Redistribution of Solute during Cellular Solidification of Single Phase Alloys

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Computer simulation of the upward cellular solidification of Al–Cu alloy was carried out considering the solidification to be a reaction controlled by diffusion. In the simulation, direct solving method of differential equation was applied to the diffusion in solid and liquid in contact with each other during cooling. The results of simulation showed that the solute distribution in liquid groove ahead of the solid-liquid interface is parabola whose bottom zenith lies at cell boundary. This result, together with the negligible diffusion in solid, induced that Scheil’s equation is approximately applicable to the solute distribution in the solid cell after the solidification. Numerical analysis of the simulated results induced also a general equation which expresses the parabolic relationship between cooling rate and the cell size. The validity of thus induced equation was verified by the experimental results obtained by other researchers. The transition of planar/cellular interface in solidification was also investigated from the standpoint of the diffusion controlled solidification.

Keywords: solute redistribution, upward cellular solidification, computer simulation, diffusion control, parabolic relation, interface transition

1. Introduction

The solidification of a single phase alloy necessitates diffusion of the rejected solute out of the interface into either or both solid and liquid. The solidification of an alloy, therefore, is related closely to the solute diffusion and considered to be a kind of diffusion controlled reaction. Although solidification theories have been stated on the various conditions of diffusion in solid and liquid,\(^1,13\) the diffusion controlled solidification has not been considered yet in most of those theories. Since the value of diffusion coefficient in liquid is low, the distance of effective diffusion from its source in a short time is usually restricted to short ranges\(^14\) such as the sizes of cell, cellular dendrite and dendrite. Accordingly, the present author planned to investigate the redistribution of solute during the cellular solidification in Al–Cu alloys by means of the computer simulation. Computer simulation is considered a powerful tool to clarify the entire process of the diffusion controlled solidification. Although the computer analysis of dendritic solidification was carried out already by Brody and Flemings,\(^15\) their work seems to be made on the unreasonable supposition. The present author applies the direct solving method of differential equation (DSM) to the diffusion in both solid and liquid. And the advancing distance of the solid/liquid interface for a minute time is calculated by equating the amount of rejected solute out of the interface to the amount of solute which is carried away into solid and liquid by diffusion for the same minute time. Al–Cu alloys are favorable to the simulation, for the solidus and liquidus lines are nearly straight and the diffusion coefficients in solid and liquid are known. To avoid the complication of diffusion by liquid motions,\(^13\) upward solidification is supposed. The results of simulation are analyzed to show the solute redistribution in solid and liquid during solidification, and to induce a general equation which formulates the sell size as a function of cooling rate and the physical properties of the alloy. The validity of thus induced equation is verified by the experimental data reported by other researchers.\(^10,11\)

2. Simulation Technique for Cellular Solidification of Al–Cu Alloy

A personal computer is used to simulate the cellular solidification of Al–Cu alloys. Liquidus and solidus lines of Al–Cu alloy system are expressed by

C_L = 0.295 \times (933 – T), \quad C_S = kC_L

where \(C_L\) and \(C_S\) denote the concentration (mass%) of solute copper in liquid and solid at temperature \(T\) (K), respectively, and \(k\) the partition coefficient in equilibrium, namely \(k = 5.65/33 = 0.1712\). Diffusion coefficient of Al–Cu alloy in liquid \(D_L\) and in solid \(D_S\) are expressed respectively as follows.\(^16–18\)

\[
D_L \text{ (cm}^2/\text{s}) = 0.0081 \exp[-38900/(RT)]
\]

\[
D_S \text{ (cm}^2/\text{s}) = 2.3 \exp[-146000/(RT)]
\]

where \(R\) expresses the gas constant, 8.3144 J/(mol K).

Figure 1 shows the cross section of a growing lamellar cell whose width is \(2L\) schematically. The cell proceeds upwards along \(z\)-axis, and its sideward fattening takes place in \(x\)-direction as the temperature falls. Instead of upward proceeding of the cell, temperature at a fixed location in
the cell is considered to fall. The cellular solidification begins at liquidus temperature $T_L$ and the width of the cell grows up to $2x^*$ when temperature falls to $T$.

