SOLUTE REDISTRIBUTION IN DENDRITIC SOLIDIFICATION

by

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ABSTRACT

Analyses that include diffusion of solute in the solid phase are developed to describe solute redistribution in dendritic solidification of metallic alloys. The analyses, applicable for a wide range of casting and ingot-making practices, are based on conditions that include negligible undercooling before nucleation of solid phases, negligible increase of solute in advance of the tips of growing dendrites, and complete diffusion within the liquid over distances the order of dendrite spacings.

The classical nonequilibrium freezing equation, \( C_s = kC_0(1-f_S)^{k-1} \), accurately describes solute redistribution between dendrite arms for the solidification processes considered, provided diffusion in the solid is negligible. To account for the effect of diffusion in the solid, an analytic expression, similar in form to the classical expression, is developed through evaluation of the materials balance. In addition, a numerical analysis procedure is employed to examine in more detail effect of diffusion both during and after solidification. For a platelike dendrite morphology, the departure from classical nonequilibrium freezing behavior is determined by evaluation of the factor \( 4D_s \theta_f /kd^2 \), where \( D_s = \) diffusion coefficient of solute in solid phase, \( \theta_f = \) solidification time, \( k = \) partition ratio, \( d = \) dendrite spacing. When the ratio \( d^2/\theta_f \) is a constant for a particular alloy, extent of microsegregation is a constant independent of cooling rate.
Results are presented of experimental work on solute redistribution in alloys solidified under controlled conditions. Results of other investigators are included for comparison. Minimum solute content in the dendrite increases during solidification as a result of diffusion in the solid, but because of coarsening of the dendrite structure, the extent of diffusion increases only slowly with solidification time. Empirical measurement of segregation ratio and amount of second phase compare favorable with computations.

Once the distribution of solute at some stage during or after solidification is determined, many casting parameters are amenable to analysis. A large group of macroscopic parameters that characterize a solidifying alloy are calculable through extrapolation of data measured on single phase alloys. The heat content and rate of heat release, and the specific volume and rate of shrinkage are computed using the solidification of an aluminum-4.5 per cent copper alloy as example.

The model developed to study redistribution of solute during solidification may also be applied to the redistribution of solute during isothermal treatments. The efficacy of homogenization treatments including "isothermal solidification" is analyzed using an aluminum-4.5 per cent copper alloy as example.

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>11</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xi</td>
</tr>
<tr>
<td>I INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II IMPORTANT TRANSPORT MECHANISMS</td>
<td>6</td>
</tr>
<tr>
<td>A. General Mass Balance</td>
<td>7</td>
</tr>
<tr>
<td>B. Equilibrium Solidification</td>
<td>9</td>
</tr>
<tr>
<td>C. Normal Nonequilibrium Solidification,</td>
<td>11</td>
</tr>
<tr>
<td>Plane Interface</td>
<td></td>
</tr>
<tr>
<td>D. Normal Nonequilibrium Solidification,</td>
<td>13</td>
</tr>
<tr>
<td>Dendritic Growth</td>
<td></td>
</tr>
<tr>
<td>III LIMITED SOLID DIFFUSION</td>
<td>20</td>
</tr>
<tr>
<td>A. Analyses and Computations</td>
<td>20</td>
</tr>
<tr>
<td>1. Solution of Materials Balance</td>
<td>21</td>
</tr>
<tr>
<td>2. Composition of Primary Solid Phase</td>
<td>29</td>
</tr>
<tr>
<td>3. Diffusion within the Dendrite</td>
<td>31</td>
</tr>
<tr>
<td>B. Comparison of Computations with Experiment</td>
<td>42</td>
</tr>
<tr>
<td>1. Thermal Analysis of Extended Solidification Heats</td>
<td>42</td>
</tr>
<tr>
<td>2. Microsegregation Measurements</td>
<td>45</td>
</tr>
<tr>
<td>3. Variation of the Value of ( \delta^2 )</td>
<td>50</td>
</tr>
</tbody>
</table>
IV  MACROSCOPIC PARAMETERS OF A SOLIDIFYING ALLOY;  
HEAT CONTENT AND SPECIFIC VOLUME  .............. 55  
A. Heat Content of a Solidifying Alloy  ....... 55  
B. Specific Volume of a Solidifying Alloy .... 59  
V  HOMOGENIZATION TREATMENTS .................. 66  
A. Isothermal Solidification .................... 66  
B. Solution Treatment ............................ 70  
C. Quantitative Results; Homogenization Treat-  
ments ........................................... 72  
VI  SUMMARY AND CONCLUSIONS ................. 78  
VII SUGGESTIONS FOR FURTHER WORK .......... 83  
REFERENCES .................................... 85  
BIOGRAPHICAL NOTE .............................. 91  
APPENDIX A: LIST OF SYMBOLS ............... 92  
APPENDIX B: ORGANIZATION OF COMPUTER PROGRAMS. 96  
APPENDIX C: INFLUENCE OF THERMAL GRADIENT ON  
SOLUTE BUILDUP IN LIQUID .................... 100  
APPENDIX D: LIMITED SOLID DIFFUSION COMPUTATIONS 103  
APPENDIX E: THERMAL DATA FOR HEAT CONTENT  
ANALYSIS OF 195 ALLOY ....................... 109  
FIGURES ....................................... 112
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Description</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equilibrium phase diagram for aluminum-copper alloys</td>
<td>112</td>
</tr>
<tr>
<td>2</td>
<td>Schematic representation of the materials balance for a small amount of solidification by the most general case and the three idealized solidification cases described in the text.</td>
<td>113</td>
</tr>
<tr>
<td>3</td>
<td>Solidification curve for equilibrium case of several aluminum-copper alloys</td>
<td>114</td>
</tr>
<tr>
<td>4</td>
<td>Solidification curve for normal nonequilibrium case of several aluminum-copper alloys</td>
<td>114</td>
</tr>
<tr>
<td>5</td>
<td>Dendritic solidification under imposed thermal gradient: (a) schematic model, (b) temperature gradient, (c) solute gradient</td>
<td>115</td>
</tr>
<tr>
<td>6</td>
<td>Method of representing curved phase boundaries by series of straight lines</td>
<td>116</td>
</tr>
<tr>
<td>7</td>
<td>Comparison of solidification curves calculated by assuming the phase boundaries straight lines to those calculated taking into account the curvature of the phase boundaries</td>
<td>117</td>
</tr>
<tr>
<td>8</td>
<td>Model of growth element selected for computations involving diffusion in the solid phase</td>
<td>118</td>
</tr>
<tr>
<td>9</td>
<td>Comparison of the solidification curve of an aluminum-4.5 per cent copper alloy for the three cases, equilibrium, normal nonequilibrium, and limited solid diffusion and some experimental data</td>
<td>119</td>
</tr>
<tr>
<td>10</td>
<td>The slope of the solidification curve at the liquidus for several compositions of the systems Al-Cu, Al-Mg, Al-Zn</td>
<td>120</td>
</tr>
<tr>
<td>11</td>
<td>The concentration profile in the solid phase of an aluminum-4.5 per cent copper alloy at several stages of solidification and after cooling to room temperature.</td>
<td>121</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Description</td>
<td>Page Number</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>12</td>
<td>The minimum solute content of the solid phases calculated as a function of $\gamma^2$ for an aluminum-4.5 per cent copper alloy cooled to just above the eutectic, to just below the eutectic, and to room temperature.</td>
<td>122</td>
</tr>
<tr>
<td>13</td>
<td>Weight per cent of the nonequilibrium eutectic formed as a function of $\gamma^2$ for six aluminum-copper alloys with less copper than the solubility limit. Parabolic growth is assumed.</td>
<td>123</td>
</tr>
<tr>
<td>14</td>
<td>Weight per cent nonequilibrium eutectic formed as a function of $\gamma^2$ for several aluminum-copper alloys with less copper than the solubility limit. Linear growth is assumed.</td>
<td>124</td>
</tr>
<tr>
<td>15</td>
<td>Value of $\gamma^2$ required for the formation of a given amount of nonequilibrium eutectic phase in cast aluminum-copper alloys.</td>
<td>125</td>
</tr>
<tr>
<td>16</td>
<td>The per cent eutectic formed in an aluminum-4.5 per cent copper alloy calculated as a function of $\gamma^2$ using (a) the numerical analysis technique and the normal nonequilibrium envelope, (b) the numerical analysis technique and limited solid diffusion envelopes, and (c) the analytic expression for limited solid diffusion, equations (D.12) and (D.22) evaluated to a temperature just below the eutectic.</td>
<td>126</td>
</tr>
<tr>
<td>17</td>
<td>Macrostructures of extended solidification ingots.</td>
<td>127</td>
</tr>
<tr>
<td>18</td>
<td>Thermal records of extended solidification ingots having overall solidification times of twelve, thirty four, and eighty two hours.</td>
<td>129</td>
</tr>
<tr>
<td>19</td>
<td>Composite figure showing results of microprobe trace and photograph of microstructure of an aluminum-4.5 per cent copper unidirectional ingot.</td>
<td>130</td>
</tr>
<tr>
<td>20</td>
<td>Dendrite spacing and $\gamma^2$ as a function of solidification time for aluminum-copper alloys (Taken from Michael and Bever).</td>
<td>131</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Description</td>
<td>Page Number</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>21</td>
<td>Comparison of calculated values of the fraction eutectic to those measured by Michael and Bever</td>
<td>132</td>
</tr>
<tr>
<td>22</td>
<td>Heat content as a function of temperature for an aluminum-4.5 per cent copper alloy solidifying according to the equilibrium and normal nonequilibrium cases</td>
<td>133</td>
</tr>
<tr>
<td>23</td>
<td>Heat content as a function of fraction solid for an aluminum-4.5 per cent copper alloy solidifying according to the equilibrium and normal nonequilibrium cases</td>
<td>134</td>
</tr>
<tr>
<td>24</td>
<td>Variation during solidification of the terms that contribute to the heat content of the solid phase, the liquid phase, the solidifying alloy.</td>
<td>135</td>
</tr>
<tr>
<td>25</td>
<td>The specific volume and shrinkage in solidifying 195 alloy plotted as a function of temperature</td>
<td>136</td>
</tr>
<tr>
<td>26</td>
<td>The specific volume and shrinkage in solidifying 195 alloy plotted as a function of fraction solid</td>
<td>137</td>
</tr>
<tr>
<td>27</td>
<td>The contribution to feed metal requirements from solid contraction, liquid contraction, and solidification contraction.</td>
<td>138</td>
</tr>
<tr>
<td>28</td>
<td>The shrinkage in 195 alloy plotted versus the temperature, the metal becomes coherent: $\beta$ - the absolute shrinkage; $\beta_a$ - solid entraps liquid, bulk feeding is considered; $\beta_b$ - solid entraps liquid, bulk feeding is not considered.</td>
<td>139</td>
</tr>
<tr>
<td>29</td>
<td>Schematic representation of model for homogenization calculations.</td>
<td>140</td>
</tr>
<tr>
<td>30</td>
<td>Solute distribution in primary phase at successive stages in the isothermal solidification of an aluminum-4.5 per cent copper alloy.</td>
<td>141</td>
</tr>
<tr>
<td>31</td>
<td>Position of the interface during isothermal heat treatment of aluminum-4.5 per cent copper alloy at several temperatures</td>
<td>142</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Description</td>
<td>Page Number</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>32</td>
<td>The index of residual segregation, $\chi$, during solution treatment of an aluminum-4.5 per cent copper alloy plotted versus the dimensionless parameter $\frac{D\chi}{L^2}$</td>
<td>143</td>
</tr>
<tr>
<td>33</td>
<td>The time to eliminate the nonequilibrium phase by homogenizing at temperatures within either the isothermal solidification or the solution treatment range.</td>
<td>144</td>
</tr>
<tr>
<td>34</td>
<td>Time to eliminate the nonequilibrium phase in an aluminum-4.5 per cent copper alloy by isothermal solidification at 549°C plotted versus the freezing time (logarithmic scales).</td>
<td>145</td>
</tr>
<tr>
<td>35</td>
<td>Time to eliminate the nonequilibrium phase in an aluminum-4.5 per cent copper alloy by isothermal solidification at 549°C plotted versus the characteristic spacing ($d/2$, logarithmic scales).</td>
<td>146</td>
</tr>
<tr>
<td>36</td>
<td>Time to eliminate the nonequilibrium phase in 195 alloy in normal castings heat treated at 548°C (using dendrite measurements of Michael and Bever), and in castings solidified so as to keep the characteristic growth element at twenty microns.</td>
<td>147</td>
</tr>
<tr>
<td>37</td>
<td>Flow diagram of executive sub-program (MAIN) of FORTRAN program MACRO for computation of macroscopic solidification parameters.</td>
<td>148</td>
</tr>
<tr>
<td>38</td>
<td>Flow diagram of executive sub-program (MAIN) of FORTRAN program MICRO for computation of microsegregation pattern of an ingot.</td>
<td>150</td>
</tr>
<tr>
<td>Table Number</td>
<td>Description</td>
<td>Page Number</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>I</td>
<td>Rate of Solid Formation</td>
<td>28</td>
</tr>
<tr>
<td>II</td>
<td>Interface Composition</td>
<td>30</td>
</tr>
<tr>
<td>III</td>
<td>Duration of Eutectic Hold</td>
<td>44</td>
</tr>
<tr>
<td>IV</td>
<td>Microsegregation Measurements (Bower)</td>
<td>47</td>
</tr>
<tr>
<td>V</td>
<td>Minimum Solute Content (Novikov)</td>
<td>49</td>
</tr>
<tr>
<td>VI</td>
<td>Data from Mollard and Flemings</td>
<td>51</td>
</tr>
<tr>
<td>VII</td>
<td>Data from Michael and Bever</td>
<td>52</td>
</tr>
<tr>
<td>VIII</td>
<td>Derivatives of Specific Volume Parameters</td>
<td>62</td>
</tr>
</tbody>
</table>
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I. INTRODUCTION

It is a thermodynamic requirement of alloys that solute be redistributed during solidification, while it is the kinetics of the particular solidification process that determine the paths the solid and liquid phases take in their attempt to comply with the thermodynamic requirement. The transport properties of metals are such that, for usual casting conditions, thermodynamic equilibrium is satisfied only locally, at the liquid-solid interface.\textsuperscript{1,2,3} The requirement for solute redistribution thus induces homogeneous liquids to transform on cooling to castings with a heterogeneous, non-equilibrium structure.

Solute partitioning in its interaction with casting parameters (such as thermal gradients, chemical catalysts) and in its interaction with metal properties (such as the discontinuous change in density and thermal conductivity that occurs between the solid and liquid states) determines the solidification structure and the final solute distribution. For example,

\* It is required that two single phase fields of a phase diagram be separated by a two phase region of finite width except at points of congruent transformation (e.g., a minimum or a maximum in the liquidus) or at points of invariant reaction (e.g., a eutectic or a peritectic).\textsuperscript{4} Solute redistribution, then, is inherent in all solidification processes except those in which solidification is suppressed until entering a single phase field and is made to take place only in that field.
the solidification phenomena listed below control the forms of the solute distribution in castings; and each phenomenon is strongly influenced by solute redistribution.

The interaction of thermal gradients with the requirement for solute redistribution controls such factors as dendrite structure and grain size in castings and ingots, microsegregation and macrosegregation, and structural and compositional homogeneity of single crystals grown from the melt. 5-20

Several manifestations of solute redistribution are considered casting defects. The form of microsegregation is determined by the dendrite morphology and grain structure. 5-8,15 Two types of macrosegregation, settling of crystals 7,21 and inverse segregation, 22,23 are the result of the interaction of solute redistribution with the difference in densities of the solid and liquid. Hot tearing, a common casting defect, has been related 24,25 to stresses induced by casting conditions (in particular, geometry and thermal gradients), solute redistribution, and the unequal load bearing characteristics of the liquid and solid.

A more complete understanding of the fundamentals of the solidification process and more complete control of casting structures would bring fruitful developments in the following areas:

1. Castings made from existing alloys would be benefited so as to increase mechanical properties, reduce sus-
ceptibility to corrosion, provide greater flexibility of casting size and shape. Substantial progress along these lines has already been made.\textsuperscript{26}

2. Improvement in ingot homogeneity and soundness would benefit forged products. Ingot characteristics persist through the working operations and into forged products. Discussion of the influence of microsegregation on banding and the importance of inclusions to mechanical properties is included in several textbooks of metallurgy.

3. Alloys, now considered non-castable, could be made acceptable through the control of the solidification structure. Many alloys having potentially superior properties exhibit such extreme brittleness in the as-cast condition that they cannot be handled or worked. For example, a class of potential aluminum base casting alloys with tensile strengths in excess of 100,000 psi has already been prepared by powder metallurgy techniques,\textsuperscript{27} and by controlled casting and working techniques.\textsuperscript{28}

4. A wider variety of materials would be fabricated from castings. At one time, materials tended to be predominantly selected from the alloys most easily fabricated (due to abundance, low melting point, ease of reduction, etc.). The more stringent requirements of the aerospace and nuclear technologies have created a demand for a wider selection of materials. The new materials present a variety of casting complexities, including high melting points, affinity for oxygen, and formation of numerous intermetallic phases.
An aluminum-4.5 per cent copper alloy (designated as 195 alloy) has been used as an example for the computations and experiments of this work. The casting characteristics of 195 alloy have been studied extensively and can be used to simulate the behavior of many other alloys. The analytical expressions derived are general and can be applied to any binary alloy system whose phase diagram is accurately known. Microsegregation is emphasized in aluminum-copper alloys by the formation of the non-equilibrium phase, CuAl₂. Even though the equilibrium phase diagram, Figure 1, predicts that the single phase, solid solution Υ should exist below 570°C, in usual solidification processes the alloy is not completely solid until the transformation of eight to ten per cent eutectic at 548°C.16,20 The Θ phase, substantially harder than the aluminum rich matrix, forms in the interdendritic space and in the grain boundaries. If microsegregation is not removed by extensive solutionizing treatments, the alloy will exhibit brittleness and directionality of properties.29,30 Added to the deleterious influence of the Θ phase on the mechanical properties of the as-cast alloy is its contribution to the microporosity of the alloy. The Θ phase forms with considerable solidification shrinkage at the stage of solidification when feeding is most difficult.21,31 The wide freezing range of this alloy also makes 195 susceptible to hot tearing,25 inverse segregation,22 and gravity segregation. The initial solid crystals tend to settle. As
the heavier component, copper, is rejected into the liquid phase, the liquid becomes more dense than the solid. During the latter stages of solidification the solid tends to float.\textsuperscript{7,21}

Detailed computer aided analyses are made of the solidification process and results are compared with experiment; primary concern is given to the redistribution of solute during dendritic solidification of alloys. Previously, laborious hand calculations were necessary to carry out this type of calculation, even with highly simplified mathematical models for phase diagram boundaries, diffusion boundary conditions, and growth element geometries. The availability of an IBM 7090 digital computer for the evaluation of the expressions made feasible calculations for representative growth models and for any binary alloy system. The organization of the general programs for computing and recording the results of the analyses is included as Appendix B.
II. IMPORTANT TRANSPORT MECHANISMS

Researchers conventionally consider and measure the redistribution of solute on three levels, macroscopic, microscopic, and atomic. Macroscopic refers to phenomena or parameters that are observed with the unaided eye and are measured by techniques that characterize a large volume (such as pyrometry, dilatometry, and drilling for chemical samples.) Microscopic refers to parameters that are observed in a common light microscope (approximately $1 \mu - 10^4 \mu$), or are measured by instruments that characterize a comparably small volume (for example, electron microprobe, microradiography). Measurements taken within grains or within dendrites are typically considered as microscopic. This designation will be used even when grain size and dendrite spacing are enlarged, by slow cooling, to normally macroscopic dimensions. Atomic parameters refer to the movement and grouping of atoms. For the most part these parameters are not observed directly; but they are inferred from larger scale observations (such as X-ray diffraction to determine crystal structure). In fact, the processes at each level are not independent and the divisions, though convenient, are artificial. During the consideration of a phenomenon of one level, it is most often necessary to take into consideration the effect of phenomenon at the other levels.
In this section a macroscopic mass balance is written that can be applied to any alloy or solidification path. Before the mass balance can be evaluated for a particular solidification path, transport and equilibria that occur on the micro-scale must be specified or assumed. On this basis, fraction solid, average phase compositions, heat content, specific volume, and the associated derivatives can be evaluated for the two limiting solidification paths (1) equilibrium and (2) normal nonequilibrium. In Section III diffusion in the solid phase is taken into account and calculations are made as to the nature of microsegregation. For these computations the solidification element and its growth geometry must be assumed in addition to specifying the micro-transport mechanisms.

