Effect of Anisotropy of Surface Energy on the Growth Direction of Solid Phase in Constrained Growth Condition

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The growth direction of solid phase, which has a great influence on the grain selection, has been investigated. Transparent organic systems, succinonitrile–H$_2$O alloy and pivalic acid–H$_2$O alloy have been used for unidirectional solidification. Essential parameters of phase diagrams, distribution coefficient of H$_2$O (k) and liquidus slope (m) have been determined experimentally. The relationship is analyzed between dimensionless growth velocity ($V/V_c$), where $V_c$ is the critical growth velocity for constitutional supercooling) and dimensionless growth direction ($\pi'$). The change in $\pi'$ with $V/V_c$ is common and similar for both alloy systems. $\pi'$ increases rapidly at low growth velocity region. Then, $\pi'$ increases slowly and approaches unity with increasing $V/V_c$. When the anisotropy of surface energy increases, the growth direction of solid phase becomes close to the preferred growth direction even at low growth velocity region, where cellular interface is observed.

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Keywords: in-situ observation, unidirectional solidification, growth direction, anisotropy of surface energy, plane, cell, dendrite

1. Introduction

In case of unidirectional solidification, the number of grains decreases with increasing the growth length via grain selection. However, the process of grain selection depends on the solidification condition. When the solid/liquid interface is dendritic, the grain selection takes place quickly. On the other hand, when the interface is cellular, the grain selection occurs slowly. The reason of this dependence is the difference in growth direction of each morphology. Namely, a dendrite grows in its preferred growth direction regardless of the heat flow direction. However, a cell grows between the heat flow direction and its preferred growth direction.

A 2-D engineering simulation model for grain selection has been constructed and the simulated results agree well with the experimental data which have been carried out using the organic substances. In this engineering model, the growth direction of solid phase can be shifted towards the heat flow direction, introducing dimensionless growth direction, $\pi'$. The shift of growth direction makes the length necessary for grain selection long. These calculated results correspond to the experimental results in the case of cellular interface. One of the excellent points of this engineering model is that it takes only a few seconds to obtain the calculated results. Therefore, this engineering model has been applied for estimation of yield rate in the single crystal casting process, such as turbine blade manufacturing.

Using as-received succinonitrile, the change in growth direction has been investigated when the solid/liquid interface varies from plane, cell and dendrite. The growth direction changes from heat flow direction to preferred growth direction with increasing growth velocity. Unidirectional solidifications with three levels of temperature gradient have been performed. Using $V/V_c$, three individual data have described with a simple, unique curve. It has been found that the non-dimensional growth velocity ($V/V_c$; growth velocity divided by the critical growth velocity for constitutional supercooling) is a good parameter for characterization of solid/liquid interfacial morphology and growth direction. Furthermore, the simulation results of phase field model have also agreed qualitatively with these experimental results.

Solid/liquid interfacial energy has an effect on the size of a dendrite, such as a dendrite tip radius. It is anisotropy of surface energy that affects the growth direction of solid phase. This study then has been carried out to investigate the effect of anisotropy of solid/liquid interface energy on the change in growth direction of the solid phase. Unidirectional solidification experiments have been carried out using two organic substances. One organic material is succinonitrile–H$_2$O (SCN–H$_2$O) system, the anisotropy of which is not strong. The other one is pivalic acid–H$_2$O (PVA–H$_2$O) system, the anisotropy of which has been reported to be strong. Comparing the relationships between growth velocity and growth direction of these alloy systems, the effect of anisotropy of the solid/liquid surface energy on the growth direction has been investigated.

2. Experimental Procedure

A unidirectional solidification apparatus has been installed on the stage of an optical microscope as shown in Fig. 1. Basically this set-up is a typical Bridgman-type furnace and one can control independently temperature gradient ($G$) and growth velocity ($V$). Right hand side of Fig. 1 is a hot stage where the resistant wires are installed and left hand side is a cooler where cooling water with a constant temperature is circulated. The temperature gradient can be regulated with changing the temperatures of hot stage and the cooler. There is a DC servomotor on the right hand side of Fig. 1 to drive a glass cell. The moving velocity of the glass cell is controlled by changing the voltage.