When the cell proceeds upwards by $dz$ during the time increment $dt$, the solute concentration of liquid is altered by diffusion and cooling. That is,

$$\frac{dC_L}{dt} = D_L \left( \frac{d^2C_L}{dx^2} + \frac{d^2C_L}{dz^2} \right) + \text{cooling effect.} \quad (1)$$

When $G$ denotes the temperature gradient along $z$-axis, it is related to the concentration gradient as follows:

$$G = \frac{dT}{dz} = \frac{dT}{dC_L} \frac{dC_L}{dz} = m \frac{dC_L}{dz}$$

where $m$ denotes the gradient of liquidus line and $m = -1/0.295 = -3.390$. If $G$ is kept constant, $dC_L/dz$ becomes constant accordingly. Then $d^2C_L/dz^2$ is equal to 0 in eq. (1). Accordingly, it is sufficient for the simulation to consider the solute redistribution only along $x$-direction during cooling. Similar condition of diffusion will hold in solid. This idea that no effective diffusion of solute along $z$-direction agrees the experimental fact\(^{13}\) that no lengthwise macro-segregation occurs in the alloy whose solute is heavier than the solvent.

For the conservation of solute, the proceeding of solid/liquid interface by $dx^*$ requires the diffusion of rejected solute ($C_i - C_0$) $dx^*$ out of the interface into both solid and liquid. This condition is written as follows:

$$[C_i(x^*) - C_S(x^*)]dx^* = \left[ \frac{dC_S(x)}{dx} \right]_{x^*} D_S dt - \left[ \frac{dC_S(x)}{dx} \right]_{x^*} D_L dt$$

(2)

where $C_S(x)$ and $C_i(x)$ express themselves to be the functions of $x$ at temperature $T$. Equation (2) shows also that the rate of solidification, $dx^*/dt$, is controlled by the solute diffusion in solid and liquid. In order to use the direct solving method of differential equation,\(^{19}\) DSM, a half cell size $L$ is divided by $n$. The dividing joints, or joint, are labeled by number of 0 to $n$ including both ends. Then the distance between the neighboring joints is $\Delta L = L/n$. The solute concentration at each joint is calculated by DSM, in which Fick’s second law of diffusion in solid is developed as follows:

$$dCS(i) = d\tau_S[CS(i - 1) - 2CS(i) + CS(i + 1)]$$

$$d\tau_S = D_S dt/\Delta L^2 = n^2 D_S dt/L^2$$

where $CS(i)$ and $d\tau_S$ express the solute concentration at $i$-th joint of solid and the dimension-less time increment, respectively. Similar calculation is carried out also in liquid, that is;

$$dCL(i) = d\tau_L[CL(i - 1) - 2CL(i) + CL(i + 1)]$$

$$d\tau_L = D_L dt/\Delta L^2 = n^2 D_L dt/L^2.$$  

When the location of the interface is halfway between neighboring joints, estimation of the solute concentration at the joint in contact with the interface is necessary. Let $p$ denote the joint number in solid in contact with the interface. Let $a$ express the distance between the interface and the joint of number $p$, and $CSI$ and $CLI$ denote $C_S(x^*)$ and $C_L(x^*)$, respectively, as shown in Fig. 2. The solute concentration of joint $p$ in solid is estimated by interpolation as follows:

$$CSI(p) = CSI - [CSI - CS(p - 1)] \frac{a}{\Delta L + a}$$

(3)

The solute concentration at the supposed joint $p$ in liquid is estimated by extrapolation as follows:

$$CLI(p) = CLI + [CLI - CL(p + 2)] \frac{a}{\Delta L - a}$$

(4)

According to eq. (2), the shift of the interface $da = dx^*$ is calculated as follows:

$$CLI(p) - CSI(p) = \frac{[CS(p) - CS(p - 1)] D_S dt}{\Delta L}$$. 