A. General Mass Balance

For a solidifying alloy of known phase diagram, the fraction solid at any temperature can be calculated by the appropriate application of mass balances. An alloy system having m components and solidifying through a region of n solid phases and p liquid phases will have m-1 independent mass balances of the form

\[ \sum_{j=1}^{n} \overline{c}_{S_{ij}} f_{S_j} + \sum_{k=1}^{p} \overline{c}_{L_{ik}} f_{L_k} = c_{0_i} \quad \cdots \quad (1) \]

where \( c_{0_i} \) = overall weight fraction of component \( i; \overline{c}_{S_{ij}}, \overline{c}_{L_{ik}} \) = the average weight fraction of component \( i \) in the \( j \) phase of

* The symbols used are tabulated in Appendix A.
of the solid and the k phase of the liquid, respectively; $f_{S_j}$, $f_{L_k} = \text{the weight fraction of the } j \text{ phase of the solid and } k \text{ phase of the liquid, respectively.}$

Consider now a solidifying alloy of a specific binary system (such as that of Figure 1). At any point in the two phase region the mass balance for solute may be written in the form

$$\overline{C_S} f_S + \overline{C_L} f_L = C_0 \quad . \quad . \quad . \quad (2)$$

where the subscripts i, j, k have been deleted, there being only one solid phase, one liquid phase, and one independent equation.

Differentiation of equation (2) gives the effect of an infinitesimal variation in the system

$$d(\overline{C_S} f_S) + d(\overline{C_L} f_L) = 0 \quad . \quad . \quad . \quad (3)$$

which is expanded to

$$\overline{C_S} df_S + f_S \overline{dC_S} + \overline{C_L} df_L + f_L \overline{dC_L} = 0 \quad . \quad . \quad . \quad (4)$$

As long as the system is closed

$$f_S + f_L = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$df_S + df_L = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and equation (4) may now be rewritten

$$(\overline{C_L} - \overline{C_S}) df_S = f_S \overline{dC_S} + (1 - f_S) \overline{dC_L} \quad . \quad . \quad . \quad (7)$$
The equality expressed by equation (7) is depicted in Figure 2a, for an infinitesimal amount of solidification, \( df_S \), at an isothermal interface. The condition before the transformation is represented by the \( L_0 \) and the condition after transformation by the line \( L_1 \). Cross-hatched area B (represented by the left side of equation 7) must equal area A plus area C (represented by the right side of equation 7).

**B. Equilibrium Solidification**

Equilibrium solidification refers to a liquid-solid transformation that occurs with complete transport within both liquid and solid phases and with compositions at the interface exactly those predicted by the phase diagram; chemical thermodynamics are completely satisfied. The compositions of the solid and liquid will be uniformly those given by the intersection of the isothermal at that temperature (tie line) with the solidus and liquidus, respectively. Figure 2b depicts the change produced by an amount of solidification \( df_S \), and equation (7) modified for this special case is:

\[
(C_L^* - C_S^*)df_S = f_SdcS^* + (1 - f_S)dC_L^* \quad \ldots \ldots \quad (8)
\]

where \( C_L^*, C_S^* \) = weight fractions of solute present at solid-liquid interface.

**Straight Phase Boundaries** - One method of solution of equation (8) is to assume that both the solidus and liquidus are straight lines described by \( m_S \) and \( m_L \) where:
\[
m_L = \frac{T_m - T_1}{c_{L_1}} \quad \quad \quad \quad \quad (9)
\]
\[
m_S = \frac{T_m - T_1}{c_{S_1}} \quad \quad \quad \quad \quad (10)
\]

where \( T_m \) = melting point of solvent; \( T_1 \) = temperature of invariant transformation; \( c_{S_1}, c_{L_1} \) = concentration of solvent in solid and liquid phases at invariant. The ratio of the equilibrium solid concentration to the equilibrium liquid concentration within the two phase region is a constant termed the equilibrium "partition ratio".

\[
k = \frac{c_{S_1}^*}{c_{L_1}^*} = \frac{m_L}{m_S} \quad \quad \quad \quad \quad (11)
\]

and

\[
dc_{S_1}^* = kdc_{L_1}^* \quad \quad \quad \quad \quad (12)
\]

Now substituting expressions (11) and (12) into equation (8), separating variables, and imposing limits of integration yields

\[
\int_0^{f_S} \frac{df_S}{1 + (k-1)f_S} = \frac{1}{(1-k)} \int_{C_0}^{c_{L_1}^*} \frac{dc_{L_1}^*}{c_{L_1}^*} \quad \quad \quad \quad (13)
\]

Integration leads either to the familiar lever rule

\[
f_S = \frac{c_{L_1}^* - C_0}{c_{L_1}^* - c_{S_1}^*} \quad \quad \quad \quad \quad (14)
\]

or the expression used for computations

\[
f_S = \frac{T_L - T}{(T_m - T)(1 - k)} \quad \quad \quad \quad (15)
\]

where \( T_L \) = liquidus temperature for alloy \( C_0 \).
Curved Phase Boundaries - Often the assumption of a straight liquidus and solidus leads to inaccurate results and/or loss of information. If the phase boundaries are not straight, equation (15) no longer holds. Equation (14), however, is still valid and may be applied at every point in the path. Results of this computation for a series of aluminum-copper alloys of differing composition are plotted in Figure 3.

Although the results obtained from the curved line calculation often differ appreciably from the results obtained from a straight line approximation (equation (15)), equilibrium solidification is rarely approached and the significance of the differences will be discussed in relation to the nonequilibrium calculations.

C. Normal Nonequilibrium Solidification, Plane Interface

The simplest quantitative approach to solute redistribution in nonequilibrium solidification, derived by Gulliver, Chipman, Scheil, and others, has been applied by Pfann and Chalmers to the case of a crystal growing with a plane, isothermal interface under the conditions (1) complete mass transport within the liquid phase (e.g., diffusion coefficient is infinite, $D_L = \infty$), (2) no mass transport within the solid phase ($D_S = 0$), and (3) equilibrium maintained at the interface. The solidification assumptions are depicted by Figure 2c. There being no mass transport within the solid phase, the change in solute content of the solid due to diffusion $f_S \Delta \bar{C}_S \text{diff}$ (i.e., $f_S \Delta \bar{C}_S - (C_S^* - \bar{C}_S) df_S$) is set equal to zero and equation (7), the
mass balance is written in the form

\[(C_L^* - C_S^*)df_S = (1 - f_S)dc_L^* \quad \ldots \ldots \quad (16)\]

Assuming the liquidus and solidus to be straight lines, substituting expressions (11) and (12) into equation (16) and integrating leads to the result

\[f_S = 1 - \left(\frac{C_0}{C_L^*}\right)^{1/(1-k)} \quad \ldots \ldots \quad (17)\]

or the expression used for computation

\[f_S = 1 - \left(\frac{T_m - T_L}{T_m - T}\right)^{1/(1-k)} \quad \ldots \ldots \quad (18)\]

The solidification curves (fraction solid versus temperature) for a series of aluminum-copper alloys of differing composition computed under normal nonequilibrium solidification conditions are plotted in Figure 4.* Less solid is formed at each temperature for this condition than for equilibrium, and liquid persists to the eutectic temperature. At this point, the equation no longer applies; remaining liquid precipitates as eutectic of average composition 33 per cent copper. For aluminum-4.5 per cent copper (195 alloy) about nine per cent by weight of eutectic is formed in the last regions to freeze.

* The curves of Figure 4 have been corrected for the curvature of the phase boundaries. The method of the corrected computation is described later in this section.
D. Normal Nonequilibrium Solidification; Dendritic Growth

Bever\textsuperscript{16}, Gulliver\textsuperscript{32}, and others\textsuperscript{19,20} have applied the normal nonequilibrium assumption to dendritic solidification. A description of the state of an alloy during dendritic growth is more complex than for plane front growth. The assumptions that must be fulfilled for this computation to be rigorous have been grouped recently by Flemings\textsuperscript{14} as follows:

1. negligible undercooling before nucleation of primary or secondary phases,
2. negligible interface supercooling from kinetic or curvature effects,
3. equilibrium partition ratio, \( k \), applies at the interface,
4. negligible constitutional supercooling,
5. partition ratio is constant,
6. no thermal gradient in the liquid,
7. no macroscopic mass flow,
8. no diffusion in the solid during solidification.

In the laboratory it is possible to undercool melts appreciably below their liquidus temperatures\textsuperscript{34}. In normal practice, nucleation takes place at temperatures close to equilibrium. Both experiment and theory have indicated that the interface supercooling that occurs is too small to influence solute redistribution\textsuperscript{1,9,35} (except by its influence on solidification morphology). Thus, assumptions (1)-(4)
will be considered valid. Assumptions (5)-(8) are discussed in more detail. Assumptions (5) and (6) are relaxed in this section. Solid diffusion accounts for the most significant deviation from normal nonequilibrium and consideration of assumption (8) forms the basis of Section III.

Effect of Thermal Gradient - The combination of assumptions (4) and (6) assure a homogeneous liquid phase. To limit the analysis to solidification processes having no appreciable thermal gradients would be a severe, and unnecessary, restriction. Flemings' has delineated the conditions for which requirement (6) may be relaxed. Consider a simple binary alloy, such as 195, freezing under a thermal gradient imposed such that all heat flow is unidirectional, as shown in Figure 5. If only assumption (6) is relaxed, the liquid composition must vary with distance in the heat flow direction as shown in Figure 5c. Solute buildup is shown at the tips of the advancing solid, \( C_t - C_0 \); solute content in the interstices between the dendrites increases with decreasing temperature to a maximum at the root of the liquid, \( C_E \). At steady state, the solute buildup in the liquid at the tips of the advancing dendrites is calculated (in Appendix C) to be

\[
C_t - C_0 = b \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (19)
\]

where

\[
b = - \frac{D_L G}{R_L m_L} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (20)
\]

and \( D_L \) = diffusion coefficient of solute in liquid, \( G \) = thermal
gradient in liquid at dendrite tip, \( R_t \) = velocity of dendrite tip.

A mass balance evaluated for these assumptions would give

\[
f_S = 1 - \left[ \frac{C_t - \frac{b}{1 - k}}{C_L - \frac{b}{1 - k}} \right] \left( \frac{1}{1 - k} \right) \ldots \ldots \ldots (21)
\]

instead of equation (17), (see Appendix C for derivation).

Except for special cases during dendritic solidification the parameter \( b \) is much less than one. Normal thermal gradients do not alter the redistribution of solute. Thus, a paradoxical diffusion condition in the liquid; diffusion over distances the size of the two phase field is negligible, diffusion within the dendritic interstices is complete.

**Macroscopic Mass Flow** - The preceding analysis indicated that the magnitude of the solute buildup in front of the advancing dendrite tips is small. It can also be shown that the extent of the solute enriched area is small. Consider dendrites growing as in Figure 5, the steady state solute content at the tips equal \( C_t \). The composition in the liquid, \( C_L \), at a distance \( X' \) ahead of the tips is given by

\[
\frac{C_L - C_0}{C_t - C_0} = \exp \left( - \frac{R_t}{D_L} X' \right) \ldots \ldots \ldots (22)
\]

The characteristic distance** of the solute enriched area is

* A reasonable value for \( b \) is \( 10^{-2} \); taking \( D_L = 10^{-5} \text{cm}^2\text{sec}^{-1} \), \( R_t = 0.1 \text{ cm.sec}^{-1} \), \( m = 0.1 \), \( C = 10^5 \text{C} \text{ cm}^{-1} \).

** Characteristic distance is the distance from the tips to the point where the solute buildup is 1/e of its magnitude at the tips. With \( D_L = 10^{-5} \) and \( R_t = 0.01 \), the characteristic distance = .001 cm.
$D_L/R$, a number less than one centimeter. Thus the concentration perturbation extends only an extremely short distance, and there can be no macrosegregation from this cause. Similar calculations by Wagner\textsuperscript{3} indicate that significant macrosegregation will result from solute flow from the enriched layer with natural convection only for relatively slow solidification rates; with forced convection for relatively slow solidification rates and/or vigorous stirring action.

Macrosegregation is, nonetheless, an important characteristic of cast structures. Macrosegregation must be the result of mass flow of solute rich or solute poor material. Examples are the sweeping of the interdendritic regions through convective flow or the formation of gas bubbles, gravity segregation, inverse segregation as a result of solidification shrinkage, and flow of solute rich liquid to relieve thermally induced or externally applied strains. When such mass flow occurs in the presence of thermal gradients, the normal non-equilibrium equation cannot apply. With the exception of inverse segregation\textsuperscript{22,23} these effects have not been quantitatively analyzed.

**Curved Phase Boundaries** - When the phase boundaries are not sufficiently straight over their entire length to justify the use of equations (17) and (18), the phase boundaries are treated as a series of straight line segments that follow the actual phase boundary within the experimental accuracy (see Figure 6). Then, for a temperature, $T$, within the
interval, \( T_j - T_{j-1} \), that the phase boundaries are considered straight, define

\[
m_{S_j} = \frac{T_j - T_{j-1}}{C_{S_j} - C_{S_{j-1}}} = \frac{T_j - T}{C_{S_j} - C_{S^*}} \quad \ldots \quad (23)
\]

\[
m_{L_j} = \frac{T_j - T_{j-1}}{C_{L_j} - C_{L_{j-1}}} = \frac{T_j - T}{C_{L_j} - C_{L^*}} \quad \ldots \quad (24)
\]

where \( C_{L_j} \) and \( C_{S_j} \) are weight fraction of solute at intersections of the isothermal at \( T_j \) (tie line) with the liquidus and solidus, respectively; \( C_{L_{j-1}} \) and \( C_{S_{j-1}} \) represent similar quantities at \( T_{j-1} \). Expressions (23) and (24) combine to yield

\[
C_{L^*} - C_{S^*} = C_{L^*} - \frac{m_{L_{j-1}}}{m_{S_j}} C_{L^*} - C_S + \frac{m_{L_j}}{m_{S_j}} C_L \quad \ldots \quad (25)
\]

Let

\[
A_j = 1 - \frac{m_{L_{j-1}}}{m_{S_j}} \quad \ldots \quad (26)
\]

\[
B_j = \frac{m_{L_j}}{m_{S_j}} C_{L_j} - C_{S_j} \quad \ldots \quad (27)
\]

and replace \( (C_{L^*} - C_{S^*}) \) in equation (16) by \( A_j C_{L^*} + B_j \)

\[
\int_{f_S}^{f'_{S}} \frac{df_S}{1 - f_S} = \int_{C''_L}^{C_{L^*}} \frac{dC_{L^*}}{A_j C_{L^*} + B_j} \quad \ldots \quad (28)
\]
Equation (28) is integrated over a short range \( T' \) to \( T \) within the interval \( T_{j-1} \) to \( T_j \), using as lower limits of integration that a fraction solid \( f_S' \) exists at temperature \( T' \) and liquid composition \( C_L' \), to give the following general expression for the classical nonequilibrium lever rule

\[
 f_S = 1 - (1 - f_S') \left( \frac{A_j C_L' + B_j}{A_j C_L^* + B_j} \right)^{1/A_j} 
\]  

(29)

To calculate the value of \( f_S \) at any temperature \( T \) within the interval \( T_{j-1} \) to \( T_j \), equation (29) must be successively evaluated within each of the intervals from the liquidus \( T_L \) to the temperature \( T_{j-1} \) and then in the interval \( T_{j-1} \) to \( T \). The results of this calculation for a series of aluminum-copper alloys are plotted in Figure 4.

In Figure 7 results obtained for several systems by using the expression for curved phase boundaries (equation 29) are compared with results obtained assuming a constant partition ratio (equation 18). The aluminum-iron system, Figure 7b, has been included as an example because the phase diagram is composed of straight lines within the experimental accuracy of the determination; hence results calculated from both expressions coincide. The main deviation for the aluminum-copper system, Figure 7a, is that the curved boundary calculation predicts a higher liquidus and thus the curve is displaced to higher temperatures. The predicted amounts of nonequilibrium second phase are only slightly different. The assumption of
a constant partition ratio is not even qualitatively applicable to the aluminum-tin system, Figure 7c. Equation (18) is valid for aluminum-zinc alloys in which zinc content is low, Figure 7d, in spite of irregularities in the phase diagram. This is due to the fact that the irregularities occur at higher zinc contents and the low zinc alloys are mostly solid before entering those regions.
III. LIMITED SOLID DIFFUSION

A. Analyses and Computations

An analysis of the extent of diffusion in the solid phase requires the assumption of a model of growth and an expression for the rate of thickening of the solidification elements. A simple platelike model, as described below, has been taken for the solidification element. (See Figure 8 for growth model.)

1. The growth forms (or dendrites) are considered to be plates separated at their centers by the final (dendrite) spacing, d. The plates start to grow smoothly at the liquidus temperature and each plane face advances a distance d/2 within the solidification time \( t \).\(^{5,6}\)

2. End and corner effects are neglected.

3. The solute transport within the solid phase is solely by volume diffusion. The diffusion coefficient, \( D_s \), is an exponential function of temperature

\[
D_s = D_0 \exp \left( - \frac{Q}{RT_K} \right)
\]

where \( D_0 \) = empirical constant; \( Q \) = heat of activation, empirical; \( R \) = gas constant; \( T_K \) = absolute temperature.

4. Density differences due to solidification shrinkage are neglected.

5. Temperature is uniform throughout the dendrite plate at any given time, \( \Theta \). Although a casting may be solidifying
under a steep thermal gradient, the temperature difference between any two dendrite plates will always be small.

