC FF experiment and appears in Figure 21. The twins on one side of the boundary continue on across the boundary into the other side; no streaks were observed in this sample.

Evidence of interfacial breakdown with increasing solidification speed is shown in Figure 22 for an Sn-Bi alloy. For this case, the solidification speed was step increased and the change from stability to instability appears approximately in the middle of the photomicrograph. The streaks were found by EMX to have a higher content of Bi than the surroundings which indicated lateral mass transport of solute resulting from interface breakdown. Figure 23 shows the streak breakdown more clearly. It is not clear if the streaks are discontinuous segregation regions (the prolate spheroids of Biloni, et al. (62)) or continuous segregation regions (rods) that were intersected by the polishing plane at an angle to their longitudinal axis. A sample that had streaks was sectioned and examined on a plane transverse to the growth direction and the resultant microstructure is shown in Figure 24. The
Figure 19. General longitudinal microstructure of an Sn-Bi alloy showing no evidence of breakdown and a nearly flat quenched solid/liquid interface. The freezing direction was to the right.
Figure 20. Twinned longitudinal microstructure of a directionally solidified Sn-Bi alloy (from left to right) showing single crystal growth.
Figure 21. Twinned longitudinal microstructure of directionally solidified Sn-Bi alloy showing a stable grain boundary along longitudinal axis, growth direction was left to right. No streaks are present indicating no CS breakdown.
Figure 22. Interfacial breakdown is exhibited resulting from an increase in solidification speed. The longitudinal streaks begin approximately in the middle of the picture. The direction of solidification was left to right.
Figure 23. General longitudinal microstructure indicating CS breakdown in an Sn-Bi alloy, the direction of solidification was left to right.
Figure 24. Transverse microstructure of Sn-Bi alloy that exhibited streaks resulting from CS breakdown. Here nodes are evident in the solid and have an internodal spacing of ~80 μm. Solidification speed is 5.5 μm/sec.
nodes have an approximately hexagonal distribution with an internodal spacing of the order of 80 µm as determined by lineal analysis.

The specimen shown in Figure 24 was from a UDS experiment in which the solidification speed initially was $-5.5 \, \mu m/sec$ then step-reduced to $-1.0 \, \mu m/sec$. The streaks were observed on that portion of the sample that was solidified at the higher speed and not observed on the other portion solidified at the lower speed, as may be seen in Figure 25 where no nodes appear. This demonstrates the reversibility of nodal formation. The quenched interface in this experiment was planar.

An examination of the breakdown conditions experienced by the specimen shown in Figure 24 can be located on a plot of the CS criterion of Tiller, et al. (58) as shown in Figure 26. At the higher speed, Point B, streaks and nodes were observed in the microstructure while at the lower speed, Point A, no streaks or nodes were seen. These points were plotted using the experimentally determined thermal gradient of $200^\circ C/cm$ in the liquid at the solid/liquid interface, the experimentally determined values of $C_0$ and $k_0$ from this project and the liquidus slope for the composition $C_0$ as given by Warner (23). While this project was not primarily concerned with stability problems, the projection of the experimental parameters onto the appropriate regions of the CS criterion graph was satisfying. However, the CS criterion can not account for the nodal morphology. To do this the stability theory of Mullins and Sekerka (69) is needed.

Using the expression developed by Mullins and Sekerka (69) as
Figure 25. Transverse microstructure of Sn-Bi alloy that exhibited no streaks following UDS at a speed of $\sim 1.0 \, \mu m/sec$. Twins may be seen crossing the specimen.
Figure 26. The CS criterion of Tiller, et al. is shown as a function of composition for an Sn-Bi alloy. The experimental points where stability and instability were observed are marked.
written in Chapter II, together with appropriate parameters from measurements and from the literature, the normalized perturbation growth parameter was plotted against the spatial frequency (Figure 27) and the wave length corresponding to the maximum \( \frac{\delta}{\delta} \) was obtained. The value for the wave length was \( \sim 30 \mu m \), somewhat less than one-half of the experimentally determined internodal spacing of \( \sim 80 \mu m \) although the latter measurement is difficult to obtain exactly. The observed \( \lambda \) of \( \sim 80 \mu m \) has a \( \left( \frac{\delta}{\delta} \right) \) value that is 61% of the maximum as shown in Figure 27. Considering the approximations in the Mullins-Sekerka theory and the experimental uncertainty in the determination of the \( C_0 \) and \( k_0 \) parameters, the comparison is reasonable.

An attempt was made to try to vary the internodal spacing by changing speed and holding other variables constant. Within the speed range investigated, the variation of spacing with speed was observed to be very weak, as may be found by comparing Figure 24 with Figure 28. In the latter figure, the internodal spacing was found to be \( \sim 70 \mu m \) even though the solidification speed in this case was \( \sim 64 \mu m/sec \). It thus appears that the variation of internodal spacing with speed in this range is very weak or negligible.

The observation of breakdown in the form of nodes indicated that the first stage of interfacial instability, as discussed in Chapter II, had occurred. The breakdown found in this project agreed with the CS criterion of Tiller, et al. (58) and the morphology of the breakdown was observed to be in fair agreement with the Mullins-Sekerka (69) instability theory. However, the occurrence of breakdown at speeds of \( \sim 3 \)
Figure 27. The instability parameter of Mullins and Sekerka (69) is shown plotted against spatial frequency for the experimental conditions pertinent to the specimen shown in Figure 23.
Figure 28. Transverse microstructure of Sn-Bi alloy showing nodes with internodal spacing ~ 70 μm. The solidification speed is ~ 64 μm/sec.
μm/sec for the composition and liquid thermal gradients encountered in this project placed severe restrictions on one of the goals of this project, viz. the verification of the Pfann-Wagner expression with their boundary conditions satisfied. In order to avoid CS breakdown at higher speeds, the liquid thermal gradient could have been increased by using water cooling instead of air cooling. Of course, using water cooling would have introduced the possibility of generating mechanically induced convection in the melt from either fluctuations in water pressure, etc. or from "stick-slip" type frictional effects between the specimen capillary and any water-tight seal used in the cooling chamber. Therefore, since the project was more concerned with the control of convection and to a lesser extent with the attainment of a large solidification speed range, it was decided to work within the speed constraints dictated by CS criterion and to use the gas cooling approach despite its shortcomings. Since the liquid thermal gradient was relatively constant from experiment to experiment, interface instability in the form of nodal breakdown restricted the solidification speeds used in this project to something less than -3 μm/sec.

C. DC-Field-Freezing Experiments.

Previous research in electrotransport had indicated that both Bi and Sb would migrate toward the positive electrode in Sn-based alloys (3), and since for these alloys no reversals in migrational direction had been reported (16, 51), the DC experiments were performed in either a "field-aiding or "field-opposing" mode. The cases where an adverse density gradient could result in convective stirring in the Sn-Bi alloys
were experiments where Bi was being driven up (since the density of Bi(1) is greater than the density of Sn(l) (79)) and, for the Sn-Sb alloys, where Sb was being driven down (since in this case, the density of Sn(l) is greater than that of Sb(1) (79)). It was anticipated that the magnetic field would inhibit convection resulting from an adverse solute concentration gradient.