Putting $L = 0.01$ cm, $n = 10$, $dt = 0.05$ s, cooling rate $V = 0.5$, 1 and 2 K/s, $T = T_L$ and $p = 0$, calculations of DSM and eqs. (3) to (5) are started and carried out repeatedly until the eutectic temperature $T_E$ is attained. The values of $L, n$ and $dt$ are chosen to satisfy the necessary conditions for DSM, $n^2D_L dt/L^2 < 0.5$, in consideration of the experimental results\(^{10,11}\). In every calculation of DSM, $da$, $d\tau_S$ and $d\tau_L$ are summed up into $a$, $\tau_S$ and $\tau_L$, respectively. Joint number $p$ is increased by 1 at every time when $a$ exceeds $\Delta L$. $x^*$ is numerated as $x^* = p\Delta L + a$, and solid fraction $f_S$ as $f_S = x^*/L$. Solute concentration of solid and liquid at each joint was printed at the desired stages of solidification.

3. Results of Simulation and Considerations

3.1 Relationship between fraction solid $f_S$ and temperature $T$

The simulated relations between fraction solid $f_S$ and temperature $T$ of Al–1, 2 and 4 mass%Cu alloys are shown in Fig. 3 when cooling rate $V = 1$ K/s. The lines in Fig. 3 are drawn according to Scheil’s equation\(^2\) in which no diffusion in solid and complete diffusion in liquid is supposed. The $f_S - T$ relations obtained by simulation shown in Fig. 3 appear in pretty good coincidence with Scheil’s relation for respective alloys. It is realized that the higher the copper content of the alloy, the wider becomes the liquid groove between the neighboring solid cells.

The depth of liquid groove, however, becomes $(T_L - T_E)/G$ and alters gently with the solute content. And it is
found that only a little change of $f_S/C_{0T}$ relation occurs when the calculation of the first term in right side of eq. (5) is omitted. For example, the first term in the right of eq. (5) is $6\times10^3/C_{10}^8/10^8$ mass%/cm$^2$s, while the second is $6\times82/C_{10}^5/10^5$ mass%/cm$^2$s when $C_0 = 4$ mass% Cu, $V = 1$ K/s and $f_S = 0.5$. The ratio of the two becomes $9/0/10^7/C_{04}$. This is the reason why the first term in the right of eq. (5) is negligible.

Figure 4 shows the effect of cooling rate on the $f_S - T$ relation of Al–4 mass% Cu alloy in comparison with the relations in equilibrium and of Scheil. Figure 4 shows almost no effect of cooling rate on the $f_S - T$ relation. Figure 4 also shows that the temperature of simulated $f_S - T$ relation lowers away from the equilibrium after the value of $f_S$ exceeds about 0.5. This super-cooling may be the driving force for the second arms of cellular dendrite to grow and the super-cooling is somewhat decreased to approach equilibrium.

3.2 Solute redistribution in solid and liquid during solidification

Figure 5 shows the solute distribution in solid and liquid at every intervals of 0.2 fraction solid during the solidification of Al–4 mass% Cu alloy. The solute concentration at each joint in liquid changes large with the progressive solidification, while the solute concentration at each joint in solid changes only a little during the solidification. Therefore, the change in solute concentration in solid after the passage of interface is not drawn in Fig. 5 to avoid confusion.

The curves of solute distribution in liquid shown in Fig. 5 are characterized by the gentle slope toward cell boundary, and by the parallel shift between the curves.

In order to examine the solute distribution in liquid more precisely, $C_L(i) - C_L(n)$ of $i$-th joint is plotted against $(1 - i/n)^2$ at every intervals of 0.2 fraction solid in Fig. 6. Figure 6 indicates that the distribution curves are parabola whose bottom zeniths lie at the cell boundary $x = L$, and that the difference in concentration $C_L(i) - C_L(n)$ is proportional to the cooling rate. The parabolic solute distribution is written in general as follows;

$$C_L(x) = C_L(n) + b(1 - x/L)^2$$

where $b$ expresses a constant. The second order derivative of eq. (6) about $x$ gives the following equation.

$$\frac{d^2C_L(x)}{dx^2} = \frac{2b}{L^2}$$

where $L$ is the length of the interface.
Fick’s second law of diffusion combined with eq. (7) turns to
\[
\frac{dC_1(x)}{dt} = D_L \frac{d^2 C_1(x)}{dx^2} = \frac{2bD_t}{L^2}
\]
(8)