The glass cell is constructed with a glass plate with 100 mm in length, 35 mm in width, 150 μm in thickness. The gap of the glass cell is adjusted to be 150 μm. The glass cells are constructed with epoxy resin.

In the case of SCN–H$_2$O alloy, to measure the temperature field during experiment fine thermocouple is installed in the glass cell, which is lied parallel to the isotherm. However, in
the case of PVA–H\textsubscript{2}O alloy alumel–chromel thermocouple is corroded because of galvanic corrosion. Therefore, the thermocouple is installed on the glass cell. Since the linear expansion coefficient of glass is not similar with the epoxy resin for PVA–H\textsubscript{2}O alloy used in this study, the glass cell would be destroyed by thermal stress with high temperature gradient. Thus, the experimental runs have been performed with rather low temperature gradient in case of PVA–H\textsubscript{2}O alloy.

As-received organic materials have been distilled 4 times. After purifying, organic materials have been handled in a glove box with argon atmosphere in order to prevent from contamination. To make alloys, distilled water degassed by argon bubbles is introduced in the glove box. Then the molten alloy is filled in the glass cell and sealed with the epoxy resin. After cured, the glass cell is used for measuring the liquidus temperature with a ring heater. The detail for this method has been described in the literature.\textsuperscript{10,11)

A CCD camera is attached to the optical microscope and \textit{in-situ} observation of the solidification of organic materials is made and the morphology of the unidirectional solidification is recorded by a DVD recorder. The most part of the alloy in the glass cell is melted and unidirectional solidification is performed from the solid phase. When the movement of solid/liquid interface stops in the observed area, it is recognized that the steady state is achieved. This situation is the same as the steady state in the solutal field in the liquid and is attained after the growth length exceeds 10 mm even at the slowest growth velocity. In order to minimize the error in measuring the angle, dendrites, the growth direction of which are deviated over 10 degrees from the heat flow direction, are selected for observation.

A schematic drawing of determining of the growth direction and preferred growth direction of the solid phase\textsuperscript{2,5)} is shown in Fig. 2. In the steady state, the growth direction of the solid phase is constant, thus the angle between the growth direction and the heat flow direction is defined as $\alpha$. To verify the heat flow direction, a line perpendicular to a tangent line of dendrite or cell tips is determined. The dendrites grow in their preferred growth direction, when the temperature gradient at the solid/liquid interface is zero. When the electronic power supplies for two heaters shown in Fig. 1 are abruptly turned off at the end of the experiment, dendrites grow from the solid phase. The growth direction of dendrites is defined as the preferred growth direction.\textsuperscript{3)} Then the angle between heat flow direction and preferred growth direction is defined as $\theta$. Then, the dimensionless growth direction is defined as $\alpha / \theta \ (= \pi')$.

3. Experimental Results

3.1 Determination of melting temperature of pure substance ($T_0$) and liquidus temperature of alloy ($T_L$)

An example of solid particle during holding the temperature is shown in Fig. 3. This is observed in measuring $T_L$ of an SCN–H\textsubscript{2}O alloy. Solid particle indicated by an arrow is a single phase and spherical. The diameter of this solid particle is approximately 300 $\mu$m and is kept constant between 200 $\mu$m to 500 $\mu$m during measurement. The thermocouple is also observed in this figure. To confirm the equilibrium, the solid particle is kept over 600 s. The temperature, where the solid particle does not melt nor grow, is defined as the
melting temperature of the pure substances or the liquidus temperature of the alloys. The experimental results are listed in Table 1.

The aimed amount of H$_2$O was about 0.1 mass%, though the real content of water was uncertain due to the experimental error, including vaporization. Thus, the content of H$_2$O in SCN and PVA would be decided in section 4.2.

3.2 Effect of growth velocity on the growth direction

3.2.1 SCN–H$_2$O system

Temperature gradients in this experiments range between 5120 to 5900 K/m and the average value is 5400 K/m. Solid/liquid interfacial morphologies of unidirectional solidification obtained in SCN–H$_2$O alloy are shown in Figs. 4–6(a).