Case I. $k_0 < 1$: Sn-Bi Alloy. A field-freezing experiment of an Sn-2 atom % Bi alloy was performed at a solidification speed of $-1.3 \mu m/sec$ without magnetic field. The alloy was directionally solidified for $-33\%$ of its length. The polarity was such that Bi was driven into the liquid ("field-aiding" mode) using a current density of $-485 A/cm^2$, and the resultant compositional profile is shown in Figure 29. The profile is similar to that shown in Figure 1(b) of Chapter II for complete convective mixing in the liquid. There is no initial transient and the solute boundary layer defined as in Chapter II is very small, $-0.5 mm$. Clearly, severe convective mixing was present in the liquid during the FF experiment. The convection could be the result of either the moderate current density, or an unstable condition resulting from an adverse solute concentration gradient, or both. The $k_0$ value was determined to be $-0.25$, in good agreement with the value of 0.26 from UDS experiments reported in Part A, and this suggests that local equilibrium existed at the solid/liquid interface during FF. The quenched interface was similar to Figure 19, i.e., it was planar. The above experiment was repeated on another Sn-2 atom % Bi alloy, with directional solidification performed over 60% of the specimen at a speed
H = 0 Gauss
CD ≈ 485 A/cm², + VE ⏬
̇R ≈ 1.3 μm/sec
Sn - Bi

Figure 29
\[ \frac{C_S}{C_0} \]

\[ \frac{C_S}{C_0} \]

\[ \frac{C_S}{C_0} \]

\[ \frac{C_S}{C_0} \]

\[ \frac{C_S}{C_0} \]
of ~1.1 \mu\text{m/sec}. Essentially the same kind of profile was obtained as shown in Figure 30. Again, the profile is typical of the case of complete convective mixing in the liquid. The determination of $\delta_{\text{sol}}$ is rather difficult due to the scatter in the probe data. An approximate value of ~1mm was obtained, but the error would be of the order of \pm 0.5 mm. Again, the $k_0$ value was found to be ~.24, in good agreement with the base-line value of 0.26 for the UDS experiment.

An attempt to control the convective mixing with the use of the magnetic field was done in another FF experiment with an Sn-2 atom % Bi alloy directionally solidified at 1.7 \mu\text{m/sec} while driving Bi into the liquid ("field-aiding" mode). The compositional profile of this experiment is shown in Figure 31, and it is clearly apparent that the magnetic field was of insufficient strength to inhibit convective mixing in the liquid. The $k_0$ value was estimated to be 0.22. The $\delta_{\text{sol}}$ is again difficult to estimate but is approximately 0.5 mm. Another Sn-2 atom % Bi alloy was field-frozen in the "field-aiding" mode with the 300 Gauss magnetic field activated; the solidification speed was 1.3 \mu\text{m/sec} and the sample was frozen for 51 % of its length, see Figure 32. Once more, evidence for convective mixing in the liquid may be seen from the nearly-flat directionally frozen portion of the compositional profile, the very narrow $\delta_{\text{sol}}$, and the level as-quenched liquid portion beyond. The $k_0$ was found to be 0.24.

In order to analyze for the probable cause of the convection, a FF experiment was performed on an Sn-2 atom % Bi alloy in the "field-opposing" mode, i.e., the Bi was driven toward the solid which was
Figure 30

\[
\frac{c_s}{c_0}
\]

\[
H = 0 \text{ Gauss}
\]

\[
CD \approx 4.85 \text{ A/cm}^2 + \text{VE}
\]

\[
\bar{R} \approx 1.1 \mu\text{m/sec}
\]

\[
\text{Sn-Bi}
\]
$H \approx 300$ Gauss

$CD \approx 485$ A/cm², + VE ↑

$\overline{R} \approx 1.7$ μm/sec

Sn-Bi
H \approx 300 \text{ Gauss}
H_{max} \approx 485 \text{ A/cm}^2, + \text{VE}
\bar{R} \approx 1.3 \mu\text{m/sec}
Sn - Bi

Figure 32

\frac{C_S}{C_0} vs. d, mm

\frac{C_S}{C_0} vs. d, mm
acting as an anode in the electrotransport circuit. The current density was kept constant at \(-485\, \text{A/cm}^2\) and the solidification speed was \(-0.93\, \text{um/sec}\). In this experiment a favorable solute induced density gradient was expected and the magnetic field was not activated. The compositional profile for this experiment is shown in Figure 33 and clearly indicates a lack of convective mixing in the liquid. This profile is explained on the basis of the relative speed ratios between the moving solid/liquid interface and the electrotransport speed of Bi in the liquid. Taking the electric mobility of Bi in the liquid Sn as \(U = 1.7 \times 10^{-3}\, \text{cm}^2/\text{sec-volt}\) (3) and the applied field as \(E = 0.025\, \text{volt/cm}\) (using the resistivity value of \(51.5\, \text{u\Omega} - \text{cm}\) from Verhoeven (16)) the Bi ET speed is \(R_{ET} = 0.43\, \text{um/sec}\) while the solidification speed is \(R_f = 0.93\, \text{um/sec}\). Thus, the interface will migrate into the liquid before much solute has been depleted by ET. Initially, the liquid adjacent to the interface "sees" an approximate \(C_0\) concentration of Bi; however, as time goes on, the ET drives Bi toward the solid while the bulk liquid is being depleted of Bi. As the liquid near the interface becomes enriched in Bi, so does the solid. Eventually, the interface starts to reach a region in the liquid where Bi flux is reduced due to earlier ET drain. Finally, the quenching operation freezes in the solid/liquid interface and liquid beyond. Measurement of \(k_0\) gave a value of \(-0.23\). Examination of the microstructure indicated no CS breakdown from the start ("0" mark on the profile graph) until approximately 5 mm into the profile where streaks were observed. These persisted until \(-25\, \text{mm}\) had solidified after which the microstructure was
$H = 0 \text{ Gauss}$

$CD \approx 485 \text{ A/cm}^2, +VE \uparrow$

$\bar{R} \approx 0.93 \mu \text{m/sec}$

Sn-Bi
clear of streaks.

Before leaving the Sn-Bi DC FF experiments, an attempt was made to obtain a plot of the $k_e$ values against solidification speed. In obtaining $k_e$, use was made of an equation derived by Verhoeven (16) from conservation principles in which $k_e$ is expressed as:

$$k_e = \frac{\ln(C_f/C_0(1 - g))}{\ln(1 - g)}$$

where $C_0$ is the initial alloy concentration, $g$ is the fraction directionally solidified, and $C_f$ is the mean composition in the quenched liquid. Values of $k_e$ were determined for the Sn-Bi FF experiments in which no CS breakdown existed and are shown in Figure 34 plotted against the solidification speed. Also in the figure are points obtained from the Pfann-Wagner (13) expression using values of $D = 1.7 \times 10^{-5}$ cm$^2$/sec, $\delta_{sol} = 500$ µm, and $k_0 = 0.24$. For the very limited speed range investigated, the experimental values appear to converge at the lower speed range with the values given by the Pfann-Wagner expression. Although the speed control was within ±5% of set-point for speeds of ~1 µm/sec, at the lower range (< 0.6 µm/sec) the variation appeared to be greater. Also, at the very slow speeds, thermotransport effects may begin to become bothersome (80). It is unfortunate that CS breakdown resulting from an insufficient liquid thermal gradient prevented using higher solidification speeds in the FF experiments, particularly in those experiments where the assumptions used in the derivation of the Pfann-Wagner expression were satisfied. However, the experimental results, albeit limited, do lend qualitative credibility to the Pfann-Wagner relationship under conditions of convective mixing in the liquid.
Figure 34. The effective distribution coefficient is plotted against solidification speed for an Sn-Bi alloy with $k_0 = .24$. Values computed from the Pfann-Wagner equation are shown.
A potential mechanism for the convective mixing encountered in this project will be discussed later.