On the other hand, \(dC_1(x)/dt\) can be written as follows:
\[
\frac{dC_1(x)}{dt} = \frac{dC_1(x)}{dT} \frac{dT}{dt} = -\frac{V}{m}
\]
(9)

Equating of two right terms of eqs. (8) and (9) results in the following relation:
\[
b = -\frac{VL^2}{2mD_L}
\]
(10)

Consequently, eq. (6) can be rewritten as follows:
\[
C_1(x) = CL(n) - \frac{V}{2mD_L}(L - x)^2
\]
(11)

Equation (11) shows that \(C_1(x) - CL(n)\) becomes zero when \(D_L\) is infinity, that is, when the diffusion in liquid is complete. This condition of diffusion in liquid agrees quite well with that of Scheil. That is, the complete mixing in liquid supposed by Scheil is taken as an extreme case of the diffusion controlled solidification.

Derivative of eq. (11) is written as follows:
\[
\frac{dC_1(x)}{dx} = -\frac{V}{mD_L}(L - x)
\]
(12)

Since the diffusion in solid is negligible, eq. (2) can be rewritten as follows by using eq. (12):
\[
(C_L - C_S)dx^* = -\frac{V}{m}(L - x^*)dt
\]
(13)

Since \(x^*/L = f_S\) and \(-Vdt/m = dC_L\) at the interface, the following equation is given.
\[
(1 - k)C_L df_S = (1 - f_S) dC_L
\]
(14)

Equation (14) is quite the same as Scheil’s equation. This is the reason why the simulated \(f_S - T\) relation coincides pretty well with that of Scheil in lamellar cells whose size \(2L\) is small enough to cause the parabolic solute distribution in liquid in a short time. In other words, Scheil’s equation is approximately applicable to the lamellar cell forming solidification of actual alloys whose diffusion is incomplete.

To examine the solute distribution in solid more precisely, an example of the simulated values of concentration at solid joint at several stages of solidification is shown in Table 1. The concentration at each solid joint calculated from Scheil’s relation is also shown in Table 1. Table 1 shows that the simulated \(C_S\) of the interface at a fixed location differs a little from that of Scheil’s relation essentially, because of the incomplete mixing of solute in liquid. Table 1 shows also a little more change in \(C_S\) caused by the diffusion after the passage of interface. The former difference in \(C_S\) is considered to increase as the cooling rate increases, because the mixing in liquid becomes more incomplete. The latter difference in \(C_S\) is considered to decrease as the cooling rate increases on the contrary. However, the cell width \(L\) is dependent on the cooling rate \(V\), that is, the parabolic relation of cellular solidification is dominant, which will be stated later.

<table>
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<tr>
<th>(x/L)</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
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<tr>
<td>Simulation</td>
<td>0.6848</td>
<td>0.6875</td>
<td>0.6942</td>
<td>0.7045</td>
<td>0.7216</td>
<td>0.7340</td>
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<td></td>
<td>0.6848</td>
<td>0.8487</td>
<td>0.8537</td>
<td>0.8550</td>
<td>0.8577</td>
<td>0.8606</td>
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<tr>
<td></td>
<td>0.6942</td>
<td>1.0580</td>
<td>1.0912</td>
<td>1.4650</td>
<td>1.5768</td>
<td>2.5727</td>
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<td>0.7216</td>
<td>1.6034</td>
<td>3.2850</td>
<td>4.4516</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Scheil
| Simulation | 0.6848 | 0.8240 | 1.0459 | 1.4637 | 2.6002 | 4.6170 |
|           |        |        |        |        |        |        |

Table 1  Solute distributions in solid at \(f_S = 0, 0.2, 0.4, 0.6, 0.8\) and 0.9 are shown in successive lines, respectively. Bottom line shows Scheil’s relation. Al–4 mass%Cu alloy, \(V = 1\) K/s.

![Fig. 7 Solute distribution in solid peculiar to respective Al–2, 4 and 8 mass%Cu alloys when eutectic temperature is attained in comparison with Scheil’s relation.](image)

Under the parabolic relation between the cell size and cooling rate, the redistribution of solute in relative location of solid was found not to vary during the solidification, however the cooling rate of an alloy may change.