6. The rate of advance of the interface is taken to be a continuous function of time.

parabolic \[ X_1 = \lambda \sqrt{\Theta} \ldots \ldots \ldots \ldots (31) \]
or

linear \[ X_1 = \eta \Theta \ldots \ldots \ldots \ldots (32) \]

where \( X_1 \) = interface position; \( \Theta \) = time from initiation of solidification; \( \lambda \) = growth rate constant, parabolic; \( \eta \) = growth rate constant, linear.

1. Solution of Materials Balance

An increase in the solute content of the solid phase due to diffusion in the solid must be the result of a flux that enters at the liquid-solid interface. To evaluate the materials balance for this case (see Figure 7d for a schematic representation of the materials balance for the limited solid diffusion conditions), the solute increase behind the interface, \( f_s \frac{dc_s}{dx} \), is equated to the flux at the interface.

\[ f_s \frac{dc_s}{dx} \bigg|_{diff} = - J_1 (\frac{2}{\eta d}) d\Theta = \left( \frac{2 D_s}{d} \frac{dc_s}{dx} \right)_1 d\Theta \ldots \ldots \ldots \ldots (33) \]

where \( J_1 \) = flux in the solid phase at the interface (gr/cm²/sec), \( \eta \) = density of alloy (gr/cm³), \( D_s \) = diffusion coefficient (cm²/sec), \( \frac{dc_s}{dx} \bigg|_1 \) = concentration gradient at interface (wt.frac./cm).
To simplify equation (33), assume that the concentration gradient in the solid is not changed significantly after the interface passes, i.e.,

\[
\frac{dc_S}{dx} \bigg|_1 = \frac{dc_S^*}{dx_1} \quad \ldots \ldots \ldots \quad (34)
\]

This assumption will result in the calculation of an upper limit on the extent of diffusion.

**Parabolic Growth** - First, let the rate of advance of the interface be parabolic in time (equation 32). Then

\[
\frac{d\Theta}{dx_1} = \frac{2x_1}{\lambda^2} = \frac{f_S d}{\lambda^2} \quad \ldots \ldots \ldots \quad (35)
\]

For the case of limited solid diffusion, platelike growth form, and parabolic growth rate, equation (7) becomes

\[
(C_L^* - C_S^*) df_S = \alpha f_S dc_S^* + (1 - f_S) dc_L^* \quad \ldots \ldots \quad (36)
\]

where

\[
\alpha = \frac{2D_S}{\lambda^2} \quad \ldots \ldots \ldots \quad (37)
\]

and equation (36) may only be applied for \(\alpha < 1\) due to the assumption (34). Integrating equation (36) for the simplest conditions, constant partition ratio and constant diffusion coefficient,

\[
f_S = \frac{1 - \left(\frac{c_O}{c_L}\right) \left[\frac{1 - \alpha \kappa}{1 - \kappa}\right]}{1 - \alpha \kappa} \quad \ldots \ldots \quad (38)
\]
or

\[ f_s = \frac{1 - \left( \frac{T_m - T_L}{T_m - T} \right)}{1 - \alpha k} \left[ \frac{1 - \alpha k}{1 - k} \right] \]  \hspace{1cm} (39)

The more general solutions of equation (36) for curved phase boundaries and using a temperature dependent diffusion coefficient* (equation (30)) are presented in Appendix D.

Transformation at the Eutectic Temperature - The limited solid diffusion case differs from the previous two cases, because solute redistribution occurring at the eutectic transformation temperature and during cooling to room temperature must be taken into account. In the equilibrium case, the phase distribution is simply obtained from the phase diagram. An aluminum-4.5 per cent copper alloy (Figure 1) is totally primary solid solution, K, after solidification, and the Θ phase only appears as the alloy crosses below the solvus line. In the normal nonequilibrium case, no mass transport within the solid phase is allowed and no diffusion controlled solid state change can occur. An aluminum-4.5 per cent copper alloy that has 90.9 per cent primary solid and 9.1 per cent liquid phase just above the eutectic temperature will form just 9.1 per cent eutectic. This requirement is relieved for the case of limited solid diffusion. An analysis of the formation of the primary phase at the eutectic temperature is presented in Appendix D. The

* The diffusion coefficient of the solute may vary by more than order of magnitude in the solidification range. For example, 195 alloy, at the liquidus \( D_s = 1.62 \times 10^{-9} \) cm² sec⁻¹, at the eutectic \( D_s = 1.99 \times 10^{-10} \) cm² sec⁻¹.
result for a constant partition ratio is

\[ f_S(T_E) = f_S'(T_E) + \frac{\alpha k}{2} \frac{1 - f_S'(T_E)^2}{1 - (1 - \alpha k)f_S'(T_E)} \ldots (40) \]

where \( f_S'(T_E) \) = weight fraction of primary crystals just above eutectic temperature, \( f_S(T_E) \) = weight fraction of primary solid just below eutectic temperature. An analysis of the extent of diffusion during cooling to room temperature is presented in Section 3, page 33.

**Evaluation for an Aluminum-4.5 Copper Alloy** - The analysis for limited solid diffusion was applied to an aluminum-4.5 per cent copper alloy using the published phase diagram (Figure 1); the following constants in the expression for the diffusion coefficient, \( D_0 = 8.4 \times 10^{-2} \text{ cm}^2 \text{ sec}^{-1} \), \( Q = 32,600 \text{ calories mole}^{-1} \); and a parabolic growth rate constant, \( \lambda = 6 \times 10^{-5} \text{ cm sec}^{-1/2} \). The fraction solid at each temperature, i.e., the solidification curve, for the limited solid diffusion condition, is compared to those for the equilibrium and normal nonequilibrium limiting cases in Figure 9.* The calculated curve falls between the limiting curves for the equilibrium and normal nonequilibrium case; the position of the curves shift in the direction from nonequilibrium to equilibrium as the value of \( \lambda \) decreases.

* Figure 9 includes some experimental data described in Section B, "Comparison of Computations with Experiment".
Linear Growth - Considering the advance of the interface to be linear in time (equation (32)),

\[
\frac{dX_s}{d\Theta} = u \quad \ldots \ldots \ldots \ldots \ldots . \quad (41)
\]

For the case of limited solid diffusion, plate-like dendrites, and linear growth, equation (7) becomes

\[
(\dot{C}_L - \dot{C}_S) \, df_S = \alpha_L dC_S + (1 - f_g) \, dC_L' \quad \ldots \ldots \ldots \ldots . \quad (42)
\]

where \(\alpha_L = 2D_g/ud\) \ldots \ldots \ldots \ldots \ldots . \quad (43)

The result of integration for the conditions of straight line phase boundaries and constant diffusion coefficient is

\[
f_S = (1 + \alpha_L k)(1 - \left(\frac{C_0}{C_L}\right)^{\frac{1}{1-k}}) \quad \ldots \ldots \ldots \ldots . \quad (44)
\]

The analysis may also be applied to the conditions of curved phase boundaries and/or temperature dependent diffusion coefficient. The method is described in Appendix D.

Again, the analytic expression (equation (44)) is valid to just above the eutectic temperature. Just below the eutectic temperature, the weight fraction of primary crystals is given by

\[
f_S(T_E) = f_S'(T_E) + \alpha_L k \left(1 - \frac{f_S'(T_E)}{1 + \alpha_L k - f_S'(T_E)}\right) \quad \ldots \ldots \ldots \ldots . \quad (45)
\]

The derivation of this expression and the analogous expression for curved phase boundaries is presented in Appendix D.
Sensitivity to Growth Geometry - The factor \( \upi \) determines the extent of diffusion in the solid for either parabolic growth (equation (36)) or linear growth (equation (42)).

Reference to the definitions (37) and (43) shows that \( \upi \) can be written

\[
\upi = 8 \frac{D_S}{\gamma^2} \quad \ldots \quad (46)
\]

\[
\upi_L = 4 \frac{D_S}{\gamma^2} \quad \ldots \quad (47)
\]

where

\[
d = \gamma \sqrt{\Theta_f} \quad \ldots \quad (48)
\]

That is, \( \gamma \) = empirically determined ratio of the solidification element (dendrite) spacing to the square root of the solidification time. (1) For \( \upi \) (or \( \upi_L \)) \( \ll 1 \), there is negligible solid diffusion; \( \upi \sim 1 \), there is significant diffusion; \( \upi \gg 1 \), the solid will be homogeneous.

(2) If the dendrite spacing is proportional to the square root of solidification time, (i.e., \( \gamma \) is a constant), varying freezing rate has no effect at all on the extent of diffusion. If \( \gamma \) decreases with increasing solidification times, then increasing solidification time increases the extent of solid diffusion; if \( \gamma \) increases with increasing solidification times, then increasing solidification time

* It is shown in Section 3 that these conclusions are valid for any power of the growth rate equation (i.e., any value of \( \theta \) when \( X_1 = \gamma \Theta^n \)).
reduces the extent of solid diffusion. The dependence of microsegregation on the growth geometry is discussed in detail in Section B.

Rate of Solid Formation - Through their description of the solidification curve, the first derivative of the fraction solid with temperature, $df_S/dT$, and with concentration, $df_S/dC_L$, are valuable quantities for (1) analyzing solidification phenomena and (2) insertion in solidification calculations (e.g., the calculations of rate of shrinkage and rate of heat release that follow). These derivatives, obtainable by rearrangement of the differential mass balances (equations (8), (16), (36), and (42)), are summarized in Table I. The reciprocals of the slope at the liquidus of the solidification curve, $(df_S/dT)_R=1$, are plotted for several solute contents of the aluminum-magnesium, aluminum-copper, and aluminum-zinc systems in Figure 10 where the reduced temperature, $T_R$, has been defined as

$$
T_R = \frac{T - T_E}{T_L - T_E} \ldots \ldots \ldots \ldots \ldots (49)
$$

Note that the rate of solid formation of the aluminum-zinc system is about five fold higher than the two former systems. The rate of solid formation decreases sharply with the fraction solid (see inset Figure 10).
<table>
<thead>
<tr>
<th>Case</th>
<th>First Derivative $\frac{df_s}{dC_L^*}$</th>
<th>Constant Partition Ratio $\frac{(1-f_s) + kf_s}{C_L^*(1-k)}$</th>
<th>Variable Partition Ratio $\frac{(1-f_s) + (1-A_j)f_s}{A_jC_L^* + B_j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
<td>$\frac{df_s}{dT}$</td>
<td>$- \frac{(1-f_s) + kf_s}{(1-k)(T_m - T)}$</td>
<td>$\frac{df_s}{dC_L^* j} \frac{1}{m_{L, j}}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{df_s}{dC_L^*}$</td>
<td>$\frac{1-f_s}{C_L^*(1-k)}$</td>
<td>$\frac{1-f_s}{A_jC_L^* + B_j}$</td>
</tr>
<tr>
<td>Normal</td>
<td>$\frac{df_s}{dT}$</td>
<td>$- \frac{1-f_s}{T_m - T} \frac{1}{1-k}$</td>
<td>$\frac{df_s}{dC_L^* j} \frac{1}{m_{L, j}}$</td>
</tr>
<tr>
<td>Nonequilibrium</td>
<td>$\frac{df_s}{dC_L^*}$</td>
<td>$\frac{1-f_s + \infty kf_s}{(1-k)C_L^*}$</td>
<td>$\frac{1-f_s + (1-A_j)\infty f_s}{A_jC_L^* + B_j}$</td>
</tr>
<tr>
<td>Limited Solid Diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(parabolic growth)</td>
<td>$\frac{df_s}{dT}$</td>
<td>$- \frac{1-f_s + \infty kf_s}{(1-k)(T_m - T)}$</td>
<td>$\frac{df_s}{dC_L^* j} \frac{1}{m_{L, j}}$</td>
</tr>
<tr>
<td>Limited Solid Diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(linear growth)</td>
<td>$\frac{df_s}{dC_L^*}$</td>
<td>$\frac{1 + \infty K - f_s}{(1-k)C_L^*}$</td>
<td>$\frac{1 + (1-A_j)\infty L f_s}{A_jC_L^* + B_j}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{df_s}{dT}$</td>
<td>$\frac{1-f_s + \infty L k}{(1-k)(T_m - T)}$</td>
<td>$\frac{df_s}{dC_L^* j} \frac{1}{m_{L, j}}$</td>
</tr>
</tbody>
</table>
2. Composition of the Primary Solid Phase

**Interface Composition as Function of Temperature** - The minimum segregation will be experienced for the equilibrium case; the maximum segregation for the normal nonequilibrium case, and an intermediate amount of segregation for the limited solid diffusion case. As an extension of the previous analyses, the composition at the interface and the average composition of the primary dendrite are calculated. The composition present at the interface must, for each solidification case, be just that given by the phase boundary at that temperature. Interface equilibrium is established between the compositions listed in Table II.

**Interface Composition as a Function of Fraction Solid** - It is of interest to express $C_s^*$ as a function of fraction solid, as this relates closely to the concentration profile within a dendrite. The relations for the three solidification cases are listed in Table II.

**Average Composition of the Solid** - For equilibrium the composition within the solid is uniformly the same as that at the interface; that is, the average composition is equal to the interface composition. For the normal nonequilibrium case, the solute content at a position within the solid does not change after the interface passes. For the limited solid diffusion case the solute content within the solid changes continuously and approaches the interface composition. But, for each of the three cases, the average composition of the
TABLE II: Interface Composition

A. Function of Temperature
   (Independent of Path)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Constant k</th>
<th>Variable k</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_L^*$</td>
<td>$\frac{T_m - T}{m_L}$</td>
<td>$C_L^*<em>{ij} - \frac{T_j - T}{m</em>{Lj}}$</td>
</tr>
<tr>
<td>$\frac{dC_L^*}{dT}$</td>
<td>$-\frac{1}{m_L}$</td>
<td>$\frac{l}{m_{Lj}}$</td>
</tr>
<tr>
<td>$C_S^*$</td>
<td>$kC_L^*$</td>
<td>$(1 - A_j)C_L^* - B_j$</td>
</tr>
<tr>
<td>$\frac{dC_S^*}{dT}$</td>
<td>$-\frac{k}{m_L}$</td>
<td>$\frac{(1 - A_j)}{m_{Lj}}$</td>
</tr>
</tbody>
</table>

B. Function of Fraction Solid
   (Constant k)

<table>
<thead>
<tr>
<th>Solidification Case</th>
<th>$C_S^*$</th>
<th>$\frac{dC_S^*}{df_S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
<td>$kC_o (1-(1-k)f_S)^{-1}$</td>
<td>$\frac{1-k}{kC_o} C_S^*^2$</td>
</tr>
<tr>
<td>Normal Non-equilibrium</td>
<td>$kC_o (1-f_S)(k-l)$</td>
<td>$\frac{1-k}{1-f_S} C_S^*$</td>
</tr>
<tr>
<td>Limited Solid Diffusion (Parabolic Growth)</td>
<td>$kC_o \frac{k-1}{1-\alpha_k}$</td>
<td>$(1-k) C_S^* \frac{1-(1-\alpha_k)f_S}{1-(1-k)f_S}$</td>
</tr>
<tr>
<td>Limited Solid Diffusion (Linear Growth)</td>
<td>$kC_o \frac{1+\alpha_k f_S}{1+C_L^*}$</td>
<td>$(1-k) C_S^* \frac{1+\alpha_k f_S}{1+\alpha_k f_S}$</td>
</tr>
</tbody>
</table>
solid at any point during the solidification is given by
the relation:

\[ \bar{c}_S = \frac{c_0}{f_S} - \frac{(1 - f_S)}{f_S} c_{L*} \ldots \ldots \ldots (50) \]

and

\[ \frac{d\bar{c}_S}{dT} = \frac{c_{L*} - \bar{c}_S}{f_S} \frac{df_S}{dT} - \frac{(1 - f_S)}{f_S} \frac{dC_{L*}}{dT} \ldots \ldots \ldots (51) \]

The value of \( f_S \) and \( \frac{df_S}{dT} \) appropriate to the solidification
condition are substituted on the right side of equations
(50) and (51).

3. Diffusion Within the Dendrite

The solution of the materials balance for the limited
solid diffusion case delineates the conditions necessary
for significant solid diffusion during solidification. En-
hancement of this diffusion reduces the severity of micro-
segregation and is, therefore, of great engineering interest.
Previous calculations, however, do not fully describe micro-
segregation in that they do not describe the distribution of
solute within the dendrite. A more complete description is
obtained by the application of numerical analysis techniques
to the diffusion equation.

The model used in the numerical analysis computation is
analogous to the model of Section 1 depicted by Figure 8.
The pertinent conditions and assumptions are described on
page 20. One additional assumption is required to describe
the interface composition at each position of the interface.

7(a) In the first analysis, diffusion behind the interface is considered not to alter the rate of growth. For this assumption, the interface composition at each position of the moving solid-liquid interface is given by the normal nonequilibrium expression for interface composition (see Table II), which becomes for the co-ordinates of this model:

\[ C_s^* = kC_0 \left(1 - \frac{2X_i}{d}\right)^{k-1} \]  

(52)

7(b) A second, more accurate analysis, but one that requires more computer time, assumes the envelope of interface composition is given by the limited solid diffusion expressions for the interface composition, parabolic growth or linear growth (see Table II). Results were obtained using both analyses.

**Solid Diffusion within the Solidification Range** - Diffusion within the solid phase for the above described model was studied using Fick's second law:

\[ \frac{dC}{d\Theta} = D \frac{\partial^2 C}{\partial x^2} \]  

(53)

with the initial and boundary conditions implied by the model: when, \( T = T_L \), then \( \Theta = 0, \ X = 0, \) and \( C_s(X_i) = kC_0 \) at \( X = 0, \ \partial C/\partial X = 0; \ X = X_i, \ C_s = C_s^* \).  

(54)

(where \( C_s^* \) is given either by the normal nonequilibrium or the limited solid diffusion expression as stated in the assumption above).
Using the method of finite differences, equation (53) is transformed to

\[
\Delta X \frac{C_{j,k} - C_{j,k-1}}{\Delta \Theta} = D \Delta X \frac{C_{j+1,k-1} - C_{j,k-1}}{\Delta \Theta} + \frac{C_{j,k-1} - C_{j-1,k-1}}{\Delta \Theta} \ldots (55)
\]

where the subscript \( j \) refers to steps in the \( X \) direction and \( k \) refers to steps in time. Solving equation (55) for \( C_{j,k} \)

\[
C_{j,k} = \frac{C_{j+1,k-1} + (M - 2) C_{j,k-1} + C_{j-1,k-1}}{M} \ldots (56)
\]

where

\[
M = \frac{\Delta X^2}{D \Delta \Theta} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (57)
\]

Equation (56) is evaluated iteratively over \( j \) and \( k \) and the boundary conditions are simulated by the sequence of the steps taken by the computer solution.

**Solid Diffusion During the Eutectic Transformation** - As the liquid remaining at the eutectic temperature is transforming, diffusion occurs within the primary solid. This diffusion is calculated by evaluating equation (56) at all the \( j \) positions within the primary solid solution for successive iterations, each \( \Delta \Theta \) in duration, from the time, \( \Theta_E \), of reaching the eutectic temperature to time \( \Theta_f \) when freezing is complete (i.e., if \( p = \) number of iterations, then \( p \Delta \Theta = \Theta_f - \Theta_E \)).