Case II. \( k_0 > 1; \) Sn-Sb Alloy. These experiments were more exploratory in nature as it was felt that a greater understanding of FF effects with convection control would be obtained from Sn-Bi rather than Sn-Sb due to the extensive literature on the former as compared to the latter. A FF experiment was performed on an Sn-2 atom % Sb alloy, driving the Sb toward the solid ("field-opposing" mode). Since the density of Sb(l) is less than that of Sn(l), some convective mixing was expected as may be seen in Figure 35. In this case, the rate of freezing was \(-1.1\) \(\mu m/sec\) \((R_f > R_{ET})\) and the magnetic field was inactive. The profile can be qualitatively explained as follows. Initially, the liquid concentration just ahead of the interface was approximately the same as the original concentration of Sb. However, as time progressed, the Sb in the bulk of the liquid ahead of the interface was driven downward toward the solid causing the Sn to be displaced upward resulting in an adverse solute concentration gradient giving rise to convection. Once the adverse solute concentration gradient was relieved, ET would build it up again and the process would be repeated. This will be discussed more thoroughly later. Apparently, the rate of build up of the Sb concentration gradient and the maximum concentration value were sufficient to maintain the solid composition above \(C_0\) as is shown in the figure, i.e., \(C_S/C_0 > 1\) along the directionally solidified solid. The \(k_0\) value was found to be \(-1.64\) in good agreement with the value of 1.66 determined by Verhoeven and Gibson (78). Using Verhoeven's expression for \(k_e\), a
Figure 35

$H = 0 \text{ Gauss}$

$CD \approx 485 \text{ A/cm}^2, + \text{VE}$

$R \approx 1.1 \mu \text{m/sec}$

$\text{Sn-Sb}$
value of ~2.1 was calculated. Thus, "field-opposing" resulted in in- 
creasing the $k_e/k_0$ ratio above unity. It is interesting to note that 
inverting the Sn-Sb profile gives the same general shape as the Sn-Bi 
profile for complete convective mixing in the liquid. Figure 36 shows 
a typical quenched solid/liquid interface for an Sn-2 atom % Sb alloy 
that was field-frozen at ~1 µm/sec under a current density of 485A/cm² 
with the solid acting as the anode. Reversing the polarity did not 
alter the morphology of the interface.

A FF experiment similar to the one just discussed was performed 
on an Sn-2 atom % Sb alloy, but with the Sb driven into the liquid 
("field-aiding" mode). Since this compositional profile would result 
in a stable solute induced density gradient, no convective mixing was 
anticipated and none was found as may be seen from Figure 37. The 
magnetic field was not needed and was not used. Qualitatively, this 
profile can be explained as follows: initially, the moving solid/liquid 
interface "sees" a liquid of composition $C_0$. Then as time goes on, the 
Sb concentration in the liquid ahead of the interface is reduced by ET 
and the interface advances into the liquid containing progressively less 
Sb. However, since $R_f > R_{ET}$, eventually the solid composition increases 
slightly until the interface is quenched. It should be noted that this 
figure shows purification by ET alone over approximately 55% of the 
length of the specimen, i.e., normal UDS would have a level plateau of 
$C_S/C_0 = 1$ over this length and severe stirring would have $C_S/C_0 > 1$, 
but for the "field-aiding" mode, $C_S/C_0 < 1$ (in fact, by a $C_S/C_L$(bulk) 
expression, $k_e = 0.60$) which demonstrates that solutes with $k_0 > 1$ 
in a given solvent can be purified by field-freezing under appropriate
Figure 36. Typical longitudinal microstructure of Sn-2 atom % Sb alloy field-frozen left to right at 1.0 μm/sec and 485 A/cm². Antimony was driven toward the solid. The structure consists of twins, a few small inclusions, and a planar solid/liquid interface.
H = 0 Gauss
CD ≈ 485 A/cm², +VE
R ≈ 1.0 μm/sec
Sn-Sb

Figure 37
conditions of minimum convective mixing in the liquid. The interface composition gave \( k_0 = 1.6 \), again this value is in good agreement with Verhoeven and Gibson (78) indicating local equilibrium at the solid/liquid interface. Thus, FF in the DC mode has been demonstrated to be able to reduce \( k_e \) below \( k_0 \) under minimum convective mixing conditions.

The convection encountered in both the Sn-Bi and Sn-Sb systems may be due to an adverse solute concentration gradient. Another possibility is that the convection may have been caused by the current density itself as suggested by Verhoeven (16) although this seems unlikely in view of the fact that no convection was seen in cases where a favorable density gradient was present.

D. AC FF Experiments.

An AC field-freezing experiment using an Sn-2 atom % Bi alloy was performed with a current density of approximately 485 A/cm\(^2\). The first experiment was done without the use of the magnetic field in order to establish the effect of the current density on convection; a solidification speed of \(-1.3\ \mu m/sec\) was used. The compositional profile of this experiment is shown in Figure 38 and is indicative of no convective mixing in the liquid. The "characteristic distances" for the initial transient and the solute boundary layer are listed in Table III.

<table>
<thead>
<tr>
<th>Magnetic Field</th>
<th>( \delta\text{int}(\text{mm}) )</th>
<th>Theory</th>
<th>Exptl.</th>
<th>( \delta\text{sol}(\text{mm}) )</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>On</td>
<td>4.4</td>
<td>5.1</td>
<td>1.5</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Off</td>
<td>5.5</td>
<td>5.7</td>
<td>1.4</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

Table III. "Characteristic Distances", \( \delta\text{int} \) and \( \delta\text{sol} \) are listed for the AC FF experiments for Sn-2 atom % Bi alloy with the magnetic field on and off.
$H = 0$ Gauss
$CD \approx 4.85 \text{ A/cm}^2, AC$
$\bar{R} \approx 1.3 \mu \text{m/sec}$
Sn-Bi
Both the experimentally determined initial transient, $\delta_{\text{int}}$ and $\delta_{\text{sol}}$ of the solute boundary layer agree well with the predicted value. The profile is consistent with a condition of negligible convective stirring in the liquid. The lack of AC induced convective stirring in the melt is different from Verhoeven's results (16) although he used a much greater current density ($\sim 2000 \text{ A/cm}^2$) and had a curved solid/liquid interface which probably contributed to convection in the liquid. In the FF and ET experiments of this project, the solid/liquid interfaces were essentially planar although the UDS experiments had a slight curvature due to heat transfer near the edges. Also from Figure 38, the $k_0$ value determined at the solid/liquid interface is approximately 0.31, in good agreement with the value of 0.33 as determined by Verhoeven and Gibson (78).