Figure 7 shows the peculiar solute distributions of three alloys with different solute content at the time when eutectic temperature is reached (open circles), together with that of Scheil’s relation. Figure 7 shows that the simulated solute concentration at each joint differs only a little from that of Scheil.

When the temperature decreases below eutectic temperature, CuAl in eutectic begins to dissolve into the primary solid solution and homogenizing diffusion of solute will take place in the cell. However, the solubility limit as well as the diffusion coefficient in solid decreases with lowering of temperature. Therefore, the change of solute concentration in the solid cell below eutectic temperature is considered to be very few. That is, the solute distribution in the cell after the solidification can be approximated by the integrated relation of Scheil’s equation, eq. (14), as follows:
\[
C_S = kC_0(1 - f_S)^{k-1}
\]

Flemings stated that the solute distribution in dendritic solid is expressed as follows:
\[
C_S = kC_0(1 - \frac{f_S}{1 + \alpha k})^{k-1}, \quad \alpha = \frac{D_s f_V}{L^2}
\]
(15)
where \( t_f \) represents local solidification time, that is the time required to cool from liquidus to solidus. Kurz and Fisher showed the mass balance equation as follows:\(^2^1\)

\[
C_L/C_0 = [1 - f_S(1 - 2\alpha k)]^\beta
\]

(16)

In the present simulation, \( dt \) was summed up into \( t_f \) until eutectic temperature is attained. The result of the simulation was \( t_f = 96.75 \text{s}, \quad t_S = \Sigma(n^2 D_{S}/L^2) = n^2 D_{S} A_v t_f/L^2 = 0.448, \quad t_L = \Sigma(n^2 D_{L}/D_{S}/L^2) = n^2 D_{S} A_v t_f/L^2 = 3631 \) when \( V = 1 \text{K/s}, \quad L = 0.01 \text{cm} \) and \( n = 10 \). Therefore, \( D_{S} = 4.63 \times 10^{-8} \text{cm}^2/\text{s} \) and the value of \( V L^2 \) is numerated to be \( 6.26 \times 10^{-4} \text{Kcm}^2/\text{s} \) for lamellar cell of Al–4 mass%Cu alloy as will be seen later. \( t_f/L^2 = 1.55 \times 10^5 \text{s/cm}^2 \) and \( \alpha = D_{S} \Delta T/V L^2 = 7.16 \times 10^{-4} \). Then the value of \( \alpha \) is very small in comparison with unity. Accordingly, both eq. (15) and eq. (16) turn to Scheil’s equation. Therefore, it contradicts neither eq. (15) nor (16) that Scheil’s equation is applicable to the result of the present simulation.

Figure 8 shows the simulated solute distribution in solid at several stages of solidification on the assumption that \( L = 0.02 \text{cm}, \quad V = -1 \text{K/s}, \quad D_{S} = 10^{-6} \text{cm}^2/\text{s} \) (\( \alpha = 0.2419 \)). Figure 8 looks like the work by Brody and Flemings\(^1^5\) at first sight. But their work seems to be made on the inadequate assumption. They supposed the complete mixing in liquid, which they misunderstood as no diffusion in liquid.

They considered, therefore, the whole amount of solute rejected out of the interface had to be carried off by the solid diffusion and calculated as \( t_f/L^2 = 3.3 \times 10^8 \text{s/cm}^2 \). And they made the work by using \( t_f/L^2 = 3.3 \times 10^8 \text{s/cm}^2 \) which is several thousands times larger than the real one. Since most of the solute is carried off by the liquid diffusion actually as described above, their assumption is inadequate. In addition, the solute concentration of solid which solidifies at the start has to be \( kC_0 = 0.77 \text{mass}\%\text{Cu} \) as shown by eqs. (15) and (16), however the value of \( \alpha \) or \( t_f/L^2 \) may change. But their figure shows 0.61 mass\%Cu. Perhaps, they would miscalculate as \( k = 4.5/33 = 0.1364 \) and \( kC_0 = 0.1364 \times 4.5 = 0.6138 \text{mass}\%\text{Cu} \).