**Diffusion in the Solid Solution Region** - As the alloy cools from the eutectic to room temperature, a certain amount of
homogenization can occur. If this homogenization is significant, then one would expect to see less second phase and more level concentration gradients at room temperature than are present immediately after solidification. Once the time-temperature path for the alloy is determined, the above analysis can be extended to the computation of the amount of solid state homogenization.

Just as for the solidification range, two classes of cooling curves are considered. The condition of linear advance of the liquid solid interface, equation (32), requires a constant rate of heat removal, \( q \); that is,

\[
q = \text{constant} = C_1 \quad \text{(58)}
\]

Such a heat flow condition would be largely true for (1) an ingot cast so that interface resistance to heat flow is the limiting factor, (2) an ingot cooled by the "differential thermocouple technique" described later in this report, and (3) for "unidirectionally" solidified ingots, solidified under steep thermal gradients, for distances not too close to the chill and temperatures not far from \( T_E \).

If the heat released in solidification were the same for each fraction solidified and equal to \( H' \) (calories/gram), then

\[
\frac{dX_i}{d\Theta} = \frac{q}{\rho H_f A} = \frac{C_1}{\rho H_f A} \quad \text{(59)}
\]

Now, in the solid region,

\[
q = - \rho c_p A \frac{dT}{d\Theta} \quad \text{(60)}
\]

where \( c_p \) = heat capacity of solid (calories).

* \( H' \) is numerically equal to average value of \( \frac{dH_T}{df_S} \), a parameter calculated in Section IV-A.
Substituting (60) into (59) and rearranging

\[
\frac{dT}{d\Theta} = \frac{2H'u}{c_{ps}d} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (61)
\]

Integrating

\[
T = T_E - \frac{H'}{c_{ps}} \left[ \frac{\Theta - \Theta_f}{\Theta_f} \right] \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (62)
\]

The condition of parabolic advance of the liquid-solid interface, equation (31), requires a parabolic rate of heat removal, that is,

\[
q = c_2 \Theta^{-1/2} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (63)
\]

Such a heat flow condition would be largely true for temperatures not too far below \(T_E\) when resistance to heat flow is primarily thermal diffusivity of the mold as in (1) sand castings, (2) chill castings, locations near the chill, mold-metal interface resistance negligible. Following a procedure analogous to that used to derive equation (62), the cooling curve is related to the solidification time for parabolic heat removal by

\[
T = T_E - \frac{H'}{c_{ps}} \left[ \frac{\sqrt{\Theta} - \sqrt{\Theta_f}}{\sqrt{\Theta_f}} \right] \quad \cdots (64)
\]

Once the appropriate time temperature path has been selected, the extent of diffusion on cooling can be determined by evaluating equation (55) iteratively from the eutectic temperature to a temperature at which the diffusion is no longer significant.

**Qualitative Results; Diffusion within the Dendrite** - The qualitative results of the numerical analysis solution are
in agreement with the solution to the materials balance. The value of \( M \), as defined by equation (57), is inversely proportional to \( \gamma^2 \) and indicates the extent of solute diffusion in the solid phase. It is a characteristic of the analysis that when \( \Delta X \) represents the amount of solid to form in a solidification time \( \Delta \Theta \); for \( M \ll 2 \), the gradients will tend to level out as fast as the dendrites grow; for \( M \gg 2 \) there will be little diffusion and segregation will approach the maximum. The parameter \( M \) is related to the growth model through \( \gamma \). As defined previously,

\[
d = \gamma \cdot \theta_f^{1/2}
\]

If a value of \( \gamma \) is known for an alloy, then it should be possible to estimate the extent of solid state diffusion by computing \( D/\gamma^2 \). If \( D/\gamma^2 \ll 1 \), tendency for maximum segregation; \( D/\gamma^2 \approx 1 \), significant reduction of segregation; \( D/\gamma^2 \gg 1 \), tendency for minimum segregation.

It is demonstrated below that, within the assumptions of the above analysis, over any range that the value of the proportionality factor \( \gamma \) for an alloy is truly a constant, the solute segregation pattern will be the same for every dendrite spacing and cooling rate.

For two ingots made from an alloy with a constant value of \( \gamma \), the solute content at dendrite centers will be identical; the solute content at equal fractions of the dendrite spacing will be identical; the amount of nonequilibrium second phase will be identical.
Let the position of the interface be proportional to the \(n\)th power of the solidification time (such as equations (31) and (32).)

\[ x_1 = \gamma \theta^n \]  

(65)

Then, the following relation exists between \(\delta^2\) and \(\gamma\)

\[ \delta^2 = (2\gamma) \frac{1}{n} d \left( \frac{2n-1}{n} \right) \]  

(66)

Consider the diffusion in the \(j\)th slice during the time the interface moves from \(X_1 = (j-1) \frac{d}{a}\) to \(X_2 = j \frac{d}{a}\), where \(\Delta X = \frac{d}{a}\) (a' = number of spaces taken across the dendrite). Then,

\[ \Delta \theta = \theta_2 - \theta_1 = \left( \frac{jd}{a\gamma} \right)^{\frac{1}{n}} - \left( \frac{(j-1)d}{a\gamma} \right)^{\frac{1}{n}} \]  

(67)

\[ \Delta \theta = \left[ (j^{1/n} - (j-1)^{1/n}) \left( \frac{d^2}{a} \right)^{\frac{1}{n}} \right] \frac{\delta^2}{\Delta X^2} \]  

Now evaluating \(M\)

\[ M = \sqrt{\frac{x^2}{D}} \]  

(68)

where \(\sqrt{=} = \left[ 2^{1/n} (j^{1/n} - (j-1)^{1/n} a^{2n-1})^{-1} \right]\) is a numerical factor dependent on the relative position of the calculation and not on the absolute distance. Thus, in equation (68), \(M\) is dependent only on \(D\) and \(\delta^2\) but not individually on \(d\) or \(\theta_f^*\).*

---

* In particular, for parabolic growth, \(n = 1/2\); \(M = \frac{1}{2j-1} \frac{\delta^2}{D} \); for linear growth, \(n = 1\); \(M = \frac{1}{2a} \frac{\delta^2}{D} \).
Previous researchers have reported $\gamma$ to be a constant over a considerable range of dendritic solidification conditions.\textsuperscript{9,40} Closer study, however, may demonstrate that $\gamma$ is not a constant but actually a function of the solidification time. Representing the relation as

$$\gamma = \gamma_0 \Theta_f^m$$ \hspace{1cm} (69)

when \( m = 0 \), $\gamma$ is a constant and the segregation pattern will not alter with solidification time. When \( m < 0 \), the value of $\gamma$ decreases as the solidification time increases and the severity of coring will be lessened for slow cooling rates; when \( m > 0 \), the value of $\gamma$ increases as the solidification time increases and coring becomes less severe for a high cooling rate.

**Quantitative Results: Diffusion within the Dendrite** - The numerical analysis technique, described above, was applied to an aluminum-4.5 per cent copper alloy assuming a parabolic rate of interface advance (condition (31)), using a limited solid diffusion envelope (condition (7b)) and using the following numerical values, \( D_0 = 0.084 \text{ cm}^2\text{sec}^{-1} \), \( Q = 32,600 \) calories mole\(^{-1} \), \( \gamma^2 = 1.2 \times 10^{-8} \text{ cm}^2\text{sec}^{-1} \).

The concentration profiles at progressive stages of solidification and cooling to room temperature, plotted in Figure 11, depict a buildup of the solute in the solid behind the advancing interface. Just above the eutectic temperature, the solute content at the center of the dendrite is predicted
at 1.32 per cent copper. This value is to be compared to the 0.61 per cent copper predicted by the normal nonequilibrium conditions. Just below the eutectic temperature, the solute content at the dendrite center is predicted at 1.34 per cent copper and, at room temperature, 1.38 per cent copper.

The amount of solute buildup within the primary solid is, of course, sensitive to the value of $\gamma$. The dependence is demonstrated by the plot of centerline composition versus $\gamma^2$, Figure 12. The transition from normal nonequilibrium behavior to equilibrium behavior occurs in the range of $\gamma^2$ from $10^{-6}$ to $10^{-10}$ cm$^2$ sec$^{-1}$, two orders of magnitude.

The solidification curves for several compositions of the systems aluminum-copper, aluminum-magnesium, and aluminum-zinc* were computed using the analytic expression of Section 1, "Solution of Materials Balance" with several values of $\gamma^2$ for both parabolic and linear growth. The fraction eutectic formed during solidification as a function of $\gamma^2$ is plotted for several compositions of aluminum-copper having parabolic growth, Figure 13, and linear growth, Figure 14. The results, as plotted in Figures 13 and 14, show the sensitivity of the segregation behavior of several aluminum-copper alloys to the value of $\gamma$ (the ratio of the growth element size, e.g., the dendrite spacing, to the square root of the solidification time). Figure 15, which delineates the value of $\gamma$ to produce a given amount of nonequilibrium eutectic, is derived by a

* Aluminum-magnesium and aluminum-zinc alloys shift from equilibrium to normal nonequilibrium behavior as $\gamma$ varies from $1 \times 10^{-3}$ to $2 \times 10^{-4}$. 
transformation of Figure 13. A horizontal line drawn on Figure 13, as shown at one per cent retained eutectic, intersects the curve for each composition at the value of \( y^2 \) just necessary to form a given amount of eutectic, e.g., one per cent. The intersections of several horizontal lines are plotted in Figure 15. Thus, the area below the curve marked 0.5 is the locus of points for which one half per cent or less eutectic will be formed; similarly, for the curves marked 2.5, 5.0, 10.0.

The fraction solid as calculated from the numerical analysis results is applicable to a wider range of \( y \). The weight fraction primary solid phase is computed by subtracting the solute content integrated over the primary phase from the overall alloy solute content, \( C_0 \), and considering the difference to be dispersed in the second phase, i.e., at the liquid or eutectic composition; e.g., at the eutectic temperature:

\[
f_S = \frac{C_E - \left[ C_0 - \frac{2}{d} \sum_{X=0}^{X=X_1} \int_{X}^{X_1} C_j \Delta X \right]}{C_E} \quad \ldots \ldots \quad (70)
\]

For the results plotted in Figure 11, the fraction of primary solid solution just above the eutectic temperature is 0.927; just below the eutectic temperature, 0.930; at room temperature, 0.935. For normal nonequilibrium, 0.909 is the predicted weight fraction primary solid.

The weight per cent of eutectic predicted at the eutectic temperature, after eutectic transformation, and at room tem-
perature are plotted in Figure 16 as a function of $\gamma^2$ for
the assumptions (1) parabolic growth, (2) straight line phase
boundaries, and (3) normal nonequilibrium envelope (condition
7b). It is clearly demonstrated by the curves that the most
significant reduction of segregation due to diffusion in the
primary solid occurs during solidification and not during
direct cooling of the solid casting.

The dotted line of Figure 16 is a comparable curve of
the fraction solid just below the eutectic temperature com-
puted by the analytic expression for limited solid diffusion,
parabolic growth, and straight line phase boundaries (developed
in Section 1: "Solution of the Materials Balance". As the
value of $\gamma$ decreases, and consequently the value of $\infty$
approaches 1, the analytic expression tends to overestimate
the amount of homogenization. This result is due to the
assumption, stated by equation (34), that solid diffusion
will not change significantly the gradient of solute at the
interface. The change that does occur is the consequence of
(1) the increased rate of solid formation and (2) the buildup
of the solute behind the interface. The analytic expression
is, nonetheless, sufficiently accurate for the common range
of values of $\gamma$.

Two envelopes were used to express the interface compo-
sitions, the normal nonequilibrium and the limited solid
diffusion. The points plotted in Figure 16 are the fraction
solid just below the eutectic calculated for a limited
solid diffusion envelope, whereas the solid curves are for a normal nonequilibrium envelope. The former envelope is expected to be more accurate and the latter more convenient; however, it is evident from Figure 16 that closely similar results are obtained by the two envelopes.

B. Comparison of Computations with Experiment

1. Thermal Analysis of Extended Solidification Heats

Several ingots of aluminum-4.5 per cent copper were solidified over extended periods, ranging from twelve to 1000 hours, at a constant rate of heat extraction using a differential thermocouple technique. A detailed description of the experimental technique and the method of alloy preparation has been presented previously.7,8 Photographs of polished and etched macrosections of ingots solidified twelve, sixty, one hundred and one thousand hours are shown in Figure 17. Thermal record of ingots solidified over twelve, thirty six, and eighty two hours are plotted in Figure 18. The plots are similar in shape to the solidification curve (Figure 9) calculated earlier for this alloy. The slope decreases sharply as the first solid appears and remains relatively shallow and linear for a good part of the solidification time. The slope just before the eutectic transformation is close to the value previous to the transformation. The horizontal hold represents the eutectic transformation. Finally the slope increases to a value
characteristic of a single phase field. Neither the amount of undercooling below the liquidus prior to the initiation of freezing nor the undercooling below the eutectic prior to the initiation of the eutectic transformation was ever measured as greater than two degrees Farenheit.

The Solidification Curve; Comparison with Computations - Due to the fact that the ingots were cooled with a constant rate of heat extraction, the abscissa of the thermal record differs from the heat content by a constant factor and the cooling curves may be compared to solidification curve (fraction solid versus temperature, Figure 9), using the method of Stonebrook and Sicha. The method assumes that the heat of fusion liberated for each per cent of transformation is the same and that the heat capacity of the solid and liquid are the same. The heat content calculations of Part IV A: "Heat Content of a Solidifying Alloy," demonstrate that these assumptions are individually inaccurate, especially so when an intermetallic, such as CuAl₂, is one of the transformation products. But the construction, when applied to an aluminum-4.5 per cent copper alloy is accurate within 15 per cent during the bulk of solidification. The converted thermal data is plotted in Figure 9 with the calculated curves for the three cases. The data is seen to agree reasonably well with the case of limited solid diffusion and a value of $y^2 = 1.2 \times 10^{-8}$.

The Amount of Nonequilibrium Second Phase - It is interest-
ing to note that there is only a very slow increase in the amount of solid diffusion when the time of solidification is increased over two orders of magnitude. The ratio of the time of the eutectic hold to the total solidification time may be, through the calculations of Part IV-A, equilibrated with the weight fraction of eutectic formed. These values, summarized in Table III, change only slightly in the runs twelve to eighty two hours. There was no hold in the cooling curve recorded for the one thousand hour heat. However, some eutectic is observed in the macrostructure.

<table>
<thead>
<tr>
<th>Solidification Time (hours)</th>
<th>Duration of Eutectic Hold (hours)</th>
<th>Weight Fraction Eutectic (calculated)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.25</td>
<td>.03</td>
</tr>
<tr>
<td>36</td>
<td>0.7</td>
<td>.03</td>
</tr>
<tr>
<td>60</td>
<td>1.3</td>
<td>.03</td>
</tr>
<tr>
<td>82</td>
<td>1.7</td>
<td>.03</td>
</tr>
<tr>
<td>1000</td>
<td>None Observed</td>
<td>-</td>
</tr>
</tbody>
</table>

* The method of relating the heat content of an alloy to the solidification curve is described in some detail in Part IV-A: "Heat Content of a Solidifying Alloy." The weight fraction eutectic listed above is derived from that heat content curve that has a ratio $H_E/H_T$ equal to the ratio $t_E/t_T$ of the cooling curve; where $H_E$=heat released at eutectic temperature, $H_T$=total heat released during solidification, $t_E$=time at eutectic temperature, $t_T$=total solidification time.
It is evident in the macrostructures (Figure 17) that the dendrite spacing is increasing along with the solidification time. Even though the time for solid diffusion to take place may be increased, the diffusion paths become extended and thus the concentration gradients, representative of the driving force for diffusion, become shallow. The somewhat simplified model and calculations of Section A indicate that if the dendrite spacing increases in a manner such that the ratio of the square of the dendrite spacing to the solidification time \( (\frac{d^2}{t}) \) remains constant, the segregation pattern will not change. The experimental evidence indicates that the extension of solidification times is not, in itself, a practical means of eliminating microsegregation in aluminum-4.5 per cent alloys.

2. Microsegregation Measurements

Microprobe Measurements; Unidirectional Ingots - The segregation pattern within the dendrites of a series of unidirectionally solidified ingots cast from aluminum-4.5 per cent copper was analyzed quantitatively with the aid of an electron microprobe by Bower.\(^{6,41}\) The photomicrograph of Figure 19 is a section taken perpendicular to the heat flow direction and seven inches from the chill from an ingot that was water chilled and unidirectionally solidified. The sample was prepared for analysis by first polishing metallographically and then placing microhardness indentation to mark the area of observation. The electron probe traces are
apparent in the photomicrograph and the results of one trace are plotted on the same figure with the scale of the abscissa such that horizontal distances are the same. The composition along the centerline of the dendrite element is fairly uniform and for this sample a minimum value of 1.3 per cent copper was obtained.

The minimum copper content measured at the centerline of dendrite elements of samples taken from locations on this and other ingots is summarized in Table IV. The minimum solute content expected if the solidification followed normal non-equilibrium conditions is 0.6 per cent copper for an aluminum-4.5 per cent copper alloy. The fact that the minimum compositions observed are about 1.3 per cent copper indicates that the assumptions of this limiting case are not completely valid and that one of the two following conditions contributes to the discrepancy: (1) there is a significant buildup of solute ahead of the initial dendrite growth forms or (2) some solutionizing occurs in the primary dendrites during solidification. If there were a buildup of solute in the liquid, the minimum solute content measured within the solid phase would be the same throughout solidification. On the other hand, solid diffusion in the dendrites would cause the minimum solute content to gradually increase during solidification similar to the prediction of Figure 11. Two experimental techniques of interrupting solidification, described below, demonstrate that the solute content within the


<table>
<thead>
<tr>
<th>Method of Chill</th>
<th>Distance from Chill</th>
<th>Minimum Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Water chill</td>
<td>1/16 inch</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>3 inches</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>7 inches</td>
<td>1.3</td>
</tr>
<tr>
<td>2. Air Chill</td>
<td>1/16 inch</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>7 inches</td>
<td>1.3</td>
</tr>
<tr>
<td>3. Air Then Water</td>
<td>1/2 inch</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>3/4 inch</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>7/8 inch</td>
<td>1.4</td>
</tr>
</tbody>
</table>

B. Slow Cooled Ingots

<table>
<thead>
<tr>
<th>Interrupted at</th>
<th>~5% Solid</th>
<th>0.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1201°F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. 1187°F</td>
<td>~40% Solid</td>
<td>1.0</td>
</tr>
</tbody>
</table>
dendrites does, indeed, increase during solidification, and the increase in copper concentration at the center of dendrite arms above the value $kC_0$ results from diffusion in the solid.

**Microprobe Measurements, Interrupted Solidification** - First, an ingot was solidified unidirectionally by air chilling until, according to thermal data, the most advanced solid reached $3/4''$ into the ingot. Then water was put through the chill to effectively quench in the existing structure. The data in Table IV show that the primary solid phase had $.8 - .9$ per cent copper at the time of quenching. The region above $3/4''$ had a normal minimum solute content for a water chilled ingot, $1.4$ per cent copper.