An AC experiment using the Sn-Bi alloy was made with the magnetic field operating at its maximum value of 300 Gauss. No effects from the field were anticipated on either $\delta_{\text{int}}$, $\delta_{\text{sol}}$, or $k_0$. The results are shown in Figure 39 which verifies this assumption. The $\delta_{\text{int}}$ and $\delta_{\text{sol}}$ values are listed in Table III and indicate again a lack of convective mixing in the liquid during AC field-freezing at a current density of $\sim 485 \text{ A/cm}^2$. The $k_0$ value was 0.29. While this value is lower than the value of 0.30 reported by Verhoeven and Gibson (78), it is still within the experimental error of $\pm 15\%$ from the EMX analysis.

E. ET Experiments.

These experiments were performed on the Sn-2 atom \% Bi alloy to observe the effect of ET alone, i.e., the solid/liquid interface did
$H \approx 300 \text{ Gauss}$
$CD \approx 485 \text{ A/cm}^2, \text{AC}$
$\bar{R} \approx 1.2 \mu\text{m/sec}$
Sn-Bi
not move during the duration of the experiment (~ 6 hours). Experiments were made in both the "field-aiding" (driving Bi into the liquid) and "field-opposing" (driving Bi toward the solid) modes at a current density of ~ 485 A/cm². Figure 40 shows the EMX profile obtained for the "field-aiding" case, and, even though the magnetic field was activated during the experiment, convective mixing had occurred and no significant separation of the Sn and Bi was obtained. Since this mode would develop an adverse solute density gradient the finding of convection was not surprising. Another ET experiment was performed in the "field-opposing" mode where Bi was driven toward the solid with the same parameters as above. The resultant compositional profile is shown in Figure 41.

Since these were static experiments, the question of the role of thermotransport (TT) in altering the profiles needs to be addressed. Specifically, since it is known that Bi will migrate toward the cold end of a temperature gradient (81), this may have contributed to the build-up at the quenched solid/liquid interface of Figure 41. In estimating the relative contribution of TT, the thermal diffusion coefficient for Bi in a dilute Sn-Bi alloy was used as \( D' = 2 \times 10^{-8} \text{ cm}^2/\text{sec-K} \), this value was from Verhoeven, et al. (81). The TT velocity with respect to the interface is given by Verhoeven, et al. (82) as \( V_{TT} = D'\nabla T \), where \( \nabla T \) is the liquid thermal gradient. Taking the ET velocity, \( v_{ET} = U_1 E \), then the ratio of the \( v_{ET}/v_{TT} \) is \( U_1^2 E/D' \nabla T = 11 \). Thus, ET contributes roughly 90% of the total build-up with TT contributing roughly 10%. While these estimates are crude, it does suggest that the
$H \approx 300 \text{ Gauss}$

$CD \approx 485 \text{ A/cm}^2, + \text{VE}$

$R \approx 0 \mu\text{m/sec}$

$Sn - Bi$

Figure 41
build-up of Bi at the solid/liquid interface is mainly due to ET. As an added note, it is believed that the contribution of TT to the profiles observed in the FF experiments was negligible since for UDS runs without convective mixing, the initial solid composition agreed with that of the quenched liquid composition within the experimental error.

In Figure 41, an estimate of the rate of build-up of the solute concentration gradient at the solid/liquid interface can be made as follows. During the course of the experiment, Bi was driven toward the interface where its concentration increased, at the solid/liquid interface the concentration gradient can be estimated as $\nabla C_{x=0} = 2.4$ weight %/cm. Since this concentration gradient is built up over the time period of ~6 hr, assuming the rate of build-up of the concentration gradient is linear, then $(\nabla C_{x=0})=(d/dt)(\nabla C_{x=0}) = 0.4$ weight %/cm-hr = 4,000 wppm/cm-hr.

The morphology of the solid/liquid interface was not affected by the polarity change in the ET experiments. Figure 42 shows the interface for the Sn-2 atom % Bi alloy. When the Bi was driven into the liquid, the region adjacent to the interface shows some dendrites with cells extending into the quenched liquid. For the case in which Bi was driven toward the solid, the morphology of the quenched interface appears the same as shown in Figure 43. In both cases, the interface was nearly planar.

F. Effect of the Magnetic Field on Convection Control.

Since the magnetic field was designed to inhibit convection caused by an adverse solute-induced gradient, only the case in which Bi was
Figure 42. The microstructure of the quenched solid/liquid interface is shown for the ET of an Sn-2 atom % Bi alloy. Bi was driven toward the liquid.
Figure 43. The microstructure of the quenched solid/liquid interface is shown for the ET of an Sn-2 atom % Bi alloy. Here Bi was driven toward the solid.
being driven into the liquid for the Sn-2 atom % Bi alloy will be discussed as this will suffice for an example. A model will be suggested to account for the appearance of complete convective mixing occurring as shown in Figure 29.

The suggested model for convective mixing in the liquid during an FF experiment under the influence of the magnetic field depends upon the interplay between the ET driven solute build-up of the solute concentration gradient in the liquid ahead of the solid/liquid interface to a critical value and the relief of the gradient through convective mixing followed by repeated build-up. From Appendix B, the critical solute concentration gradient for the onset of convection for an Sn-Bi alloy in a capillary of the diameter used in this project is - 970 wppm/cm at a magnetic field strength of ~300 Gauss. This is the threshold gradient above which convection will occur, thereby relieving the gradient. From the ET experiment discussed in the last section for the case of driving Bi toward the solid, the rate of build-up of the concentration gradient was of the order of 4,000 wppm/cm-hr. Thus, from the beginning of the FF experiment driving Bi into the liquid, for a time period of approximately \( t = \frac{970 \text{ wppm/cm}}{4000 \text{ wppm/cm-hr}} = 0.24 \text{ hr.} = 15 \text{min} \), no convective mixing was occurring in the melt and the solid profile was that for no mixing. At a typical solidification speed used, this gives a distance of the order of 1.1 mm before convection begins. For some distance, convection would occur then cease and ET would again start to build up the gradient until the cycle repeated itself. The length of the convective mixing distance can not be
estimated since the speed of convection and its effectiveness is not known. Therefore, it is difficult to ascertain the wave length of the cycle. The FF experiments with Bi going to the liquid did not show any undulations, at least within the EMX error limit of ± 15%. The fluctuations may be below the EMX limit as the following suggests. For the distance of 1.4 mm, the solid compositional profile is given from the expression for no mixing as written in Chapter II. Using the appropriate parameters, the solid composition is roughly 1.5 weight % Bi; for complete mixing, the solid composition is roughly 0.97 weight % Bi. The difference is approximately 0.53 weight % Bi which would not necessarily be detected by EMX.

A cyclic fluctuation in composition driven by ET and relieved by convection seems plausible in light of the fact that convection needs to be driven and would tend to level out any adverse density gradients with time. This model would also suggest no convective stirring during the AC FF experiments, as was observed, since no "driving force" for mixing could exist.
CHAPTER V. CONCLUSIONS AND RECOMMENDATIONS

This project has demonstrated that enhanced purification can be obtained by direct current field-freezing when convective mixing in the liquid is minimized. Also it has been demonstrated that solutes with $k_0 > 1$ in a given solvent can have their concentration lowered while field-freezing with no convective mixing in the melt.