Fine dendrites grown from the solid phase after turning off the heaters are also shown in Figs. 4–6(b). Figure 4 shows a planar solid/liquid interface at a growth velocity of 0.75 μm/s, which grow from left to right. After turning off the heaters, typical, well-developed dendrites grow form the solid. As seen the planar solid phase grow perfectly along the heat flow direction regardless of the preferred growth direction.

Figure 5 shows an example of cellular interface at $V = 3.61 \mu$m/s. It is found that slight perturbations are visible on some primary trunks. However, there are no secondary dendrite arms. At the tip of the cell, it is a little bit distorted. This is due to a weak anisotropy of the surface energy of SCN. The growth direction of cells (Fig. 5(a)) and that of dendrites observed after turning off the heaters (Fig. 5(b)) are found to be clearly different. Figure 6 shows an example of dendritic interface at $V = 8.93 \mu$m/s. It has been found that well-developed secondary dendrite arms form on the primary trunks. The growth directions in Fig. 6(a) and 6(b) are similar, but that in Fig. 6(a) shifts towards the heat flow direction to some extent.

Dimensionless growth direction has been determined comparing these photographs as defined in Fig. 2. The relationship between the growth velocity and the dimensionless growth direction ($\pi'$) is shown in Fig. 7. At low growth velocity region, $\pi'$ rapidly increases with increasing $V$. Then, $\pi'$ increases slowly and gradually approaches unity with increasing $V$. The cell-to-dendrite transition is determined from the morphology of solid/liquid interface, and indicated with a dotted line in Fig. 7.

3.2.2 PVA–H$_2$O system

Temperature gradients in this series range between 1400 to 1750 K/m and the average value is 1630 K/m. Solid/liquid interface morphologies of unidirectional solidification in PVA–H$_2$O alloy are shown in Figs. 8–10(a). Fine dendrites grown from the solid phase after turning off the heaters are also shown in Figs. 8–10(b). Figure 8 shows a planar solid/liquid interface at a growth velocity of 0.28 μm/s. Slight perturbations are observed at grain boundaries. After turning off the heaters some solid phase nucleate in the liquid because of low temperature gradient. An arrow indicates dendrite grown

<table>
<thead>
<tr>
<th>pure substances</th>
<th>alloy</th>
<th>melting temperature</th>
<th>liquidus temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinonitrile</td>
<td>Succinonitrile–H$_2$O</td>
<td>331.1 K</td>
<td>330.1 K</td>
</tr>
<tr>
<td>Pivalic acid</td>
<td>Pivalic acid–H$_2$O</td>
<td>308.3 K</td>
<td>307.9 K</td>
</tr>
</tbody>
</table>

Table 1 Melting temperature and Liquidus temperature measured.
from a grain paid attention. In this case again, the planar interface grows along the heat flow direction regardless of the preferred growth direction. Figure 9 shows an example of cellular interface observed at $V = 0.925 \text{ mm/s}$. It is found that the growth direction of cell is shifted to the heat flow direction to some extent from the preferred growth direction. It is also found that cell tip is strongly asymmetric and is pointed to its preferred growth direction, which is due to strong anisotropy of the surface energy of pivalic acid.

Figure 10 shows a dendritic interface observed at $V = 8.98 \text{ mm/s}$. The dendrites grow almost along its preferred growth direction but slightly shift towards the heat flow direction.

The relationship between $V$ and $\pi'$ is shown in Fig. 11. The changes in $\pi'$ with $V$ are very similar to the result in SCN–H$_2$O alloy. At lower growth velocity, $\pi'$ increases steeply. On the other hand, at high growth velocity, $\pi'$ gradually increases and approaches unity. The cell-to-dendrite transition determined from the solid/liquid interfacial morphology is also shown in Fig. 11.

### 4. Discussions

#### 4.1 Validity in the measurement of $T_0$ and $T_L$

Outer diameter of the ring heater is 20 mm. At around the center of the ring heater, a small solid particle is held in the melt controlling the temperature of the center region. The temperature, where the solid phase did not melt nor grow, is defined as the liquidus temperature. In order to ensure the equilibrium, the small solid particle is kept holding at least 600 seconds.