Second, ingots were slow cooled to temperatures below the liquidus, and then lead at the same temperature as the alloy was poured into the ingot to displace the liquid. In this case an ingot that had its solidification interrupted at $1201^\circ F$, equivalent to $5$ per cent solid, had a solute content of $0.7$ per cent copper within the primary dendrites. An ingot that had its solidification interrupted at $1187^\circ F$, equivalent to $40$ per cent solid, had a solute content of $1.0$ per cent copper.

The experimental results substantiate the results of calculations which indicate that limited solid diffusion can occur during normal solidification. The value of the minimum solute contents measured is consistent with a value of
\[ \gamma^2 = 1.2 \times 10^{-8} \text{ cm sec}^{-1} \]

**Quantitative Microradiography: Varied Solidification Rates**

Other authors, including several Russians, have reported comparable results; the solid solution composition in the center of dendrite arms is independent of the cooling rate over a wide range.\(^ {42} \) However, few have taken the care of Bower to orient the dendrites before analysis and to record cooling conditions during the entire solid diffusion range. For example, microhardness measurements and quantitative microradiography were employed by Novikov et al.\(^ {43} \) to determine the minimum solute content of aluminum-2 per cent copper and aluminum-5 per cent copper alloys solidified over a wide range of cooling rates. Their results presented in Table V, indicate a minimum solute content of 0.5 for the 2 per cent alloy and 1.6 for the 5 per cent alloy.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>24,000</th>
<th>4400</th>
<th>925</th>
<th>430</th>
<th>230</th>
<th>146</th>
<th>60</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-2% Cu</td>
<td>0.6</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al-5% Cu</td>
<td>3.5</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
<td>-</td>
<td>1.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**TABLE V: Minimum Solute Content**

(Novikov\(^ {43} \))
3. Variation of the Value of $\gamma^2$

Mollard and Flemings\textsuperscript{40} measured the secondary dendrite arm spacings for several ingots of iron-26 per cent nickel with solidification times ranging from 240 to 25,000 seconds. The reported values of $d$, $\Theta_f$, and the calculated value of $\gamma^2$ are presented in Table VI. A plot of $d$ and $\Theta_f$ on a logarithmic scale has a slope of 0.46, very close to a slope of 0.5 for which no change in segregation pattern would be expected for different cooling rates (refer to page 38). The actual segregation ratio, measured by an electron microprobe, is included in Table VI. Measurements made on samples quenched from temperatures at varying amounts below the non-equilibrium solidus demonstrated that the slight variation in the segregation ratio was due to different amounts of diffusion after solidification.

Michael and Bever\textsuperscript{16} solidified a series of aluminum-copper ingots with solidification times ranging from two seconds to 7,600 seconds. "Selecting the dendrite formations having the maximum spacings from any given microsection," they reported dendrite spacings for each ingot. Their values of $d$, $\Theta_f$, and a calculated value of $\gamma^2$ are presented in Table VII. A plot of $d$ and $\Theta_f$ on a logarithmic scale, Figure 20, has a slope of 0.36 and a similar plot of $\gamma^2$ and $\Theta_f$, also Figure 20, has a negative slope. Thus, for aluminum-copper increased solidification time is expected to decrease microsegregation(m 0, refer
### TABLE VI: Data from Mollard and Flemings

<table>
<thead>
<tr>
<th>Cooling rate °F/min</th>
<th>Solidification time (seconds)</th>
<th>Secondary arm spac. (microns)</th>
<th>( \delta^2 \times 10^3 ) (cm²/sec)</th>
<th>Segregation ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.70</td>
<td>240</td>
<td>77</td>
<td>25</td>
<td>1.23</td>
</tr>
<tr>
<td>6.85</td>
<td>500</td>
<td>145</td>
<td>42</td>
<td>1.25</td>
</tr>
<tr>
<td>0.49</td>
<td>6,600</td>
<td>280</td>
<td>12</td>
<td>1.29c</td>
</tr>
<tr>
<td>0.47</td>
<td>6,600</td>
<td>280</td>
<td>12</td>
<td>1.17c</td>
</tr>
<tr>
<td>0.46</td>
<td>6,600</td>
<td>280</td>
<td>12</td>
<td>1.15c</td>
</tr>
<tr>
<td>0.13</td>
<td>25,200</td>
<td>605</td>
<td>14</td>
<td>1.00</td>
</tr>
</tbody>
</table>

(a) Estimated: \( 55^\circ \times (\text{cooling rate})^{-1} \times 60 \text{ sec./min.} \)

(b) Segregation ratio = \( \frac{C_M}{C_m} \); where \( C_M \) = maximum value of solute content measured, \( C_m \) = minimum value of solute content measured.

(c) Samples quenched at different temperatures in the solid solution region.
<table>
<thead>
<tr>
<th>Composition C_0 (wt%)</th>
<th>Nominal Composition C_0 (wt%)</th>
<th>Solidification Time (sec)</th>
<th>Dendrite Arm Spacing (microns)</th>
<th>( \gamma^2 \times 10^8 )</th>
<th>Eutectic calculated^a (wt%)</th>
<th>Eutectic measured^b (wt%)</th>
<th>Eutectic corrected^c (cm^2/sec)</th>
<th>Eutectic calculated^d (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.07</td>
<td>2</td>
<td>2</td>
<td>12</td>
<td>72</td>
<td>3.57</td>
<td>2.71</td>
<td>12.3</td>
<td>2.71</td>
</tr>
<tr>
<td>2.07</td>
<td>2</td>
<td>20</td>
<td>24</td>
<td>29</td>
<td>3.33</td>
<td>1.92</td>
<td>5.2</td>
<td>1.80</td>
</tr>
<tr>
<td>2.08</td>
<td>2</td>
<td>120</td>
<td>63</td>
<td>33</td>
<td>3.38</td>
<td>1.42</td>
<td>6.0</td>
<td>1.90</td>
</tr>
<tr>
<td>1.96</td>
<td>2</td>
<td>7440</td>
<td>250</td>
<td>8.4</td>
<td>2.39</td>
<td>0.66</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>2.94</td>
<td>3</td>
<td>6</td>
<td>23</td>
<td>88</td>
<td>5.90</td>
<td>4.67</td>
<td>15.8</td>
<td>5.3</td>
</tr>
<tr>
<td>2.96</td>
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<td>35</td>
<td>56</td>
<td>5.84</td>
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<td>10.0</td>
<td>4.78</td>
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<tr>
<td>2.97</td>
<td>3</td>
<td>156</td>
<td>81</td>
<td>42</td>
<td>5.76</td>
<td>3.69</td>
<td>7.6</td>
<td>4.4</td>
</tr>
<tr>
<td>2.81</td>
<td>3</td>
<td>6360</td>
<td>220</td>
<td>7.6</td>
<td>4.68</td>
<td>2.54</td>
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<tr>
<td>3.93</td>
<td>4</td>
<td>2</td>
<td>21</td>
<td>220</td>
<td>8.39</td>
<td>7.18</td>
<td>39.0</td>
<td>8.2</td>
</tr>
<tr>
<td>3.96</td>
<td>4</td>
<td>20</td>
<td>31</td>
<td>48</td>
<td>8.22</td>
<td>6.95</td>
<td>8.7</td>
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</tr>
<tr>
<td>3.94</td>
<td>4</td>
<td>110</td>
<td>60</td>
<td>33</td>
<td>8.12</td>
<td>5.72</td>
<td>6.0</td>
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</tr>
<tr>
<td>4.06</td>
<td>4</td>
<td>5540</td>
<td>250</td>
<td>11</td>
<td>7.63</td>
<td>3.50</td>
<td>2.0</td>
<td>3.7</td>
</tr>
<tr>
<td>4.71</td>
<td>4.8</td>
<td>6</td>
<td>18</td>
<td>54</td>
<td>10.05</td>
<td>9.64</td>
<td>9.7</td>
<td>9.6</td>
</tr>
<tr>
<td>4.79</td>
<td>4.8</td>
<td>26</td>
<td>27</td>
<td>28</td>
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<td>9.66</td>
<td>5.1</td>
<td>9.5</td>
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<tr>
<td>4.82</td>
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<td>9.78</td>
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<td>4.8</td>
<td>7600</td>
<td>250</td>
<td>8.2</td>
<td>9.15</td>
<td>5.05</td>
<td>1.5</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Notes:  
(a) Taken from Figure 13 at reported value of C_0 and \( \gamma^2 \).  
(b) Lineal analysis  
(c) \( \gamma^2 = (0.425d)^2/\Theta_f \)  
(d) Taken from Figure 13 at reported value of C_0 and corrected value of \( \gamma^2 \).
Lineal analysis estimates of the weight fraction eutectic that Michael and Bever reported for their ingots are presented (Table VII, column F) together with the weight fraction eutectic selected from Figure 13 for the reported values of $C_o$ and $Y^{a^2}$ (column G). Indeed, the amount of eutectic diminishes with lengthening solidification times. Nonetheless, there are substantial differences between the calculated and experimental values. The discrepancy, i.e., more rapid decrease of eutectic with increase of solidification time than calculated, could have several explanations; including experimental factors, such as, the metal was poured into hot molds and the homogenization period after solidification would be extended. But, the major factor is considered to be the assumption of a too simple geometry for the growth model. Even though dendrites are "platelike" through much of their growth $^{5,44}$, the spacings of the several orders of branches (i.e., primary dendrite element spacing, secondary dendrite element spacing, etc.) do not differ by more than a factor of five $^{41,45}$. The branches are not accurately described as infinite plates. Corner effects are not negligible.

The introduction of corner effects in the analysis of solidification will tend to increase the amount of homogenization of the solid phase during solidification; in effect, to reduce the dendrite spacing. To account for corner effects,
the Michael and Bever values of dendrite spacing have been multiplied by a geometric correction factor 0.425. The new values of $\gamma^2$ are then listed in Table VII (column H).

The weight fraction eutectic selected from Figure 13 for the reported value of $C_0$ and the corrected values of $\gamma^2$ are listed in Table VII (column I). In Figure 21, the weight fraction eutectic reported by Michael and Bever are compared to the values of column I. The dotted line of slope 1.0 would represent perfect correspondence.
IV. MACROSCOPIC PARAMETERS OF A SOLIDIFYING ALLOY; HEAT CONTENT AND SPECIFIC VOLUME

The determination of the solidification curve for an alloy makes possible calculation of a variety of solidification parameters, the actual measurement of which is often extremely difficult. The computation of two such groups of properties has been included in the FORTRAN program for macroscopic properties described in Appendix B. These are

1. The heat content of the phases and the rate of the heat release.
2. The specific volume of the phases and the amount and rate of shrinkage.

A. Heat Content of a Solidifying Alloy

The total heat released during the liquid to solid transformation of a binary alloy of components A and B depends only on the initial and final states of the alloy. The heat released at any temperature during the transformation, however, is intimately dependent on the solidification path. This dependence on the path is significant when the composition changes of the solid and liquid phases during solidification are considerable.

General - The heat content of a binary alloy at any temperature in a two-phase region is expressed by the following relations:
\[ H_T = f_S H_S + f_L H_L \]  \hspace{1cm} (71) 

where

\[ H_S = \bar{c}_S H'_S + (1 - \bar{c}_S) H''_S + H_S^M (T, \bar{c}_S) \]  \hspace{1cm} (72) 

\[ H_L = c_L^* H'_L + (1 - c_L^*) H''_L + H_L^M (T, c_L^*) \]  \hspace{1cm} (73) 

Having used the following expressions for the solute

\[ H'_S = \int_{T_B}^{T} c'_P S \, dT \]  \hspace{1cm} (74) 

\[ H'_L = \int_{T_B}^{T'} c'_P S \, dT + H'^F + \int_{T'}^{T_M} c'_P L \, dT \]  \hspace{1cm} (75) 

Analogous expressions were used for the solvent parameters, \( H''_S, H''_L \), where single primes refer to solute and double primes refer to solvent and

\[ H_T = \text{total heat content of alloy relative to a base temperature, } T_B \text{ (calories/gram alloy)} \]

\[ H_S, H_L = \text{heat content of solid and liquid phases (calories/gram phase)} \]

\[ T'_M, T''_M = \text{melting point of pure component (°C)} \]

\[ c'_P S, c'_P L = \text{heat capacity of pure solute in the solid and liquid states, respectively (calories/gram °C)} \]

\[ H'^F = \text{heat of fusion of pure solute (calories/gram)} \]

\[ H^M_{S}(T, \bar{c}_S), H^M_{L}(T, c_L^*) = \text{heat of mixing of solid and liquid phases at temperature } T \text{ and average compositions } \bar{c}_S \text{ and } c_L^*, \text{ respectively (calories/gram).} \]
The assumption has been made that the properties of a phase are accurately represented by its average composition. This is essentially use of the Kopp-Neumann rule of heat capacities.

Equally general as the previous expressions are the following derivates that are the rate of heat release of the phases and the aggregate,

\[
\frac{dH_T}{dT} = f_S \frac{dH_S}{dT} + (1 - f_S) \frac{dH_L}{dT} + (H_S - H_L) \frac{df_S}{dT}
\]

\[
\cdots \cdots \cdot (76)
\]

\[
\frac{dH_S}{dT} = \overline{c}_S c'_p (1 - \overline{c}_S) c''_p (H'_S + H''_S) \frac{dC}{dT} + \frac{\partial H_S}{\partial T} \frac{dC}{dT} + \frac{\partial H_S}{\partial C} \frac{dC}{dT}
\]

\[
\cdots \cdots \cdot (77)
\]

\[
\frac{dH_L}{dT} = c'L c'_p (1 - c'_L) c''_p (H'_L + H''_L) \frac{dC}{dT} + \frac{\partial H_L}{\partial T} \frac{dC}{dT} + \frac{\partial H_L}{\partial C} \frac{dC}{dT}
\]

\[
\cdots \cdots \cdot (78)
\]

The rate of heat release with increase of solid fraction \((dH_T/df_S, dH_L/df_S, dH_S/df_S)\) is simply obtained by multiplying the appropriate derivative above by \(dT/df_S\) (see Table I).

For a dendritically freezing alloy the liquid is considered to be homogeneous on the microscale and thus the terms that depend on the solidification path are \(f_S, \overline{c}_S, d\overline{c}_S/dt, dT/df_S\). The method of evaluation of these parameters has been discussed previously.
Evaluation for an Aluminum-4.5 Per Cent Copper Alloy - The analysis has been applied to the particular case of an aluminum-4.5 per cent copper alloy. The method of evaluating each of the thermal parameters using data from K. K. Kelley\textsuperscript{46} and from O. Kubashawski and J. A. Catterall\textsuperscript{47} is summarized in Appendix E.

The heat content is plotted as a function of temperature in Figure 22 and as a function of the solid fraction in Figure 23. The heat content curves of Figure 22 are shaped similarly to the solidification curves for the same alloy (Figure 9). However, the curves differ in detail.

The curves are extended in the direction of the abscissa. During solidification of an alloy, the sensible heats of the solid and liquid phases must be removed, in addition to the heat of fusion of the solidifying fraction.

The ratio heat released during the eutectic transformation to heat released over entire solidification interval does not equal the weight fraction of eutectic formed. No sensible heat is removed from the solid or liquid phases during the eutectic transformation. Also contributing to the discrepancy, the $\ominus$ phase, which is one of the eutectic constituents, has an appreciably negative heat of formation.

If the heat released for each fraction solidified were constant, then a heat content curve could be transformed to a solidification curve using the construction of Stonebrook and Sicha.\textsuperscript{38} The slope of the curve in Figure 23 equals the
amount of heat that need be extracted to form one gram of solid at a particular stage of solidification. The slope is not a constant throughout the solidification interval of 195 alloy; rather $dH_T/df_S$ continuously increases as solidification progresses. For some calculations (e.g., qualitative application of the Stonebrook and Sicha construction) a value of $dH_T/df_S$ averaged over the solidification interval is a reasonable first approximation.

The composition of each phase and of the fraction freezing increases continuously during solidification. The heat capacity of each phase, the heat of mixing of the liquid, and the heat of fusion of the solidifying fraction are each dependent on the composition. The contribution of each of these components to the heat content and the rate of heat release is summarized in Figure 24.

B. **Specific Volume of a Solidifying Alloy**

The solid state of the common metals has a smaller specific volume than the liquid state. Much of the porosity in cast structures is a direct consequence of this shrinkage and the inability to compensate properly by liquid feeding. If feeding is to be better understood, the first step is to determine the total amount of shrinkage and the various stages of solidification in which shrinkage occurs. Empirical determination is made difficult due to the "mushy" mode typical of alloy solidification.
Specific Volume of Solid and Liquid Phases - Analytical expression of the shrinkage is made complex by the dependence of the specific volume on both solute concentrations and temperature. Data gathered for the solid and liquid phases adjacent to the transformation range often show the specific volume of the phases to be linear functions of solute content and temperature. Such a relation is assumed to hold within the transformation region and the data are extrapolated from the single phase regions by the expressions

\[ V_S = V_S^0 + \bar{C}_S + XT \]  \hspace{1cm} (79)

\[ V_L = V_L^0 + \bar{C}_L* + ZT \]  \hspace{1cm} (80)

where \( V_S, V_L \) = specific volume of solid and liquid at temperature \( T \) and average solute contents \( \bar{C}_S \) and \( \bar{C}_L* \), respectively, and \( V_S^0, V_L^0, W, X, Y, Z \) = empirical constants. Thus, the specific volume of either phase at any temperature within the solidification range is immediately evaluated by insertion of the average composition of solid or liquid phases appropriate to the solidification path (Note: Part 2 of Section III-A: "Composition of the Primary Solid Phase.")

Specific Volume of Alloy - The overall volume of the alloy is then given by inserting the appropriate value of the fraction solid, \( f_S \), into the relation

\[ V_T = f_S V_S + (1 - f_S) V_L \]  \hspace{1cm} (81)

where \( V_T = \) specific volume of both phases.
Shrinkage - The total shrinkage from the liquidus temperature to a temperature, \( T \), within the solidification range can now be computed

\[
\beta = \frac{V_T(T_L) - V_T(T)}{V_T(T_L)} \quad \ldots \ldots \quad (82)
\]

Derivatives - The rate of change of the specific volume of the phases and the rate of shrinkage are closely related to the rate requirement of feed metal. These parameters are evaluated for a specific solidification path by inserting the appropriate values for the derivative of compositions and of fraction solid into the expressions summarized in Table VIII.

Evaluation for Aluminum-4.5 Per Cent Copper Alloy - Specific volume and shrinkage parameters were computed for an aluminum-4.5 per cent copper alloy. Using the least squares method, the data of Ellwood and Silcock\(^{49}\) and of Gerbhart, Becker, and Corner\(^{50}\) were converted to expressions of the form of (79) and (80).

\[
V_S = 0.3663 - 2.9 \times 10^{-3} \, c_S + 3.83 \times 10^{-5} \, T
\]

\[
V_L = 0.3965 - 3.21 \times 10^{-3} \, c_L^* + 3.92 \times 10^{-5} \, T
\]

The specific volume and shrinkage of the alloy are plotted as a function of temperature in Figure 25 and as a function of fraction solid in Figure 26.*

As is expected the solid that forms first is more dense.