This work has shown that a solute-induced adverse density gradient is an effective means of generating convection, and that for the current density investigated ($\sim 485 \text{ A/cm}^2$), alternating current field-freezing does not cause convection. Also a model based on the cyclic behavior of electrotransport and convection induced by an adverse solute density gradient has been proposed to account for the apparent complete convective mixing observed for an alloy with $k_0 < 1$ and with an adverse solute density gradient in the liquid. It has also been observed that neither alternating current nor direct current field-freezing alter local equilibrium at the solid/liquid interface.

If performed carefully, the electron microprobe X-ray analysis can be used to obtain quantitative data on compositional profiles obtained by field-freezing. This analytical technique allowed for interfacial compositions to be determined.

It has been shown that interface instability resulting from
constitutional supercooling occurs in the form of nodes in an Sn-Bi alloy, and that the morphology of the nodes can be largely explained by instability theory.

Finally, it has been shown that the inhibition of convection caused by an adverse solute density gradient of the order of 1300 wppm/cm requires a vertical DC magnetic field strength greater than 300 Gauss.

From the analysis of the results of this project, some areas of future research were uncovered. Specifically, the model suggested as an explanation for the convection encountered in the \( k_0 < 1 \) case should be pursued.

The nodal breakdown of the solid/liquid interface should be studied more thoroughly, especially the effects of solidification speed changes on internodal spacing for speed ranges greater and smaller than those used here.

Finally, the effect of field-freezing under controlled convection during the unidirectional solidification of eutectic and off-eutectic alloys should be pursued.
Appendix A: Vibration Control

In general, during unidirectional solidification experiments, one wishes to isolate the system from any sources of mechanical vibration which could manifest themselves as solute "banding" from local velocity fluctuations at the solid/liquid interface or result in mixing of the solute in the bulk of the liquid which would be particularly annoying if one were attempting to control liquid convection as in this study.

Early in the design and setting up of the equipment for this project, it was observed that the floor of the laboratory was experiencing vibration from nearby mechanical equipment. This vibration was detected by placing a partially filled beaker of water upon the equipment table and observing the standing waves. Vibration control pads ordered early in the program did not eliminate this vibration, and it was considered impractical to move the power supplies, etc., to another room (which would not eliminate the effects of vibration). Therefore, a more thorough examination of the cause of the vibration and its isolation was warranted.

According to Tse, Morse and Hinkel (83), if the excitation agent causing the vibration is operating in a sinusoidal manner, vibration control can be achieved by 1) varying the mass and spring constant of the system such that its natural frequency is much less than the
excitation frequency or by 2) using what is called a dynamic absorber. The former approach was used in this program. The isolation from random or non-sinusoidal vibrations is more difficult, if obtainable at all.

Since the author believes that others may find this subject relevant for their own projects, the following paragraphs review the theory of vibration control in the context that it was used in this program. The interested reader should consult texts such as references (84,85 ) for more details.

I. Brief Review of the Theory of Vibration Control

A brief review of vibration theory follows so that the concepts can be used to intelligently design equipment to be as nearly free as possible from the adverse effects of mechanical vibration. The following definitions are needed:

Mass: Assumed rigid body following Newtonian mechanics, (M).

Spring: Negligible mass, entirely elastic following Hooke's law with the spring force proportional to the deflection, (k).

Damper: Negligible mass and elasticity, usually assumed viscous, damper force proportional to velocity, (c).

Excitation: Externally imposed disturbance, if periodic results in forced vibration, if aperiodic results in transients.
Free Vibration

Undamped case. For free vibration, the spring-mass system is a simple harmonic oscillator vibrating about the equilibrium position with a frequency of \( f_n = \frac{\sqrt{k/M}}{2\pi} \). Consider the spring-mass system in Figure 44 (a) under static equilibrium; the forces resulting from its displacement from the equilibrium (Figure 44 (b)) may be analyzed in a free-body diagram shown in Figure 44 (c). Upon the release of the body from the displaced configuration, the resultant sinusoidal motion with time is shown in Figure 44 (d).

Damped case. The addition of a damper in the system alters the motion depending upon the degree of damping. This may be seen in Figure 45 where the motion of a system containing various degrees of damping is schematically shown. An example of the use of the critically damped case would be the stopping of the recoil motion of an artillery piece where the recoil must be limited in extent.

Forced Vibration

Undamped case. In this situation, the linear superposition of the natural frequency of the system and the forcing function (external excitation) contribute to the motion except for the special case where both frequencies are the same whereupon the idealized system goes into resonance and the amplitude increases without limit (until failure of the equipment occurs).

Damped case. When damping exists in the system subjected to a forcing function, the motion may be characterized for the case away from resonance as an initial transient which decays with time leaving
Figure 44. The static equilibrium position is shown in (a). Displacement of the mass from equilibrium position downward by distance $x_0$ in (b) may be analyzed by the free-body diagram in (c). The resultant motion upon release of the mass is simple harmonic shown in (d).
Figure 45. The effect of viscous damping upon the motion of the spring/mass system shown in (a) may be seen in (b).
a steady-state component vibrating at the same frequency as the excitation or forcing function. When the system is being excited by a frequency such that resonance exists (i.e. $f_{ex} = f_n$), then the amplitude again increases but not to the extent as for the resonance/undamped case. However, the exact nature of the resonance depends on the degree of damping in the system.

II. Details of the Single-Degree of Freedom System in Free Vibration.

Consider the single-degree of freedom system (one spatial coordinate is required to define the configuration of the system) with a Hookean spring and linear damper under the influence of an external vibration (forcing function), see Figure 45 (a). The equation of motion is $M\ddot{x} + c\dot{x} = kx = 0$ ($\ddot{x} = d^2x/dt^2$, $\dot{x} = dx/dt$). A solution to this second order, ordinary, linear, homogeneous differential equation is identified as the "complementary solution" and is $x(t) = x_c(t) = A_1e^{m_1t} + B_1e^{m_2t}$, where $m_{1,2} = (1/2M)(-c \pm (c^2 - 4MK)^{1/2})$, or $m_{1,2} = -\delta \omega_n \pm (\delta^2 - 1)^{1/2} \omega_n$. The natural radian frequency, $\omega_n$, is related to the mass (M) and the spring constant (k) as $\omega_n = 2\pi f_n = (k/M)^{1/2}$ rad/sec. The damping factor is $\delta = c/(2kM)^{1/2}$. Several kinds of the response of the system to the initial displacement can occur depending upon the magnitude of $\delta$, as may be seen in the following.

Case 1. $\delta > 1$ (i.e., $c^2 > 4MK$). In this case, the system is over damped and no oscillatory motion can exist, see Curve 1 of Figure 45 (b). Any imparted motion decays exponentially.
Case II. $\delta = 1$ (i.e., $c^2 = 4Mk$). For this case, the system is critically damped and no oscillatory motion exists, Curve 2 of Figure A-2 (b).

Case III. $\delta < 1$ (i.e., $c^2 < 4Mk$). Here the roots $m_{1,2}$ are complex conjugates, i.e. $m_{1,2} = -\delta \omega_n \pm j(1 - \delta^2)^{1/2} \omega_n$ or defining the damped natural frequency $\omega_d = (1 - \delta^2)^{1/2} \omega_n$ ; then $m_{1,2} = -\delta \omega_n \pm j\omega_d$. The motion is oscillatory but decays with time and the damped frequency is less than the undamped frequency, see Curve 3 of Figure 45 (b).