Broken lines in Fig. 8 show solute distributions of solid calculated by eq. (15) using \( \alpha = 0.2419 \) and by Scheil’s relation. The broken line of eq. (15) indicates the approximate solute concentration in solid at a given relative location in the cell when the interface passes over, but it does not show the solute distribution at or after the passage of the interface. Equation (16) shows almost similar pattern of the solute distribution curve to that of eq. (15).

Figure 9 shows the solute distributions in solid with varied values of \( D_{S} \) when eutectic temperature is just attained. The value of \( D_{S} \) is increased much to get a comparable value of \( \alpha \) to unity instead of the \( t_f/L^2 \). The figure shows that the larger the diffusion coefficient of solid, the more gentle becomes the slope of solute distribution. Although the solidification in equilibrium is expected when \( \alpha = 0.5 \) from eq. (16),\(^2^1\) the solute distribution d \( (\alpha = 0.4839) \) in Fig. 9 seems still far from the equilibrium or homogeneous solute distribution.

### 3.3 Parabolic law of cellular solidification

The processes of cellular solidification with varied cooling rate are shown in Fig. 10, in which dimension-less time \( D_{S} A_v t/L^2 \) is taken as abscissa. \( D_{S} A_v t/L^2 \) is numerated by elimination of \( n^2 \) from \( n^2 D_{S} A_v t/L^2 \) as follows:

\[
D_{S} A_v t/L^2 = \Sigma(\Sigma n^2 D_{S} A_v t/L^2)/n^2 = \Sigma(dT)/n^2 = \tau/n^2
\]

It is natural that the dimension-less time required to attain a definite temperature fall (a) and a definite fraction solid (b) is inversely proportional to the cooling rate. The slopes of the solidification curves shown in Fig. 10(b) are written as follows:

\[
L^2 df_s/\Sigma D_{S} A_v t = V L^2 df_s/\Sigma D_{S} A_v t = V L^2 df_s/\Sigma D_{S} A_v t = \Sigma(dT)/n^2 = \tau/n^2
\]

Use of eq. (14) gives \( df_s/\Sigma dT \) as follows:

\[
\frac{df_s}{\Sigma dT} = \frac{dC_L}{\Sigma dC_L} = \frac{1 - f_s}{m(k - 1)C_L}
\]

Combination of above two equations results in following equation:

\[
\frac{L^2 df_s}{\Sigma D_{S} A_v t} = \frac{V L^2 (1 - f_s)}{m(k - 1)C_L D_{S} A_v t}
\]
The solid line in Fig. 11 shows the dimension-less rate of solidification calculated by using eq. (17) for Al–4 mass% Cu alloy, and the plots are the results of simulation. Details about the drawing of Fig. 11 are as follows.

The values of right side of eq. (17) are numerated to be 0.178, 0.143, 0.117, 0.094, 0.072 and so forth at \( f_s = 0.1, 0.2, 0.3, 0.4 \) and so forth, respectively by the use of \( C_L \) and \( D_L \) at each stage when \( V = 1 \) K/s, Al–4 mass% Cu alloy. Solid line is made using these data. In the simulation of the same conditions, the required \( \tau/n^2 \) or \( D_{Av}/t/L^2 \) to attain \( f_s = 0.1, 0.2, 0.3, 0.4 \) and so forth becomes 0.8928, 1.6031, 2.4702, 3.6090 and so forth, respectively. Use of these data gives \( L^2 df_s/Dt = 0.112, 0.141, 0.115, 0.088 \) and so forth at \( f_s = 0.05, 0.15, 0.25, 0.35 \) and so forth in average, respectively. Simulations of the solidification with \( V = 0.5 \) and 2.0 K/s are carried out similarly. These data are plotted in Fig. 11.

Although the rate of solidification at the start calculated by using eq. (17) is 0.178 for the alloy, the simulated rates appear about 25% decrease as shown in Fig. 11 and also in Fig. 10. The misfit is partly attributable to the unskilled technique of simulation, but most of the misfit is considered to be caused by the transition of solute distribution, from complemental error function to parabola.