* The solidification contraction of liquid of eutectic composition was estimated at 8 per cent based on data taken by Takase\(^{53}\)
<table>
<thead>
<tr>
<th>TABLE VIII: Derivatives of Specific Volume Parameters</th>
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<tr>
<td></td>
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<td>Solid</td>
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<tr>
<td>$V_S$</td>
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<td>Liquid</td>
</tr>
<tr>
<td>$V_L$</td>
</tr>
<tr>
<td>Alloy</td>
</tr>
<tr>
<td>Shrinkage</td>
</tr>
</tbody>
</table>
than the liquid from which it formed (the solid volume is 94.4 per cent of the liquid volume). For this system, however, the density of the liquid increases very quickly as it is enriched in the more dense constituent, copper. Initially 4.5 per cent copper, the liquid becomes 33 per cent copper before the final eutectic transformation. As a result, after the alloy is six tenths solid, the freezing metal has a greater volume than the liquid from which it originates. The total volume still decreases, nonetheless, due primarily to the thermal contraction.

The shrinkage, $\beta$, as defined by equation (82), is the absolute shrinkage of the alloy and is the same no matter how the porosity is dispersed. In practice the shrinkage is distributed as macropores, micropores, uniform contraction from the mold wall, dishing, cracks, and/or shrinkage pipe. The actual distribution of porosity is determined by the physical properties and solidification characteristics of the alloy, the casting procedure, the casting geometry, the rigging of risers and gates, the stress distribution, and the thermal gradients. It is the aim of risering and directional solidification to limit -- by liquid feeding -- the formation of internal pores.

For purposes of discussion, the complexity of the problem is reduced by eliminating most of the variables listed above. Consider a metal of high elastic modulus cast into an ingot mold without appreciable thermal gradients.
The specific volume calculation gives a good idea of feed metal requirements. The individual contributions to feed metal requirement can be seen more clearly from an expansion for \( \frac{d\beta}{df_S} \) (Table VIII).

\[
\frac{d\beta}{df_S} = \frac{1}{v_L(T_L)} (v_l - v_s) - f_S \frac{dv_s}{df_S} - (1 - f_S) \frac{dv_L}{df_S}
\]  

\ldots \ldots (83)

The first term in brackets represents the solidification contraction, the second and third terms represent the contraction of the solid and liquid phases; thermal and solidification contraction each are functions of temperature and composition. The individual terms of equation (83) are plotted in Figure 27.

Early in solidification, shrinkage in ingots cast with shallow temperature gradients is readily fed by bulk movement of liquid and solid.\textsuperscript{21,31} At some stage during solidification (near 30 per cent solid\textsuperscript{21}) the solid becomes coherent, and feeding is solely by liquid flow. Once the solid becomes coherent, it will contract as a mass and actually reduce the internal volume. Thus solid contraction, the second term of (83), will not represent a tendency for porosity; rather, it will reduce the tendency for porosity -- less feed metal will be required. If the solid, when it is coherent, forms so as to entrap the liquid and if it contracts uniformly, the effective shrinkage (and the feed metal require-
ment) will be given by

$$
\beta_a = \frac{V_T(T_c) - V_S(T_c)}{V_S(T)} \frac{V_T(T)}{V_T(T_c)}
$$

(84a)

where $T_c$ is the temperature that the solid becomes coherent. $\beta_a$ is the measure of the requirement for liquid feed metal if feeding by bulk movement is perfect up to the time of coherency. If we include the shrinkage that occurs before the solid becomes coherent,

$$
\beta_b = \frac{V_T(T_L) - V_S(T_c)}{V_S(T)} \frac{V_T(T)}{V_T(T_L)}
$$

(84b)

$\beta_a$ and $\beta_b$ are compared in Figure 28 to the absolute shrinkage, $\beta$, as a function of the temperature, $T_c$, that the solid becomes coherent.

The maximum benefit from solid contraction will be obtained when the metal becomes coherent at the liquidus (note curve of $\beta_b$). On the other hand, bulk flow is active longer if the metal becomes coherent at a low temperature. The difference between the curves for $\beta_b$ and $\beta_a$ represents the feeding possible by bulk flow.

The solidification that takes place at the eutectic temperature is accompanied by appreciable porosity. Near the end of solidification, thermal gradients are generally lowest and channels for liquid feeding are tortuous even when continuous.31
V. HOMOGENIZATION TREATMENTS

Metal properties, including fracture strength, susceptibility to corrosion, deformability, and surface character have been correlated with the degree of homogeneity of the alloy.\textsuperscript{29,30,36,51,52} During the solidification process solute redistribution is required; and the kinetics of solidification limit the approach of the alloy to equilibrium. Thus, the initial pattern of segregation is determined during solidification. The efficacy of homogenization heat treatments, in turn, are dependent on the initial solidification structure; i.e., on the size of the solidification element and on the solute distribution within the solidification element. The numerical analysis technique, described above, which was applied to the redistribution of solute during solidification can be employed to evaluate the efficiency of homogenization treatments, provided the rate limiting step is diffusion of solute within the primary solid phase. Two homogenization treatments, isothermal solidification and solutionizing, have been considered.

A. Isothermal Solidification

Very slow solidification, by itself, is not an effective method for eliminating nonequilibrium phases and coring in aluminum alloys (refer to Section III). Comparable conclusions may also be drawn for the solidification behavior of
several ferrous alloys.\textsuperscript{40,45} Of importance is not solidification time, per se, but the relation of solidification time to the size of the solidification element, expressed by a quantity such as $\gamma$ (equation 48, page 26). (Reference to Figure 13 demonstrates the effect of a reduction of $\gamma$ on the amount of nonequilibrium eutectic formed in aluminum-copper alloys.) One method* of reducing microheterogeneities by the reduction of $\gamma$ is isothermal solidification; a fine dendrite arm spacing is obtained in conjunction with a long solidification time.

In practice, for an alloy such as 195, the ingot is cooled relatively rapidly to a temperature below the solidus but above the eutectic, achieving a fine dendrite spacing. The ingot is maintained, isothermally, above the eutectic until solidification is complete. At such a temperature below the solidus, the liquid is a nonequilibrium phase and will disappear at a rate determined by diffusion of solute through the primary dendrite. When this procedure is employed for 195 alloy, the ingot will pass through the eutectic temperature, on further cooling, without the formation of the $\ominus$ phase and the concomitant porosity.

\textsuperscript{*} More complex thermal treatments may also be employed to reduce $\gamma$. In addition, $\gamma$ may be altered through combinations of mechanical, chemical, and thermal treatments during ingot solidification. Several of these treatments, described elsewhere,\textsuperscript{15} give confirmation of the relation of microsegregation to $\gamma^2$. 
The temperature that will promote isothermal solidification in the shortest time for a particular alloy is dependent on the solidification structure and the diffusion parameters. Typically, as the temperature selected for isothermal solidification is decreased toward the eutectic, the diffusion coefficients of the alloying elements decrease; on the other hand, the driving potential for diffusion increases and the quantity of liquid to be eliminated diminishes. The balance between these factors sets the optimum temperature for isothermal solidification.

Method of Calculation* - In the application of numerical analysis to the consideration of isothermal solidification, the limiting factor is taken to be the ability of the primary dendrites to accommodate solute from the unstable liquid. The solute distribution resulting from the initial, relatively rapid cooling of the alloy from the liquidus to the isothermal solidification (holding) temperature is computed by the numerical analysis technique of Section III (pages 32-35). The calculation (see Figure 29) is made for a particular dendrite spacing, d, and solidification time, $\Theta_f$, and cooling is interrupted at the isothermal solidification temperature, $T_I$, at a time after the initiation of freezing, $\Theta_C(\Theta_f > \Theta_C)$. The position of the interface, $X_I$, the solute

* Organization of the computer program to perform this calculation is included in Appendix B.
concentration in the liquid, \( C_L^* \), and the solute content in the solid at the interface, \( C_S^* \), and the distribution of solute within the solid phase at time \( \Theta C \) constitute the initial condition for the isothermal solidification calculation. The boundary conditions are

\[
\frac{\partial C_S}{\partial x} = 0, \text{ at } x = 0; \quad C_S = C_S^*, \text{ at } x = x_1 \quad \ldots . \quad (85)
\]

where \( x_1 \), the position of the interface, is continually increasing as solidification proceeds. The amount of diffusion in the solid phase during a time interval \( \Delta t \) (where \( \Delta t \sim \Delta x^2 / 2D_S \)) is computed by iteratively evaluating the expression

\[
C_{S,J-1,k-1}^{\ast} + (M-2)C_{S,J,k-1}^{\ast} + C_{S,J+1,k-1}^{\ast}
\]

for steps in \( J \) from the center line, \( x = 0 \), to the interface, \( x = x_1 \) (\( J = 1 \) to \( J = x_1 / \Delta x \)), while the interface remains stationary and at the equilibrium concentration, \( C_S^* \). This diffusion gives rise to a new solute distribution within the primary dendrite, see Figure 29. Then the total amount of solute that entered the primary dendrite during \( \Delta t \), shaded area of solid phase in Figure 29, is computed and an equivalent amount of solute is considered to be removed from the liquid, shaded area in liquid phase in Figure 29. The interface is moved ahead an increment, \( \Xi \), proportional to the amount of liquid removed during \( \Delta t \). If \( \mathcal{J} \) is the new solute
in the solid phase, then

\[ \varepsilon = \sum \frac{d}{C_L^* - C_S^*} \cdot \frac{d}{2} \]  \hspace{1cm} \text{(86)}

Diffusion within the primary dendrite is computed for another \( \Delta t \), and the procedure continues until the primary dendrites impinge at \( X = d/2 \) or until an equilibrium ratio of phases is reached.

B. Solution Treatment

Metal alloys are often given high temperature solution treatments either as a necessary preliminary to a working operation or as a first step in a heat treatment schedule; as examples, prior to martensitic transformation and prior to precipitation hardening. The goal of solutionizing is to produce a homogeneous, stress free material. Microsegregation resulting from the nonequilibrium nature of solidification is the most difficult to eliminate of the removeable inhomogeneities. Solidification segregation is generally present on a coarser scale than other heterogeneities, for example, phases resulting from solid state transformations. Usual commercial solution treatments remove only a fraction of the microsegregation in most cast metals,\(^30\) and in many wrought materials.\(^31\)

In 195 alloy the \( \Theta \) phase (or the transition precipitates, \( \Theta', \) GP I, GP II) must be eliminated from the structure. By the time the \( \Theta \) phase has disappeared, the copper will have been quite evenly distributed through the matrix. Particles
of \( \Theta \) that precipitate at temperatures below the solvus will cause short range depletions of the lattice, and this fine precipitate will be dissolved near the beginning of solutionizing. Macrosegregation is not removed, in general, by solutionizing. Reduction of the solidification microsegregation is the slowest step in the solutionizing of 195 alloy.

**Method of Computation** - When the interdiffusion coefficient in the phase to be dissolved is higher than in the primary solid or when the dimensions of the second phase are narrow in comparison to the primary phase, the rate limiting parameter of solutionizing will be the ability of the primary solid phase to accommodate solute. Under such conditions, the mathematical description of solutionizing is analogous to that of isothermal solidification. The initial condition is specified as the solidification structure. When there is a second phase present after solidification the boundary conditions are

\[
\frac{\partial C_s}{\partial X} = 0, \text{ at } X = 0; \quad C_s = C_s^*(\text{Max. solubility}), \text{ at } X = X_1
\]

The finite difference method is employed to compute the diffusion in the solid during the time interval \( \Delta t \), the increase of solute is integrated over the primary solid, a corresponding amount of second phase is considered to disappear, the interface is advanced \( \varepsilon \), and diffusion is calculated for another interval \( \Delta t \), restarting the chain of
computations. When no second phase is present but a non-uniform single phase solid is to be homogenized, the boundary conditions are

\[ \frac{\partial C_S}{\partial x} = 0, \quad \text{at} \quad x = 0; \quad \frac{\partial C_S}{\partial x} = 0, \quad \text{at} \quad x = \frac{d}{2} \]  

(88)

and again the amount of diffusion is computed by the finite different solution of Fick's second law, now using (88) for the boundary conditions.

C. Quantitative Results: Homogenization Treatments

The time to completely eliminate the second phase by isothermally solidifying or by solutionizing an aluminum-4.5 per cent copper alloy was computed for a variety of conditions that represent a wide range of casting practice. The results are summarized by Figures 30 to 36.

The distribution of solute in the primary solid phase, K, is shown in Figure 30 at successive stages during isothermal solidification of 195 alloy at 548°C (i.e., just above the eutectic temperature). The lowest curve depicts the solute distribution when cooling is interrupted at time \( \Theta_c \). During the isothermal hold, the solute content at each point within the primary solid approaches the average alloy concentration, \( C_o = 4.5 \) per cent copper, and the solid-liquid interface advances in the direction of the liquid. At time \( \Theta_H \) the liquid is eliminated and the average composition of the solid is 4.5 per cent. The copper content varies across the dendrite from 3.85 to 5.64 per cent.
The computed average composition of the alloy after homogenization will differ, for some values of $\delta$, from the original solute content due to the approximate nature of the model; in particular, assumption 7, page 32. Refining the analysis to satisfy exactly the material balance would alter only slightly the calculated results for aluminum-copper alloys (and such a refinement is not justified by the available data).

The advance of the solid-liquid interface is depicted by Figure 31 for heat treatments of 195 alloy at several temperatures in the isothermal solidification and solutionizing range. The weight fraction of nonequilibrium phase corresponding to the interface position is indicated on the right ordinate axis. The effect on the homogenization time of the decrease in amount of liquid phases as the temperature is lowered within the isothermal solidification range is strikingly apparent. The rate of interface advance, indicated by the slopes of the curves in Figure 31, is dependent on the diffusion coefficient of the solute in the primary solid, on the steepness of the concentration gradient in the primary solid, and on the difference in solute content in liquid and solid phases. In the isothermal solidification range, the variation of these factors with decreasing temperature is such, for aluminum-copper alloys, that at the temperature plotted the rate of advance of the interface is about the same. The minimum homogenization time for this
alloy is at the temperature where the least amount of liquid phase must be eliminated, just above the eutectic.

In the solutionizing range, the initial concentration gradient and the initial amount of second phase are the same at each temperature. The time to eliminate the \( \Theta \) phase quickly increases with decreasing temperature, i.e., as the diffusion coefficient diminishes. In Figure 31, the decrease in the rate of advance of the interface is apparent at the end of solutionizing, when the concentration gradients approach zero. For a given alloy with a given solidification structure characterized by \( y^2 \), one homogenization curve can be drawn for all temperatures within the solutionizing range by plotting a "segregation factor" versus the dimensionless factor \( D_S t / \ell^2 \), where \( D_S \) is the solute diffusion coefficient; \( t \) is the time the structure has been at the homogenization temperature; and \( \ell \) is a characteristic spacing, such as one half the dendrite spacing, \( d/2 \). The temperature dependence is incorporated in \( D_S \) and the structure dependence in \( \ell^2 \).

* The boundary conditions for the analysis of solution treatment, condition (87), fix the solute content in the primary solid at the interface at the solubility limit; i.e., the solvus is considered a vertical line. If the second phase (in 195 alloy, the \( \Theta \) phase) does not have difficulty nucleating and the primary and secondary phase can adjust their proportions and their compositions to satisfy equilibrium locally; for systems with gradually sloping solvus lines, homogenization kinetics will not differ significantly from the analysis.
The "segregation ratio", $S$, of a solute element distributed in a dendritic structure, has been defined as

$$ S = \frac{C_M}{C_m} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (89) $$

where $C_M$ is the maximum solute concentration of the primary solid phase and $C_m$ is the minimum solute concentration. For calculation of homogenization kinetics, it is useful to define an "index of residual segregation", $\delta_S$, as

$$ \delta_S = \frac{C_M - C_m}{C_M - C_m^o} = \frac{S - 1}{S^o - 1} \frac{C_m}{C_m^o} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (90) $$

where the superscript $^o$ refers to the as-cast structure. The index of residual segregation will be one for the as-cast structure and will be zero when the primary solid phase has a uniform composition. In Figure 32, $\delta_S$ is plotted versus the dimensionless parameter $D_S t / \ell^2$ for a 195 alloy with $\gamma^2 = 2.0 \times 10^{-7}$. Similar curves would be obtained for other values of $\gamma^2$.

The time to eliminate the nonequilibrium phase in a 195 alloy by homogenizing at temperatures within either the isothermal solidification or the solutionizing range is plotted in Figure 33 for several values of $\gamma^2 ( = d^2 / \Theta_p )$. The curves clearly indicate that the time for homogenization is minimized if heat treatments are performed at the eutectic temperature.
Plotted on the ordinate of Figure 33 is the homogenization time parameter

\[ \Theta \frac{H}{H} = \frac{\Theta}{\Theta_f} = \frac{\Theta H^2}{d^2} \quad \ldots \ldots \ldots \quad (91) \]

where \( \Theta_H \) = time to eliminate the unstable phase and \( \Theta_f \) = solidification time. For a given alloy that is homogenized at a chosen temperature, the value of \( \Theta_H \) is a constant over the range of cooling rates that \( H^2 \) is a constant; i.e., \( \Theta_H \) is a function of the alloy, the homogenization temperature, and \( H^2 \).

\[ \Theta_H = f(\text{alloy}, T_H, H^2) \quad \ldots \ldots \ldots \quad (92) \]

In Figure 34 a plot on log-scale of \( \Theta_H \) and \( \Theta_f \) has a slope of unity for each value of \( H^2 \), demonstrating the linear relationship. Thus, within a range that \( H^2 \) is a constant, the homogenization time is obtained by multiplying solidification time by \( \Theta_H \).

A plot on a log scale of the isothermal solidification time versus the characteristic growth element spacing, Figure 35, has a slope of two (note: \( d^2 = H^2 \Theta_f \)). The fact that the lines plotted for several values of \( H^2 \) are so close indicates that homogenization time is more sensitive to the characteristic growth element spacing than the amount of homogenization that may have taken place during solidification.
As long as the dendrite spacing is proportional to the square root of solidification time, i.e., as long as $\sqrt{t}$ is a constant, homogenization times will increase in proportion to the solidification time. For example, a casting that solidified in one half hour would take sixty times as long to homogenize as one solidified in thirty seconds. For aluminum-copper alloys, $\sqrt{t}$ decreases as the solidification time increases and, thus, the extent of segregation in the as-cast structure becomes less. In Figure 38, the homogenization time predicted for a 195 alloy, is plotted on log scale as a function of solidification time, using the dendrite spacing measurements of Michael and Bever\textsuperscript{16} (note: Figure 20). A line of slope one is drawn to indicate the advantage due to solid diffusion during solidification.