III. Details of the Single-Degree of Freedom System in Forced Vibration

Assume that a sinusoidal force of frequency $\omega$ acts upon a single degree of freedom system. The resultant equation of motion is $M\ddot{x} + c\dot{x} + kx = F \sin \omega t$. The complementary (or homogeneous) solution of the equation of motion is the same as for the free vibration case but in addition a particular solution must be added to the complementary solution to give the general solution. In this case, the particular solution is of the form $x_p = A \sin \omega t + B \sin \omega t$. Using $x_p(t)$ in the equation of motion and solving for $A$ and $B$,

$$x_p(t) = \frac{F}{(k - M\omega^2)^2 + (c\omega)^2} (k - M\omega^2) \sin \omega t - c\omega \cos \omega t,$$

or

$$x_p(t) = \frac{F}{((k - M\omega^2)^2 + (c\omega)^2)^{1/2}} \sin (\omega t - \phi),$$

where $\tan \phi = \frac{c\omega}{(k - M\omega^2)}$, or $x_p(t) = X \sin (\omega t - \phi)$, where $X$ is the steady-state amplitude response (after the transient portion has decayed to zero) and $-\phi$ is the phase lag of $x_p(t)$ with respect to $F \sin \omega t$. 
Therefore, the complete solution consists of the complementary and particular solutions, \( x(t) = A e^{-\delta\omega t} \sin(\omega\tau + \psi) + F/k \sin(\omega t - \phi) \). As the initial transient decays to zero, the system responds to the excitation by vibrating at the same frequency as the excitation. \( K \) is defined as the magnification ratio of the steady-state amplitude response to the static deflection, \( K = (1 - r^2) + (2\delta r)^2)^{-1/2} \) where \( r = \omega/\omega_n = \) the frequency ratio = \( f/f_n \).

IV. Vibration Transmissibility and Isolation

Consider a damped single-degree of freedom system undergoing forced vibration and responding with the displacement given in the preceding section. If the total transmitted force to the system after the initial transient has decayed to zero is \( F_t = kx + cx \), then the steady state displacement response is \( F_t = kx \sin(\omega t - \phi) + cX \cos(\omega t - \phi) \), or \( F_t = X (k^2 + c^2\omega^2)^{1/2} \sin(\omega t - \phi + \gamma) \), where \( \tan \gamma = c\omega/k = 2\delta r \). The total force may be expressed as \( F_t = FK (1 + (2\delta r)^2)^{1/2} \sin \omega t - \phi + \gamma \). The ratio of the transmitted force to that of the impressed force is the transmissibility ratio, \( TR \), i.e.,

\[ TR = FK(1 + (2\delta r)^2)^{1/2}/F = K(1 + (2\delta r)^2)^{1/2} \]

and is schematically shown in Figure 46 as a function of the frequency ratio, \( r = f/f_n \) for various degrees of damping. It may be observed that for low \( TR \), the frequency ratio must be large. In particular, the smaller \( \delta \) is and the larger \( r \) is, the lower \( TR \) becomes. This forms the basis for vibration control through isolation. As an example, consider the case of protecting a delicate piece of equipment (eg., a balance) from external
Figure 46. The transmissibility ratio, TR, is shown as a function of the frequency ratio, $r = f/f_n$ for various degrees of damping.
vibration such as that coming from a motor. The impressed force varies sinusoidally with time. Figure 47 shows schematically the displacements involved in the vibration mode being considered. The instrument is of mass M with a spring constant k and a damper c resting upon a surface undergoing a displacement \( y = Y \cos (\omega t) \), (this displacement may be acting on the balance via the table upon which it rests). The equation of motion of \( M\ddot{x} = c(\dot{y} - \dot{x}) + k(y - x) \), or \( M\ddot{x} + c\dot{x} + kx = kY \cos (\omega t) + Y\omega c \cos (\omega t + \pi/2) \). The steady-state component of the motion results in a displacement ratio of the mass to the support (eg., table) of \( X/Y = (1 + (2\delta r)^2)^{1/2} / ((1 - r^2)^2 + (2\delta r)^2)^{1/2} \), or \( X/Y = K(1 + (2\delta r)^2)^{1/2} = TR \). The displacement ratio is the same as the transmissibility ratio and Figure 46 may be used to show the variables that need to be changed to effectively isolate the mass M from external vibration. That is, if the excitation frequency is known or measurable, then the natural frequency of the system must be varied in some manner (increase M, decrease k, or both) so as to obtain a large r. Then with a small \( \delta \), a low TR will be obtained.

V. Application of Vibration Control

In the following discussion, the concepts developed in the section on vibration control through isolation which were used in the project to effectively isolate the field-freezing equipment from vibration will be discussed. The experimental equipment consisting of the field-freezing apparatus and supportive structure were idealized as a mass M supported on four springs giving a combined spring constant K (in
Figure 47. The relative displacements for a mass excited by a sinusoidal displacement is shown.

EOM: \[ M \ddot{x} = c (\dot{y} - \dot{x}) + k (y - x) \]
Newtons/meter) and are schematically shown in Figure 47. For purposes of analysis, the excitation was assumed to be sinusoidal of radian frequency $\omega \sec^{-1}$ and amplitude $Y_0$. The response of the system to the steady-state vibration after the initial transient was assumed to be the same frequency as the excitation. Of course, the actual frequency of the excitation had to be determined in some manner in order to utilize the above assumptions.

Analysis of the source of the vibration was done by using a vibration detector constructed by mounting an SR-4\(^a\) strain gage on a cantilever beam and following the SR-4 output on an oscilloscope. Figure 48 shows the physical arrangement. The cantilever beam and its holder were placed on the laboratory floor and a sine wave of frequency 17 cps was observed on the display screen. The cantilever beam was "tuned" by adding small weights to its free end so that the strain gage output was a maximum in order to increase its sensitivity. Using the internal strain calibration for the SR-4 strain gage and a known deflection of the end of the cantilever beam, an estimate of the amplitude of the displacement of the floor was obtained. An approximate value of the displacement of the floor was found to be $2 \times 10^{-6}$ meters. Since the excitation frequency was found to be 17 cps, and using the graph from Figure 46, it was decided to try to obtain and $r$ value of 10. For $r = 10$ and negligible damping, the $TR$ value was estimated to

\(^a\) SR-4 Type A-AF strain gage manufactured by Baldwin-Lima-Hamilton Corp., Waltham, Mass.
Figure 48. The position of the SR-4 strain gage on the cantilever beam is shown. The output of the SR-4 strain gage was observed on an oscilloscope.
be 0.009.

In order to have and \( r = 10 \), the natural frequency of the system, \( f_n \), had to be 1.7 cps. In order to obtain this frequency, both the mass and the spring constants were varied such that the target frequency was 1.7 cps. Each of the four springs used to support the apparatus table had a spring constant of 1489 Newtons/meter. In addition to the field-freezing equipment, lead bricks were added to the apparatus table to increase the total mass to 238 KGM. Thus, the natural frequency of the system was computed to be 1.6 cps giving as an \( r \) value 10.6.