However the variables in eq. (17) may change, eq. (17) must be valid always. Then the left term of eq. (17) can be regarded as a proportional constant. Putting \( V = 1 \) K/s, \( f_s = 0, \ k = 0, \ m = -1 \) K/mass%, \( C_L = 1 \) mass% and \( L^2/D_L = 1 \) s as fundamental values of the variables, the left term of eq. (17) becomes 1. Accordingly, the following equation is obtainable.

\[
VL^2(1 - f_s) = m(k - 1)C_LD_l \tag{18}
\]

Equation (18) is a general equation which shows that the cellular solidification is a kind of diffusion controlled reaction showing parabolic relation between \( V \) and \( L \).

Taking into account of the decrease in solidification rate in early stage, eq. (18) gives the following:

\[
0.75V_0L^2 = m(k - 1)C_0D_L \tag{19}
\]

where \( V_0 \) denotes the cooling rate at the start, and \( C_0 \) the original solute content of the alloy.

So far, the lamellar cell forming solidification is supposed. In the experiments by other researchers,10–12) however, crossed cells were observed in columnar crystals. Then two-dimensional solute diffusion should be considered during solidification. However, the cellular solidification is considered to progress by fattening of the crosses, which is expressed as follows:

\[
f_s = 1 - (L - x^2)^2/L^2 = 2x^2/L - (x^2)/L^2
\]

In the early stage of solidification, the second term in the right \( (x^2)/L^2 \) is negligible. Accordingly, the rate of the crossed cell forming solidification in early stage is estimated to be twice as fast as that of the lamellar cell forming solidification. That is,

\[
1.5V_0L^2 = m(k - 1)C_0D_L \tag{20}
\]

Figure 12 shows plots of the crossed cell size \( L \) against \( [m(k - 1)C_0/V_0]^{1/2} \) for Al–Cu,10) Al–Si10) and Cu–Zn11) alloys obtained experimentally by other researchers. Two straight lines express \( L \) vs. \( [m(k - 1)C_0D_L/V_0]^{1/2} \) relations calculated by the use of eq. (19) and eq. (20) on the supposition that \( D_L = 5 \times 10^{-5} \) cm/s, which may be roughly admitted for the low temperature dependence of \( D_L \). Experimental results shown in Fig. 12 appear roughly in good coincidence with the calculated relation in alloys which have their own \( m \) and \( k \).

Ibaraki et al. derived a theoretical equation for the cellular solidification with crossed cells10) as follows:

\[
L = a_0 [m(k - 1)D_L]^{1/2}/k - [C_0/V_0]^{1/2}
\]

where \( a_0 \) denoted a constant. Equation (21) indicates that the cell size \( L \) is proportional to the square root of \( C_0/V_0 \), which was proved by their experimental data of Al–Cu and Al–Si alloys.10) However, eq. (21) contains a unknown constant, \( a_0 \), and, therefore, it is unable to prove the experimental results quantitatively. Sugiyama et al.12) carried out similar experiments on Cu–Sn alloys and derived an experimental equation to explain the results as follows:
But \( V_0 \) is taken as the ratio of the difference between the casting temperature and liquidus temperature by the time passed in their experiment. Therefore, eq. (22) is not a general equation for the cellular solidification. Donaghey and Tiller\(^{22}\) calculated the size of lamellar cell on the assumption of the simplified morphology of liquid groove between cells. The result was in accord with what was expected in a special condition.

Consequently, eqs. (18), (19) and (20) seem superior to other theories quoted above, for these equations are in good quantitative coincidence with the experimental results without containing any unknown variable.

4. Transition of Planar/Cellular Interface

B. Chalmers introduced the constitutional super-cooling to explain the transition of planar/cellular interface as follows:\(^{23}\)

\[
G = \frac{mC_0(1 - k)}{kD_L} \quad \text{(23)}
\]

Tiller stated an equation on the supposition of the constitutional super-cooling caused by the partial solute mixing in liquid under constrained solidification as follows:\(^{24}\)

\[
G = \frac{mC_L(i)(1 - k)}{D_L} \quad \text{(24)}
\]

where \( C_L(i) \) denoted solute concentration in liquid at the interface.