It is of interest to see the variation in homogenization time as the size of the growth element is kept constant and the solidification time is increased.\textsuperscript{15} In Figure 36 the time to eliminate the nonequilibrium phase in 195 alloy by isothermal heat treatment at 565°C, 549°C, and 526°C is plotted for ingots in which the characteristic spacing is kept at twenty microns and the solidification time is increased. At the shorter freezing times, solidification segregation is identical and the homogenization times the same. When solid diffusion during solidification is significant, the homogenization time, which includes solidification time, is less. At sufficiently long solidification times 195 alloy will be one phase.
VI. SUMMARY AND CONCLUSIONS

An analytic study has been made of solute redistribution in dendritic solidification of binary alloys with substantial amounts of solute. The solidification process has been idealized, for the sake of analysis, by selection of microscopic transport conditions and of a growth model; this description proves to be applicable to a wide range of casting and ingot-making practice. Major characteristics of the model are: no undercooling before nucleation of solid phases, negligible increase of solute in advance of the tips of growing dendrites, complete diffusion within the liquid over distances the order of dendrite spacings, and a platelike growth geometry. Quantitative results of the analysis were successfully correlated with observations of microsegregation in castings and ingots.

Results of the analyses include:

1. The solidification curve (fraction solid as a function of temperature) for binary alloys has been described and quantitative results have been presented for 195 alloy. This method is applicable to systems with a variable partition ratio and may be extended to ternary (and more complex) alloy systems provided adequate phase diagram information is available.

2. Analyses account for limited diffusion in the solid phase during solidification and during cooling to room
temperature. These analyses allow more accurate description of the solidification conditions and more useful analysis of the solidification structure than computations based on the usual assumption, (a) complete diffusion in the solid (equilibrium), or (b) no diffusion in the solid (normal nonequilibrium).

3. The amount of nonequilibrium phases and coring present in the final solidification structure is shown to be dependent on the ratio of the square of the size of the growth element (for example, dendrite arm spacing) to the solidification time, expressed as \( \frac{S^2}{D} \); for \( \frac{S^2}{D} \ll 1 \), microsegregation is a maximum; \( \frac{S^2}{D} \approx 1 \), significant diffusion in the solid occurs during solidification; \( \frac{S^2}{D} \gg 1 \), phases are homogeneous. Further, the amount of coring and nonequilibrium phases will be the same over the range of solidification times that \( \frac{S^2}{D} \) is a constant. If \( \frac{S^2}{D} \) is a negative function of freezing time, then solidification segregation is reduced at extended solidification times.

In 195 alloy a value of \( \frac{S^2}{D} \) greater than \( 1 \times 10^{-6} \) would result in maximum segregation; a value less than \( 1 \times 10^{-10} \) in an equilibrium structure. A value of \( \frac{S^2}{D} \) ranging between these limits would result in varying amounts of solid diffusion, and curves that describe the amount of nonequilibrium eutectic formed in aluminum-copper alloys as a function of \( \frac{S^2}{D} \) have been presented.
4. As a consequence of solid diffusion, the solute content within the primary solid will increase during the solidification process. A numerical analysis technique has been described which computes the concentration profile at various solid fractions and during cooling to room temperature. The analysis applied to an aluminum-4.5 per cent copper alloy demonstrates:
(a) the dependence of the microsegregation on $\sqrt{t}$
(b) the copper concentration of the primary solid phase is quite uniform during the initial stages of solidification
(c) whenever there is substantial solid diffusion the reduction of microsegregation during cooling in the solidification range will be more significant than the reduction that will occur during the eutectic hold and during cooling of the solid structure to room temperature.

Through reported measurements on aluminum-copper alloy, experimental verification was obtained for the major assumptions and for the results of the analyses. These measurements include:
1. Thermal analysis of ingots solidified by a differential thermocouple technique indicate that the solidification curve of aluminum-4.5 per cent copper alloy is more aptly described by the limited solid diffusion conditions than either the equilibrium or normal nonequili-
brium conditions.

2. Electron microprobe measurements of the copper distribution within dendrites from unidirectionally solidified ingots showed a minimum value of 1.3 - 1.4 per cent copper rather than the 0.6 per cent predicted by the phase diagram. Examination of dendrites from ingots that had their cooling interrupted at various stages of solidification demonstrated that initial solid to form did have a composition close to 0.6 per cent and that the solute content of the solid increased during the solidification process.

3. Lineal analysis measurements of the eutectic fraction in aluminum-copper alloys and measurements of dendrite spacings for a wide range of solidification rates indicate that the extent of nonequilibrium second phases varies with $\gamma^{1/2}$ as predicted by the analysis; that is, when $\gamma^{1/2}$ decreases with solidification time, the degree of micro-segregation becomes less as solidification times are increased.

4. Observation of ingots cooled with solidification times ranging from seconds to one thousand hours demonstrate that the dendrite structure coarsens with increasing solidification time at such a rate that the resulting decrease in concentration gradient hinders solid diffusion to an extent comparable to the enhancement brought about by the increased time available for diffusion.
The reduction of microsegregation resulting from extended solidification times is too slight to be, in itself, a practical means for eliminating the nonequilibrium micro-inhomogeneities from solidification structures.

Once the solidification curve for an alloy has been computed, the behavior of many physical properties of a solidifying alloy may be described using data measured in single phase alloys. As examples, expressions have been derived for the heat content and rate of heat release, and the specific volume and rate of shrinkage of a binary alloy in the solidification interval. The expressions have been evaluated for 195 alloy.

The analyses used to describe the solute distribution within the primary phase of an alloy as it freezes and as it cools to room temperature can also be applied to determine the effectiveness of isothermal heat treatments. Results are presented for the isothermal solidification and solution treatment of a 195 alloy.
VII SUGGESTIONS FOR FURTHER WORK

1. Extension of analyses on the solid phase:
   a.) The finite difference solution to diffusion in the solid during solidification requires as input an envelope of interface compositions as a function of solid fraction. In addition to inconvenience, this method presents inaccuracies in the solution which, though not important for 195 alloy, become important in alloy systems that exhibit substantial solid diffusion in solidification. A mass balance incorporated into the finite difference solution would eliminate the need for an input envelope.

   b.) A geometric factor is sometimes needed for quantitative agreement of computations and experimental measurement of microsegregation -- dendrites are not infinitely long plates. The analytic expressions and the growth models could be extended to growth models that are simple shapes, boxes, cubes, spheres, and to the actual geometry once the interface shape and position are known with time.

   c.) Description of solute redistribution in ternary (and more complex) alloy systems is of commercial importance.

2. The numerical analysis method is suitable for studying mass transport in the liquid; diffusion between dendrite plates; diffusion between sub-dendrites.
3. Microsegregation measurements in alloys of several base metals will further confirm the analyses and make them of immediate practical importance, explaining ingot properties and predicting heat treatment requirements.

4. Measurements of the dependence of dendrite spacing on solidification rate for particular alloy systems yields information as to microsegregation tendency and suggests casting procedure.

5. The solidification curve summarizes many casting parameters of an alloy. If these are plotted on a reduced temperature scale, the characteristics of several alloys can be compared. Relating, perhaps statistically, casting phenomena, such as hot tearing and fluidity to a generalized solidification curve may yield a guide to foundry practice.
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BIографICAL NOTE

Harold David Brody was born April 13, 1939 in Boston, Massachusetts, received his secondary school education at The High School, Swampscott, and entered M.I.T. in September, 1956. He received a Bachelor of Science degree in Metallurgy in June 1960. As an undergraduate, the author received a Foundry Educational Foundation Scholarship and an American Smelting and Refining Company Scholarship. In June 1960, he started graduate study at M.I.T. as an American Brake Shoe and F.E.F.-Wheelabrator Fellow, receiving a Master of Science degree in Metallurgy in June 1961. After working for a short period in the Solidification Laboratory, M.I.T., for the Division of Sponsored Research, the author began work on a Doctorate in September 1961.

The author is a member of Phi Lambda Upsilon, Sigma Xi, Tau Beta Pi, and the American Society for Metals.

His publications are:


APPENDIX A

List of Symbols

\[ A_j = \text{constant descriptive of a binary phase diagram in the } j^{th} \text{ interval} \]

\[ b = -\frac{D_L G}{R m_L} \quad (\text{wt } \%) \]

\[ B_j = \text{constant, descriptive of a binary phase diagram in the } j^{th} \text{ interval} \]

\[ C_m, C_M = \text{minimum and maximum solute concentration in solid (wt } \%) \]

\[ C_O = \text{overall weight fraction of solute in a binary alloy} \]

\[ C_{pS}, C_{pL} = \text{heat capacity of solid and liquid states, respectively} \]

\[ C_S^*, C_L^*, C_E^* = \text{weight fraction solute at interface of solid and liquid phases, and eutectic, respectively} \]

\[ \bar{C}_S, \bar{C}_L, \bar{C}_E = \text{average weight fraction solute in solid and liquid phases, and eutectic, respectively} \]

\[ C_{S_j}, C_{L_j} = \text{equilibrium solid and liquid weight fraction at reference temperature } T_j \text{ of the } j^{th} \text{ interval of the phase diagram} \]

\[ C_t = \text{solute content in liquid at tip of advancing dendrites} \]

\[ d = \text{growth element spacing (cm.)} \]

\[ D_L = \text{volume diffusion coefficient of solute in liquid (cm}^2/\text{sec}) \]

\[ D_O = \text{frequency constant for diffusion} \]

\[ D_S = \text{volume diffusion coefficient of solute in solid} \]
$f_S, f_L, f_E$ = weight fraction solid, liquid, and eutectic, respectively

$G$ = actual thermal gradient in liquid ($^\circ$C/cm.)

$H'$ = heat released for each fraction solidified (cal./gr.)

$H^F$ = heat of fusion

$H_S, H_L$ = heat content of the solid and liquid phase, respectively

$H'_S, H'_L$ = heat content of pure solid and pure liquid solute, respectively; double primes refer to solvent

$H^M_S, H^M_L$ = heat of mixing of the solid and liquid phases, respectively

$H_T$ = heat content of a binary alloy

$j_i$ = flux at the interface in the solid phase (gr./cm$^2$sec.)

$k$ = partition ratio

$l$ = characteristic spacing in solidification structure, such as, d/2. (cm.)

$M$ = finite difference method constant, $\Delta X^2 / D \Delta \Theta$

$m_S, m_L$ = slopes of liquidus and solidus ($^\circ$C/wt. %)

$m_S^j, m_L^j$ = slopes of liquidus and solidus in the $j$th interval

$N_A$ = atom fraction of A in alloy

$Q$ = heat of activation of diffusion (cal./mole)

$q$ = rate of heat transfer (cal./cm$^2$ sec.)

$R$ = gas constant (cal/mole $^\circ$C)

$R_t$ = rate of advance of dendrite tips (cm./sec.)

$S$ = segregation ratio
T = temperature (°C)

T_B = base temperature for heat content measurements

T_i = temperature of an invariant reaction, e.g., eutectic transformation temperature

T_k = temperatures in degrees kelvin

T_L = liquidus temperature

T_j = reference temperature of jth interval of phase diagram

T_m = melting point of pure solvent

u = growth rate constant, linear growth

V_L, V_S, V_T = specific volume of solid and liquid phases and binary alloy (cm³/gr.)

V_L^0, V_S^0, W, X, Y, Z = empirical constants for variation of specific volume in single phase field

X = distance along growth element (cm.)

X = distance measured from dendrite tips

X_I = position of solid-liquid interface

X_R, X_T = position of root and tips of dendrites

\[ \Upsilon = \frac{2D_S}{2} \]

\[ \Upsilon_L = \frac{2D}{ud} \]

\( \beta \) = alloy shrinkage, absolute

\( \beta_a \) = alloy shrinkage, solid entraps liquid and bulk feeding effective

\( \beta_b \) = alloy shrinkage, solid entraps liquid, no bulk feeding
\[ \gamma^2 = \text{empirical ratio of square of dendrite spacing to solidification time, } \frac{d^2}{\Theta_f} \text{ (cm}^2/\text{sec.}) \]

\[ \Theta = 1 - (1 - A_j) \]

\[ \delta_S = \text{index of residual segregation} \]

\[ \lambda = \text{growth rate constant, parabolic growth (cm/sec}^{1/2}) \]

\[ \psi^{-1} = \text{grams liquid/gram atom liquid} \]

\[ \rho = \text{density of alloy (gr/cm}^3) \]

\[ \Theta = \text{time since beginning of solidification (sec)} \]

\[ \Theta_f = \text{total solidification time} \]

\[ \Theta_H = \text{time to homogenize an alloy, includes solidification time} \]

\[ \Theta_H = \frac{\Theta_f}{\Theta_f} \]
APPENDIX B

Organization of Computer Programs

Quantitative evaluation of the solidification parameters discussed in this work has been achieved, primarily with two FORTRAN programs. The first, MACRO, computes the parameters that are descriptive of an entire phase or the entire alloy and are, at least hypothetically, amenable to macroscopic measurement, (e.g., pyrometry, calorimetry, dilatometry, chemical analysis, etc.). Bases of the calculations are discussed in detail in Sections III and IV. The second program, MICRO, computes the concentration profile in a growth element on the basis of microscopic diffusion conditions as described in Sections III and V. The organization of each is described by a flow diagram of the executive routines; for MACRO, Figure 37, for MICRO, Figure 38.

MACRO consists of an executive sub-program (MAIN) that calls a sequence of computational and input/output subroutines. The calling sequence of (MAIN) is presented in Figure 37. Many variations have been compiled for each computational and output subroutine and the particular series of subroutines selected to build a deck for a computer run is a choice dependent on the nature of the alloy system (e.g., real or imaginary), the assumed solidification conditions, and the parameters to be evaluated and/or compared. By building a program from selected versions of
subroutines, computer tasks are defined and limited. The general purpose of each subroutine is indicated in Figure 37. A program of this design was deemed most suitable for a research project in which the assumptions, parameters, and systems taken under consideration are continually changing and expanding.

The basic information input is obtained from a phase diagram. For specific calculations, empirical data measured on single phase alloys is input. Through the proper evaluation of the materials balance, MACRO determines the fraction solid at a particular temperature for an alloy of composition $C_0$ taking a solidification path determined by equilibrium, normal nonequilibrium, and/or limited solid diffusion conditions. The simplest solution of the materials balance assumes the phase boundaries to be single, straight lines. MACRO will also compute fraction solid, and the other parameters, for an alloy with an irregular phase diagram and/or a phase diagram that requires an alloy to pass through more than one two-phase region during solidification (e.g., peritectic). Once fraction solid has been calculated for a binary alloy the following parameters are readily calculated: composition at interface of solid and liquid phases, average compositions of the solid and liquid, the specific volumes, the shrinkage, the heat content, and the associated derivates (e.g., rate of heat release with decreasing temperature).
MICRO consists of an executive sub-program (MAIN) and several computational and input-output subroutines. The calling sequence of (MAIN) is delineated by the flow diagram, Figure 38, as are the functions of each subroutine. The scope of job to be run on the computer is read in as part of the data and thus with the exception of subroutine CHICO only one subroutine of each name is needed. Because output is a relatively slow computer step, the output routines have been designed to be easily altered by octal correction cards whenever computer time must be conserved.

The basic input to MICRO are specification of the scope of the problem; specification of the values and the character of the physical properties of the alloy (e.g., is the diffusion coefficient a function of both temperature and composition), which include the diffusion parameter, the heat capacity and heat of fusion; the size of the growth element and the freezing time; and a relation between fraction solid and solute content of the solid at the advancing interface. The latter may be computed by MICRO (in subroutine CHICO) or may be input as punched data computed by the program MACRO.

MICRO will compute the change in the concentration profile occurring within the primary phase as an alloy is cooled through the solidification interval; as the alloy undergoes eutectic transformation; as the alloy cools to room temperature from the solidus -- for either a single phase or two
phase structure; during isothermal solidification; and during solution treatment.
APPENDIX C

Influence of Thermal Gradients on Solute Buildup in Liquid

A. Buildup at the Tips

The magnitude of the solute buildup in the liquid at the tips of advancing dendrites is estimated for steady state conditions following the procedure of Flemings.\textsuperscript{14,36} With reference to Figure 5c, consider a differential element of liquid at the dendrite tips; element width in the heat flow direction is $dX$ and element area normal to heat flow is unity. Fick's second law written for such an element is

$$ R_t \frac{dc_L}{dx} = D_L \frac{d^2 c_L}{dx^2} \quad \ldots \ldots \ldots \ldots \ldots (C.1) $$

where steady state conditions allow the use of total differentials and $R_t$ = rate of advance of the tips into liquid region, $D_L$ = diffusion coefficient of the solute in the liquid, $C_L$ = solute concentration in the liquid, $X$ = distance measured parallel and opposite in sense to heat flow. Equation (C.1) is valid over the entire enriched zone in advance of the dendrite tips. Integration of (C.1) from $X = X_t$ to $X = \infty$ yields

$$ R_t (C_t - C_0) = D_L \left( \frac{dc_L}{dx} \right)_{X_t} \quad \ldots \ldots \ldots \ldots \ldots (C.2) $$

* Flemings\textsuperscript{14} reached the identical relation considering the liquid plus solid region as his volume element.
Provided supercooling at the solid-liquid interface is small, the interface compositions are given by the equilibrium phase diagram and the actual temperature gradient in the liquid, \( G \), can be expressed as \( \frac{dT_L}{dx} \) and

\[
\left( \frac{dC_L}{dx} \right)_{x_t} = \left( \frac{dC_L}{dT_L} \right) \left( \frac{dT_L}{dx} \right)_{C_L = C_0} = - \frac{G}{m_L}, \quad \ldots \quad (C.3)
\]

Substituting (C.3) in (C.2) and rearranging yields equation (19) of Section II.

\[
(C_t - C_0) = - \frac{D_L G}{R_t m_L}, \quad \ldots \quad \ldots \quad (C.4)
\]

### B. Mass Balance

Consider\(^{36}\) now a differential volume in the liquid plus solid region fixed with respect to the mold wall; the element width parallel to heat flow is \( dx \) and area normal to heat flow is \( A_0 \). Then, the material balance (note: equation (7)) written to account for diffusion in the liquid is

* That supercooling is small for the range of solidification conditions typical of casting and ingot making processes has been noted in Section II. Supercooling that arises from kinetic effects, from curvature effects and from the requirement of solute transport from the growing tip has been treated by several authors.\(^{12}\) Recent measurements in unidirectional solidification of aluminum-copper \(^{41}\) alloys and of tin alloy \(^{48}\) ingots have shown that the supercooling at the tips is less than the experimental accuracy -- less than one per cent of the solidification interval.
\[(C_L^* - C_S^*) ds \frac{J_Y A d \Theta}{A_0 dX} = \frac{J_{X+dX} (A+dA) d \Theta}{A_0 dX} + f_L dC_L^* \quad \ldots \ldots \quad (C.5)\]

where \(J_X\) and \(J_{X+dX}\) are the diffusion fluxes flowing in and flowing from the element. Using equation (C.2) with Fick's first law

\[J_X = \frac{D \rho G X}{m_L} \quad ; \quad J_{X+dX} = \frac{D \rho G_{X+dX}}{m_L} \quad \ldots \ldots \quad (C.6)\]

By imposing a constant temperature gradient, the fluxes \(J_X\) and \(J_{X+dX}\) are made equal. However, there is a net diffusive flow opposite in direction to heat flow. Using the relations

\[df_L = - df_S = \frac{dA}{A_0} \quad \ldots \ldots \quad (C.7)\]

\[\frac{dX}{d \Theta} = R_t \quad \ldots \ldots \quad (C.8)\]

and separating variables, the materials balance yields

\[\int_0^{C_L^*} \frac{df_S}{1 - f_S} = \int_{C_t}^{C_L^*} \frac{df_L^*}{C_L^* (1 - k) - b} \quad \ldots \ldots \quad (C.9)\]

Integration of (C.9) yields equation (21) of Section II

\[f_S = 1 - \left[ \frac{C_t - \frac{b}{(1 - k)}}{C_L^* - \frac{b}{(1 - k)}} \right] \quad \ldots \ldots \quad (C.10)\]

setting

\[b = - \frac{D_L G}{R_t m_L} \quad \ldots \ldots \quad (C.11)\]
APPENDIX D

Limited Solid Diffusion Computations

A. General Solutions to Mass Balance; Parabolic Growth

The mass balance for the case of limited solid diffusion and parabolic growth, equation (36) of Section III,

\[(c_L^* - c_S^*) \, df_S = \alpha f_S dC^*_S + (1 - f_S) dC^*_L \ldots \ldots \ldots (D.1)\]

is evaluated to account for phase diagrams with curved boundaries, and to account for temperature dependent diffusion coefficients.