The vibration detector was placed on top of the apparatus table after completing the above vibration isolation steps and attempts were made to detect vibration either with the power drive motor running or not running and no vibration was detected in either case. The estimated amplitude threshold of the vibration detector was on the order of \( 10^{-5} \) meter. The estimated vibration amplitude was computed from the TR and the floor displacement to be \( 1.6 \times 10^{-8} \) meter which is in fairly poor agreement with the estimated threshold limit.

Of course, as discussed in Chapter III, the observation of solute banding in the EMX profiles could constitute evidence for local solid/liquid interface velocity fluctuations arising from vibrational effects and, if not observed would be final proof of vibration control through isolation.
Appendix B: Inhibition of Liquid Metal Convection by a DC Magnetic Field

In this section, a brief outline of Chandrasekhar's paper (49) is given, together with a discussion of its use, in combination with Verhoeven's work (42, 43), for the prediction of the critical solute concentration gradient for the onset of convection in the presence of a DC magnetic field.

Chandrasekhar treated the problem of the calculation of the critical Rayleigh number for the onset of convection in an electrically conducting fluid subjected to an adverse temperature gradient and a DC magnetic field. An analysis for the critical Rayleigh number under similar conditions except without the magnetic field was made by Pellew and Southwell (86) and is more general than Rayleigh's analysis (40). Chandrasekhar's values for $H = 0$ agree with those of Pellew and Southwell for the same boundary conditions. In all of the above cases, the fluid was treated as being of finite thickness and infinite extent, i.e., the aspect ratio was $= 0$. Of course, this condition is not realistic for a capillary type of experiment, but the results can be adjusted, as shown later in this section.

Chandrasekhar starts his analysis by using the equations of motion (EOM), Maxwell's equations (ME), and heat conduction (HC) with the
assumption that the density variation of the fluid with temperature is
negligible except so far as its action on the effect of gravity is con­
cerned. His equations are:

\[
\begin{align*}
\text{EOM:} & \quad \rho (\partial \mathbf{u} / \partial t) - \rho (\mathbf{u} \cdot \nabla) \mathbf{u} - \mathbf{u} \mathbf{J} \times \mathbf{H} = -\nabla \rho - \rho \nu \nabla^2 \mathbf{u} - \rho \nabla V \\
\text{ME:} & \quad \nabla \times \mathbf{H} = 4 \pi \mathbf{J} ; \nabla \times \mathbf{E} = -\mathbf{u} (\partial \mathbf{H} / \partial t) ; \nabla \cdot \mathbf{H} = 0 ; \mathbf{J} = \sigma (\mathbf{E} - \mu \mathbf{u} \times \mathbf{H}) \\
\text{HC:} & \quad \partial T / \partial t + (\mathbf{u} \cdot \nabla) T = \kappa \nabla^2 T
\end{align*}
\]

where the definitions are: (all units are cgs-emu)

\begin{align*}
\rho & = \text{fluid density} \\
P & = \text{fluid pressure} \\
T & = \text{fluid temperature} \\
V & = \text{gravitational potential} \\
E & = \text{intensity of the electric field} \\
H & = \text{intensity of the magnetic field} \\
J & = \text{current density} \\
u & = \text{magnetic permeability} \\
\nu, \kappa, \sigma & = \text{coefficients of kinematic viscosity, thermal conductivity and} \\
& \quad \text{electrical conductivity, respectively.}
\end{align*}

The displacement current is ignored generally in magnetohydrodynamic
calculations. After much algebra, Chandrasekhar reduced the EOM, ME,
and HC to the following forms:

\[
\begin{align*}
\text{EOM:} & \quad \partial \mathbf{u} / \partial t = (\mu \mathbf{H} / 4\pi \rho_0) r_j (\partial h / \partial x_j) + \gamma \Theta - \nu \nabla^2 \mathbf{w} - \lambda \left( \partial \mathbf{w} / \partial x_i \right) \\
\text{ME:} & \quad \partial h / \partial t = H r_j (\partial \mathbf{w} / \partial x_j) + \eta \nabla^2 h \\
\text{HC:} & \quad \partial \Theta / \partial t = -\mathbf{w} + \kappa \nabla^2 \Theta
\end{align*}
\]
where use was made of the equation of state, viz. \( \rho = \rho_0(1 - \alpha \Delta T) \)
where \( \alpha \) is the coefficient of volume expansion. The main point is
that the case for marginal stability (critical Rayleigh number) was ob-
tained by the use of the "principle of the exchange of stabilities"
where the \( \frac{d}{dt} \) terms are set equal to zero. The above equations are
then solved for various boundary conditions and the results are repre-
sented as a graph of the critical Rayleigh number, \( R_c \), as a function
of the parameter \( Q (Q = \mu^2 H^2 \sigma d^2 / \rho_0 \nu) \). The boundary conditions are
(I) both upper and lower bounding surfaces are free, (II) both upper
and lower bounding surfaces are rigid, and (III) the upper bounding
surface is free while the lower bounding surface is rigid. The last
boundary condition is pertinent to the conditions for capillary work.
In the expression for \( Q \), \( d \) is the major dimension of the convection
cell and \( \sigma \) is the electrical conductivity of the fluid. Figure 49
shows the functional relationship between \( R_c \) and \( Q \) for the case of fin-
ite thickness in the fluid of infinite extent; the boundary conditions
are those for Case III. From the figure, it may be seen that for a
magnetic field with a flux density of \( \sim 300 \) Gauss, the \( R_c \) is \( \sim 1780 \) or
the ratio of \( R_c^{H \neq 0} / R_c^{H=0} \) is 1.63, i.e., the magnetic field increased
the critical Rayleigh number by \( \sim 63 \% \). This can be rationalized as
follows: for a cell to form and thus convection to commence, the lines
of flux must be cut by conducting fluid which will be difficult (sim-
lar to Lenz's Law) and therefore, a kind of "static coefficient of
friction" effect will delay convection.

For this project, the aspect ratio as discussed in Chapter II
Figure 49. The log of the critical Rayleigh number is shown as a function of the log of Q for the boundary conditions prevalent for a capillary type experiment.
is greater than 20 where, for \( H = 0 \), Verhoeven (42,43) reports the critical Rayleigh number as approaching 68. Assuming the application of the magnetic field does not alter the form of the variation of the critical Rayleigh number with aspect ratio, then the 300 Gauss field should give a critical Rayleigh number of \((1.63)(68) = 111\) for a capillary type of aspect ratio. This essentially amounts to shifting the curve of Figure 3 upward by a constant multiplier of 1.63.