However, when the diffusion controlled solidification with planar interface perpendicular to \( z \)-axis is considered, another criterion for the transition appears. Neglecting the first term in the right side of eq. (2) and putting the growth rate \( R = dL/dt \) along \( z \)-axis turns to

\[
R = -\frac{dC_L}{dz} \frac{D_L}{C_L(z^*) (1 - k)}
\]

The concentration gradient of liquid in contact with the solid-liquid interface is converted to the gradient of corresponding liquidus temperature \( G_C \) as follows:

\[
G_C = \frac{dT}{dz} \quad \text{(25)}
\]

\[
G_C = \left[ -\frac{dC_L}{dz} \right] \frac{dC_L}{dz} \quad \text{and} \quad mC_L(z^*)(1 - k) \frac{D_L}{D_L}
\]

Hence, the combination of above two equations gives the following equation:

\[
G \frac{R}{G_C} = \frac{mC_L(z^*)(1 - k)}{D_L} \quad \text{(26)}
\]

\[
C_L(z^*) \text{ increases as the solidification progresses and so } G_C/R. \text{ Supposing the upward solidification in a furnace with its fixed temperature gradient } G, \text{ the solidification with planar interface will become unstable when } G_C \text{ exceeds } G, \text{ and protrusions of the interface will grow into the liquid, and cellular interface will be formed. And the solute diffusion in liquid along } z \text{-direction will change to the diffusion along } x \text{-direction at the same time. That is, the transition of planar/cellular interface is expressed as follows:}
\]

\[
G = \frac{mC_L(z^*)(1 - k)}{D_L}
\]

Equation (25) is quite the same as eq. (24). The coincidence between the two is convincible when the partial solute mixing model by Tiller is considered to play the role of the parabolic solute distribution in liquid.

The transition of ‘‘No Cell/Cell’’ interface in Pb–Sn alloys stated by Rutter\(^{25}\) shows that the ratio of \( C_0 \) to \( G/R \) is \( 3.2 \times 10^{-3} \text{ mass}\% \text{cm}^2/\text{Ks} \). Since \( m = -2.32 \text{ K/mass}\% \text{ and } k = 0.31, \text{ } D_L \text{ is numerated to be } 5.1 \times 10^{-4} \text{ cm}^2/\text{s} \text{ by eq. (25) and } 1.7 \times 10^{-4} \text{ cm}^2/\text{s} \text{ by eq. (23). The former value of } D_L \text{ seems more plausible than the latter, although the exact value of } D_L \text{ for the alloy is not known.}

Equation (25) indicates also the condition for the formation of cellular structure. For example, the right term of eq. (25) is from about \( 5 \times 10^2 \) to \( 5 \times 10^3 \text{ Ks/cm}^2 \) for Al–Cu alloys of low solute content, while the left term of eq. (25) in the experiment done by Ibaraki \textit{et al.}, was about 100 to 400 Ks/cm\(^2\). The smallness of the latter in comparison with the former seems to be the reason why the cellular structure was formed in their experiment.

5. Conclusion

In order to study the solute redistribution in solid and liquid during the upward cellular solidification of Al–Cu alloy, computer simulation was carried out by using the direct solving method under the supposition of the diffusion controlled solidification. The simulated results were analyzed and summarized as follows:

1. The solute distribution in liquid ahead of the solid-liquid interface was found parabola whose bottom zenith lies at cell boundary. Hence, the increasing rate of solute concentration becomes equal everywhere in liquid during the solidification on linear cooling.
(2) Most of the solute rejected out of the interface on solidification diffuses into liquid, and only a small amount of solute diffuses into solid. Therefore, the cellular solidification is controlled mainly by the solute diffusion into liquid.

(3) The diffusion in solid during and after the solidification is inactive, because the diffusion coefficient is small and time is short.

(4) Since the situation of solidification is such as described above, the solute distribution in the upwards solidified cell is expressed approximately by Scheil’s relation.

(5) The parabolic relation between the cell size and cooling rate of a single phase alloy was formulated, which indicated that the cellular solidification is a kind of diffusion controlled reaction.

(6) Thus derived formula was verified by the experimental cell sizes obtained by other researchers in Al–Cu, Al–Si and Cu–Zn alloys.

(7) The transition of planar/cellular interface was investigated in consideration of the diffusion controlled solidification and a new condition for the transition was formulated.

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