Curved Phase Boundaries, Constant Diffusion Coefficient: Equation (D.1) can be evaluated for a system with curved phase boundaries by dividing the liquidus and solidus into a series of straight line segments (as done previously for the normal nonequilibrium case). Using definitions (25), (26), and (27) and the relation

\[dC^*_S = (1 - A_j) \, dC^*_L \ldots \ldots \ldots \ldots \ldots (D.2)\]

equation (D.1) can be rewritten

\[(A_j C^*_L + B_j) \, df_S = (1 - A_j) \alpha f_S dC^*_L + (1 - f_S) dC^*_L \ldots \ldots (D.3)\]

Separating variables and integrating \(\int^{1/A_j}_{1 - \delta f_S} \ldots \ldots (D.4)\)
where \[ \varphi = (1 - [1 - A_j] \alpha) \ldots \ldots \ldots \ldots \] (D.5)
and
\[ f_S = \frac{1}{\delta} \left\{ 1 - (1 - \varphi f_{S_1}) \left[ \frac{A_j C_{L_1} + B_j}{A_j C_{L_1}^* + B_j} \right] \right\}^{\varphi/A_j} \ldots \ldots \ldots \ldots \] (D.6)

**Straight Phase Boundaries, Temperature-Dependent Diffusion Coefficient** - The diffusion coefficient of solute may vary by more than an order of magnitude over the temperature range of solidification of an alloy. A closer approximation is made by allowing the diffusion coefficient to be an exponentially varying function of temperature of the form
\[ D_S = D_0 \exp \left( -\frac{Q}{RT_k} \right) \ldots \ldots \ldots \ldots \] (D.7)

where \( D_0 \) = empirical constant, \( Q \) = heat of activation, empirical, \( R \) = gas constant, and \( T_k \) = absolute temperature.

Now \( \alpha \) becomes a function of temperature of the form
\[ \alpha(T) = \frac{2D_0}{(\lambda)^2} \exp \left( -\frac{Q}{RT_k} \right) \ldots \ldots \ldots \ldots \] (D.8)

and equation (D.1) is integrated over short temperature ranges between the liquidus temperature and the temperature of consideration. At each interval the proper value of \( \alpha(T) \) is substituted

\[ f_S = \left( \frac{1}{1 - \alpha(T)k} \right) \left\{ 1 - \left[ 1 - (1 - \alpha(T)k)f_S \left[ \frac{T_M - T_i}{T_M - T} \right] \right]^{(1-\alpha(T)k)/1-k} \right\} \ldots \ldots \ldots \ldots \] (D.9)
Curved Phase Boundaries, Temperature-Dependent Diffusion Coefficients - For this computation the dependence of $D_S$ on temperature is inserted into the analysis by relating $\alpha$ to the liquid composition. The absolute temperature at some position within the interval between $T_{j-1}$ and $T_j$ is given by:

$$T_k = T_j - m_{L_j} (C_{L_j} - C_{L^*}) + 273.0 \quad \ldots \ldots \quad (D.10)$$

and $\alpha(T)$ is defined as in equation (D.8). Now setting

$$\delta(T) = 1 - (1 - A_j) \alpha(T) \quad \ldots \ldots \quad (D.11)$$

Use for each successive interaction:

$$f_S = \frac{1}{\delta(T)} \left\{ 1 - (1 - \int(T)f_S') \left( \frac{A_j C_{L_j}^l + B_j}{A_j C_{L^*} + B_j} \right) \right\} \quad (D.12)$$

B. The Eutectic Transformation; Parabolic Growth

Considering the eutectic to be a pseudophase and evaluating the materials balance, equation (1), for three phase equilibrium of a binary alloy

$$\overline{C}_S f_S + \overline{C}_E f_E + \overline{C}_L f_L = C_0 \quad \ldots \ldots \quad (D.13)$$

where $\overline{C}_S$, $f_S$ refer to the primary solid, $\overline{C}_E$, $f_E$ refer to the eutectic solid, $\overline{C}_L$, $f_L$ refer to the eutectic liquid for an infinitesimal change

$$d(\overline{C}_S f_S) + d(\overline{C}_E f_E) + d(\overline{C}_L f_L) = 0 \quad \ldots \ldots \quad (D.14)$$
Expanding equation (D.14) but taking into account
\[ \frac{d\overline{C}_E}{df_E} = 0; \quad \frac{d\overline{C}_L}{df_L} = 0; \quad \overline{C}_L = \overline{C}_E = C_L^* \quad \ldots \ldots \quad (D.15) \]

\[ df_E = -dS_S + df_L \quad \ldots \ldots \ldots \quad (D.16) \]

it simplifies to
\[ (C_S^* - C_E^*) dS_S + f_S dC_S = 0 \quad \ldots \ldots \ldots \quad (D.17) \]

The second term of equation (D.17) is evaluated by referring to equation (33)
\[ f_S dC_S = \frac{2D_S(T_E)}{d} \left( \frac{dC_S}{df_S} \right) \frac{df_S}{dT_E} d\Theta \quad \ldots \ldots \quad (D.18) \]

Again, the assumption is taken that the solid diffusion does not change significantly the concentration profile at the interface, equation (34), and
\[ f_S dC_S = \frac{4D_S(T_E)}{d^2} \frac{C_S^*(1-k)}{1 - (1-\alpha_k)f_S'(T_E)} \quad \ldots \ldots \quad (D.19) \]

where \( f_S'(T_E) \) refers to the solid fraction just above the eutectic temperature. Rewriting equation (D.17) and setting limits
\[ \int_{f_S(T_E)}^{f_S'(T_E)} \left( C_S^* - C_E^* \right) df_S + \int_{\Theta_f = \left( d^2/4\lambda \right)^2}^{\Theta_f = f_S'(T_E)^2 \left( d^2/4\lambda \right)^2} \frac{4D_S(T_E)C_S^*(1-k)}{d^2 \left[ 1 - (1-\alpha_k)f_S'(T_E) \right]} \ d = 0 \]

\[ \ldots \ldots \quad (D.20) \]
and integrating

\[ f_S(T_E) = f_S'(T_E) + k \frac{1 - f_S'(T_E)^2}{1 - (1 - k)f_S'(T_E)} \]  \quad (D.21)

for curved phase boundaries the analogous expression is

\[ f'(T_E) = f_S'(T_E) + k \frac{(1 - A_j)}{2 \frac{1 - f_S'(T_E)^2}{1 - f_S'(T_E)}} \]  \quad (D.22)

C. Linear Growth

The mass balance for the case of limited solid diffusion and linear growth, equation (42) of Section III, can be evaluated for phase diagrams with curved phase boundaries and for temperature dependent diffusion coefficients in a manner analogous to that used for parabolic growth.

Curved Phase Boundaries, Temperature Dependent Diffusion Coefficient - Again the temperature dependence of \( D_S \) is expressed by (D.7), \( \lambda \) becomes a function of temperature of the form

\[ \lambda = \frac{2D_0}{ud} \exp\left\{ -\frac{Q}{RT_k} \right\} \]  \quad (D.23)

and \( \lambda(T) \) is defined in the same manner. The expression to be evaluated iteratively from the liquidus to the temperature of consideration is

\[ f_S = \lambda(T) - \left( \lambda(T) - f_S' \right) \left\{ \frac{A_j C_L^j + B_j}{A_j C_L^* + B_j} \right\}^{1/A_j} \]  \quad (D.24)
Eutectic Transformation - The expression for $f_s d\bar{c}_S$ (equation (D.18)) is evaluated for linear growth rate

$$f_s d\bar{c}_S = \frac{4D_s(T_E)}{\alpha^2} \frac{(1 - k) C_s^* (T_E)}{1 + \alpha L k - f_s}.$$  \hspace{1cm} (D.25)

Upon substitution for this term in the materials balance for the eutectic temperature (equation (D.17)) and integrating

$$f_s(T_E) = f'_s(T_E) + \alpha L k \frac{1 - f'_s(T_E)}{1 + \alpha L k - f'_s(T_E)}.$$ \hspace{1cm} (D.26)

Similarly for curved phase boundaries:

$$f_s(T_E) = f'_s(T_E) + \alpha_L (1 - A_j) \frac{1 - f'_s(T_E)}{1 + \alpha_L (1 - A_j) - f'_s(T_E)}.$$ \hspace{1cm} (D.27)

D. Parallel Phase Boundaries

Whenever the term $C_L^* - C_S^*$ is a constant, the above solutions to the mass balance do not hold and in their place exponential relations must be used. For example, equation (D.12) becomes

$$f_s = \frac{1}{\delta(T)} \left\{ 1 - (1 - \delta(T) f'_s)^\delta \right\} \left[ \frac{(C_L' - C_L^*) \delta(T)}{B_j} \right]$$ \hspace{1cm} (D.28)
APPENDIX E

Thermal Data for Heat Content Analysis of 195 Alloy

1. Thermal Properties of the Pure Elements

K. K. Kelley\textsuperscript{46} fits the temperature variation of heat content of an element to an expression of the following form

\[
H(T) = aT + bT^2 + c
\]  \hspace{1cm} (E.1)

The evaluation of this expression for liquid and solid aluminum and copper are

\[
H^\text{Al}_S = \left\{ (4.94)T + (1.48 \times 10^{-3})T^2 + (-1,604) \right\} / (26.98) \text{ (cal/gr)}
\]

\[
H^\text{Cu}_S = \left\{ (5.41)T + (0.75 \times 10^{-3})T^2 + (-1,680) \right\} / (63.54)
\]

\[
H^\text{Al}_L = \left\{ (7.00)T + (330) \right\} / (26.98)
\]

\[
H^\text{Cu}_L = \left\{ (7.50)T + (-20) \right\} / (63.54)
\]

and the heat capacity expression is the fit to the derivative of the above expressions, that is

\[
C_p = a + 2bT
\]  \hspace{1cm} (E.3)

and

\[
C_p^\text{Al}_S = \left\{ (4.94) + (2.96 \times 10^{-3})T \right\} / (26.98) \text{ (cal/gr°C)}
\]

\[
C_p^\text{Cu}_S = \left\{ (5.41) + (1.50 \times 10^{-3})T \right\} / (63.54)
\]

\[
C_p^\text{Al}_L = (7.00) / (26.98)
\]

\[
C_p^\text{Cu}_L = (7.50) / (63.54)
\]
2. Heat of Mixing Data

(a) Assume $H^M_S$ to be negligible. The average copper content of the primary solid is less than two per cent (less than one atomic per cent).

(b) From O. Kubasewski and J. A. Catterall\textsuperscript{47} the heat of mixing of the liquid up to 33 weight per cent fits the relation

$$H^M_L = -(9000)N_{Cu} \text{ (cal/gram atom)} \quad (E.5)$$

where $N_{Cu} =$ atom fraction copper

$$N_{Cu} = \frac{C_L^*(26.98)}{C_L^*(26.98) + (1 - C_L^*)(63.54)} \quad (E.6)$$

Define $\psi$ such that

$$\psi - 1 = N_{Cu}(63.54) + (1 - N_{Cu})(26.98) = \frac{\text{grams liquid}}{\text{gram atom-liquid}} \quad (E.7)$$

Then

$$H^M_L = -(9000) N_{Cu} \psi \text{ (cal/gram liquid)} \quad (E.8)$$

To evaluate $dH^M_L/dC_L^*$

$$\frac{dH^M_L}{dC_L^*} = -(9000) \frac{dN_{Cu}}{dC_L^*} + N_{Cu} \frac{d\psi}{dN_{Cu}} \frac{dN_{Cu}}{dC_L^*} \quad (E.9)$$

which becomes

$$\frac{dH^M_L}{dC_L^*} = \frac{63.54}{9,000} \frac{H^M_L}{C_L^*} \quad (E.10)$$
(c) For the intermetallic phase CuAl₂ (Θ)

\[ H^M_{\Theta} = -3250 \text{ (cal/gr atom)} \]  \hspace{1cm} (E.11)

and

\[ H^M_{\Theta} = -3250 \psi \text{ (cal/gr)} \]  \hspace{1cm} (E.12)
Figure 1: Equilibrium phase diagram for aluminum-copper alloys (A.S.M., Metals Handbook, 1948).
Figure 2: Schematic representation of the materials balance for a small amount of solidification by the most general case and the three idealized solidification cases described in the text.
Figure 3: Solidification curve for equilibrium case of several aluminum-copper alloys.

Figure 4: Solidification curve for normal non-equilibrium case of several aluminum-copper alloys.
Figure 5: Dendritic solidification under imposed thermal gradient: (a) schematic model, (b) temperature gradient, and (c) solute gradient.
Figure 6: Method of curved phase boundaries by a series of straight lines.
Figure 7: Comparison of solidification curves calculated by assuming the phase boundaries straight lines to those calculated taking into account the curvature of the phase boundaries.
Figure 8: Model of growth element selected for computations involving diffusion in the solid phase.
Figure 9: Comparison of the solidification curve of an aluminum-4.5 per cent copper alloy for the three cases, equilibrium, normal non-equilibrium, and limited solid diffusion and some experimental data. The derivation of the experimental data from time-temperature records is described in the text.
Figure 10: The slope at the liquidus for several compositions of the systems Al-Cu, Al-Mg, Al-Zn. Inset the slopes as a function of fraction solid for four compositions from the Al-Cu system.
Figure 11: The concentration profile in the solid phase of an aluminum-4.5 per cent copper alloy at several stages of solidification and after cooling to room temperature. Calculation is based on a value of $\gamma^2 = 1.2 \times 10^{-8}$ cm$^2$ sec$^{-1}$. 
Figure 12: The minimum solute content of the solid phase calculated as a function of $\gamma^2$ for an aluminum-4.5 per cent copper alloy cooled to just above the eutectic, to just below the eutectic, and to room temperature.
Figure 13: Weight per cent of the non-equilibrium eutectic formed as a function of $\gamma^2$ for six aluminum-copper alloys with less copper than the solubility limit. Parabolic growth.
Figure 14: Weight per cent non-equilibrium eutectic formed as a function of $\gamma^2$ for several aluminum-copper alloys with less copper than the solubility limit. Linear growth is assumed.
Figure 15: Value of $\chi^2$ required for the formation of a given amount of non-equilibrium eutectic phase in cast aluminum-copper alloys.
Figure 15: The per cent eutectic formed in an aluminum-4.5 per cent copper alloy calculated as a function of $\gamma^2$ using (a) the numerical analysis technique and the normal non-equilibrium envelope, (b) the numerical analysis technique and limited solid diffusion envelopes, and (c) the analytic expression for limited solid diffusion, equations (0.12) and (0.22) evaluated to a temperature just below the eutectic.
Figure 17: Photographs of the macrostructure of polished sections of ingots solidified over (a) twelve hours, (b) sixty hours, (c) one hundred hours and (d) one thousand hours (concentrated Keller's etch, 0.6 of original size).

(a) twelve hours

(b) sixty hours
Figure 17 (cont'd): Macrostructures of extended solidification ingots.

(d) one thousand hours
Figure 18: Thermal records of extended solidification ingots having overall solidification times of twelve, thirty four, and eighty two hours.
Figure 19: Composite figure showing results of a microprobe trace and photograph of microstructures of an aluminum-4.5 per cent copper unidirectional ingot. Both photograph and graph have the same scale in the horizontal direction.
Figure 20: Dendrite spacing and $\sqrt{\gamma}$ as a function of solidification time for aluminum-copper alloys. (Taken from data of Michael and Bever.16)
Figure 21: Comparison of calculated values of the fraction eutectic to those measured by Michael and Bever.\textsuperscript{16}
Figure 22: Heat content as a function of temperature for an aluminum-4.5 per cent copper alloy solidifying according to equilibrium and normal nonequilibrium conditions.
Figure 23: Heat content as a function of fraction solid for an aluminum-4.5 per cent copper alloy solidifying according to equilibrium and normal non-equilibrium conditions.
Figure 2b: Variation during solidification of the terms that contribute to the heat content of the solid phase, the liquid phase, and the solidifying alloy.
Figure 25: The specific volume and shrinkage in solidifying 195 alloy plotted as a function of temperature.
Figure 26: The specific volume and shrinkage in solidifying 195 alloy plotted as a function of fraction solid.
Figure 27: The contribution to feed metal requirements from solid contraction, liquid contraction, and solidification contraction.
Figure 28: The shrinkage in 195 alloy plotted versus the temperature the metal becomes coherent: $\beta$ - the absolute shrinkage; $\beta_a$ - solid entraps liquid, bulk feeding is considered; $\beta_b$ - solid entraps liquid, bulk feeding is not considered.
Figure 29: Schematic representation of model for homogenization computations.
Figure 30: Solute distribution in primary phase at successive stages in the solidification of an aluminum-4.5 per cent copper alloy.
Figure 31: Position of the interface during isothermal heat treatment of aluminum-4.5 per cent copper alloy at several temperatures.
Figure 32: The index of residual segregation, $\delta_s$, during solution treatment of an aluminum-4.5 per cent copper alloy plotted versus the dimensionless parameter $\frac{\delta \theta}{l^2}$.
Figure 33: Time to eliminate the non-equilibrium phase by homogenizing at temperatures within either the isothermal solidification or solution treatment range.
Figure 34: Time to eliminate the non-equilibrium phase in an aluminum-4.5 per cent copper alloy by isothermal solidification at 549°C plotted versus the freezing time (logarithmic scales).
Figure 35: Time to eliminate the non-equilibrium phase in an aluminum-4.5 per cent copper alloy by isothermal solidification at 549°C plotted versus the characteristic spacing (d/2, logarithmic scales).
Figure 36: Time to eliminate the non-equilibrium phase in 195 alloy in normal castings heat treated at 548\(^\circ\)C (using dendrite measurements of Michael and Bever\(^{16}\)), and in castings solidified so as to keep the characteristic growth element at twenty microns.
Figure 37: Flow diagram of executive sub-program (MAIN) of FORTRAN program MACRO for computation of macroscopic solidification parameters. (Second part of program follows on next page.)
Figure 37: Flow diagram for MACRO.
Figure 38: Flow diagram of executive sub-program (MAIN) of FORTRAN program MICRO for computation of micro-segregation pattern of an ingot.