Using the data from Verhoeven (42) with the new \( R_c \) for a magnetic field of 300 Gauss, \( R_c = \nabla C_g a' r^4 / \nu \) \( D \) = 111, where \( g = 980 \text{ cm/sec}^2 \); \( a' = 0.22 \) atom fraction Bi in Sn-Bi at 500 C; \( D = 1.7 \times 10^{-5} \text{ cm}^2/\text{sec} \); \( \nu = 2.51 \times 10^{-3} \text{ cm}^2/\text{sec} \). The critical solute concentration gradient, i.e., the change in concentration over 1 cm is

\[
\nabla C_{\text{crit}}^{H\neq 0} = \nu D R_c H^{0} / g a' r^4 = (2.51 \times 10^{-3})(1.7 \times 10^{-5})(111)/(980)(.22)(.0794)^4
\]

\[
= 550 \text{ appm/cm}
\]

\[
= 968 \text{ wppm/cm}
\]

Thus, convective mixing should commence when the solute concentration gradient equals or exceeds 968 wppm/cm. For \( H = 0 \), the critical solute concentration gradient reduces to 593 wppm/cm. Thus, the magnetic field does increase the critical solute concentration gradient, but apparently not enough to inhibit convection.
Appendic C: Design, Construction, and Characterization of
Magnet Coil

Using the formulation given in Appendix B (which was based on Chandrasekher's treatment (49) of the modified Rayleigh-Jeans instability problem) and physical properties of a dilute tin-bismuth liquid alloy, a flux density of ~500 Gauss was determined to be the design flux density for the magnetic field. Since the necessary temperature gradient required for the constitutional supercooling criterion would lead to local temperatures above the Curie point for iron, the magnetic field had to be generated by an air solenoid of a geometry such that the furnace and cooling chamber were contained within the solenoid. Of course, the magnet coil, furnace, and capillary container were vertical and coaxial.

MAGNET COIL DESIGN

The selection of the magnet wire gage size, number of turns of the solenoid, and operating current of the solenoid were obtained by using an IBM 370 computer operating on a simple program that took wire gage size, and resistance per unit length as input and computed flux density ( \( |\mathbf{H}| \) ampere-turns), power generation, external power dissipation, and solenoid weight as output for a given coil length and internal diameter. The computer program was based on information taken from the literature (87). In this program, it was assumed that the wire was close packed and that the coil temperature was uniform with a 50°C temperature.
increase over ambient. The final coil design selection was obtained by considering those wire parameters that 1) gave a power dissipation approximately 20% greater than power input ($I^2R$ heating for a DC coil), and 2) gave a minimum coil weight (the upper limit of coil weight was set at 50 lbs. since this was considered to be a "comfortable" weight to handle during assembly and did not result in an excessively large piece of equipment such that further fabrication problems would be encountered). Using the above criteria, it was decided to construct the solenoid from 18 gage enameled copper magnet wire\textsuperscript{a} using 3,860 turns wrapped on a 6.5 inch diameter by 7.6 inch length mandrel (the dimensions computed in Chapter III for the mullite insulating tube surrounding the furnace). Figure 50 shows the configuration of the furnace, solenoid, and allied parts in the final design arrangement.

**MAGNET COIL CONSTRUCTION**

The details of the auxiliary equipment needed in the construction of the coil are shown in Figure 51. The bottom wooden end plug was cut to partially fit inside the mullite tube yet leave approximately one inch sticking outside the tube for chucking into the head stock of the lathe upon which the coil was to be wound. The top end plug was similarly mounted on the mullite tube but required a centered recess to receive the tail stock arbor. Three austenitic stainless steel threaded rods were symmetrically positioned inside the mullite tube to facilitate holding the asbestos retainer rings and help

\textsuperscript{a} Magnet wire was obtained from Complete Readie Electric Co, Cleveland, OH.
Figure 50. The spatial arrangement of the magnet coil, furnace, cooling chamber and heat pipe "ears" are schematically shown.
Figure 51. The arrangement of the magnet wire, copper girdle, mullite tube, asbestos retainer rings and wooden jig fixtures are shown in the assembly ready for winding with magnet wire.
stabilize the austenitic stainless steel furnace support inside the mullite tube. Essentially, after tightening the austenitic stainless nuts onto the threaded rods, the mullite tube and asbestos retainer rings took on the appearance of a large spool.

A 0.125 inch thick copper girdle was cold roll-formed to a diameter slightly smaller than the mullite tube (a smaller diameter was used to allow for elastic spring-back), then the two receptacles (ears) for the two heat pipes were brazed onto the girdle in diametrically opposing positions half-way along the girdle length (which ran the full length of the mullite tube). The copper girdle was used to hold the heat pipes and to help obtain a uniform temperature on the inside surface of the magnet coil. After giving the copper girdle an acid pickel in a concentrated HCl (aq.) solution, it was placed about the mullite tube giving a snug fit. The tips of the "ears" were taped so as to prevent damage to the magnet wire during the winding operation.

The actual winding of the magnet coil was done on a lathe using a counter to insure the requisite number of turns were laid down. The assembly was placed in the lathe and the counter was indexed. While the lathe was hand-turned, magnet wire was carefully guided onto the copper girdle being watchful to achieve close-packing of each coil without incurring damage to the wire during the winding of 3,860 turns. After completion of the winding operation, the leads were carefully secured about the spool before removing the assembly from the lathe.
MAGNET COIL CHARACTERIZATION

In order to determine the strength and shape of the magnetic field of the coil, the wooden end plugs were removed and the coil was placed in an upright position on a wooden support free from the influence of any ferromagnetic materials. The characterization of the magnetic field flux density was accomplished with the aid of a Bell Model BH-206 Hall probe\(^a\). The Hall probe was held in a balsa wood fixture such that the solenoidal flux would be perpendicular to the probe and its Hall current. Figure 52 shows schematically the arrangement used in the characterization of the coil.

The Hall probe was calibrated with the help of a large, well-calibrated electromagnet in the NMR laboratory of the Physics Department at The Ohio State University. Essentially, the calibration consisted of plotting the Hall voltage at a fixed Hall current against the magnetic flux density passing through the probe. Figure 53 shows the calibration curve obtained for the BH-206 Hall probe operating at \(I_H = 200\) ma.

Mapping of the magnetic flux density consisted of obtaining a centerline profile and several transverse plots for field symmetry. The centerline profiles were obtained at several coil currents. The excitation circuit of the coil consisted of a 350 kilo-ohm resistor in parallel with the coil and driven with a precision regulated SCR power supply with a maximum voltage output of 120 volts. The BH-206 Hall probe was purchased from F. W. Bell, Inc. Columbus, Ohio

\(^a\) Bell Model BH-206 Hall probe was purchased from F. W. Bell, Inc. Columbus, Ohio
Figure 52. The coil and BH-206 Hall probe are schematically shown in the configuration used to characterize the magnetic flux density profiles.
Figure 53. The calibration curve of Hall voltage with flux density for a Hall current of 200 mA is shown.
Hall probe was powered by another precision regulated SCR DC power supply, and the Hall current was observed on a precision DC milliammeter. Longitudinal centerline profiles consisted of lowering the Hall probe in increments from top to bottom while the coil was energized and recording the Hall voltage as measured on a VTVM. For the transverse profiles, a N-S-E-W index was marked on the top of the asbestos retainer ring and for a given elevation, the Hall probe was moved in increments along the N, S, E, or W directions with the Hall voltage being recorded. After obtaining the longitudinal and transverse Hall voltage profiles, the flux density was obtained from the calibration curve, Figure 53 and the flux density profiles were plotted out as shown in Figures 11 and 12. The reproducibility of obtaining the same flux density from any given current setting was approximately 3%.
REFERENCES


75. T. S. Lakshmanan: Ph.D. Thesis, The Ohio State University Library, Columbus, Oh., 1972.