The volume fraction of solid in a solid/liquid mixture can be estimated with the Lever Rule when the solid/liquid mixture is in equilibrium. Therefore, using the Lever Rule, the temperature, where the solid/liquid mixture is held, can be obtained. The fraction solid is then estimated as follows: (volume of solid particle held in a liquid)/(volume of the solid and liquid mixture). Assuming the diameter of liquid phase is that of the outer diameter of the ring heater, the volume of liquid phase is calculated as $47.1 \text{ mm}^3$. The volume of the solid phase is $1.1 \times 10^{-2} \text{ mm}^3$, assuming that it is a cylinder in shape. Then, the volume fraction is approximately 0.02%. This is so small that the temperature can be regarded as the liquidus temperature of this composition.

Argon gas may be dissolved and this may lower the melting temperature. It can be concluded that the purities of SCN and PVA used in this study are fairly high, compared with the data in the literature.$^7,8,12$)

#### 4.2 Determination of compositions and parameters of phase diagrams

The essential parameters of a phase diagram are the equilibrium distribution coefficient ($k$) and the liquidus slope ($m$). These parameters are very important to predict scales of solidification, however these are unknown in SCN–H$_2$O and PVA–H$_2$O systems. In making alloys, the expected concentration of H$_2$O was 0.1 mass%, though, the actual quantity was uncertain, because of the experimental error including vaporization of water during alloying. Thus the solute content itself is unknown in this study. Therefore, these three parameters would be determined in this study.
4.2.1 Formulation

The quantity of solute, degree of temperature drops and equilibrium distribution coefficient are correlated and this equation can be derived from the well-known Van’t Hoff’s equation.13)

\[
\frac{M_A}{99M_B}(1-k) = \frac{\Delta H^0}{RT^2} \frac{\Delta T}{C_0}
\]

(1)

Where \(M_A\) and \(M_B\) are molecular weight of solvent and solute, respectively, \(\Delta T\) is the difference in liquidus temperature of pure substance and an alloy and \(T\) is the melting temperature of pure substance, \(k\) is the equilibrium distribution coefficient, \(C_0\) is the solute content of an alloy, \(\Delta H^0\) is the latent heat for solidification of pure substance and \(R\) is the gas constant.

\(m\) is the slope of liquidus line and can be obtained from the quantity of solute and temperature drop, supposing that the liquidus line is straight. This equation is shown as follows.

\[
m = \frac{\Delta T}{C_0}
\]

(2)

The growth velocity, where a planar solid/liquid interface breaks, can be obtained under the condition of constitutional undercooling14) and is indicated in eq. (3).

\[
V_c = \frac{kDG}{mC_0(1-k)}
\]

(3)

Where \(G\) is the temperature gradient at the solid/liquid interface and \(D\) is diffusion coefficient of solute in the liquid.

Then, unknown parameter, \(k\), \(m\) and \(C_0\) can be calculated. Combining eqs. (1)–(3), the solute content is finally obtained as eq. (4).

\[
C_0 = \frac{99M_B\Delta H^0\Delta T}{RT^2M_A} \left(1 + \frac{\Delta TV_c}{DG}\right)
\]

(4)

4.2.2 Calculation

Since there is no data of the diffusion coefficient of H\(_2\)O in molten SCN or PVA in the literature, the diffusion coefficient of acetone in molten SCN reported by Chopra et al.15) is assumed to be applicable to the present alloy systems. \(V_c\) is originally the growth velocity where a planar interface starts to break. Since it is rather difficult to determine \(V_c\) experimentally, the growth velocity, where a planar solid/liquid interface is observed, is assumed to be \(V_c\). The melting temperature of the pure substances and the liquidus temperature of alloys have been measured and listed in Table 1. Then, the temperature drop in each alloy system (\(\Delta T\)) is obtained.

The physical parameters necessary for calculation and the experimental data of \(V_c\), \(G\), \(T\) and \(\Delta T\) are listed in Table 2 and Table 3, respectively.

The calculated results for both alloy systems are shown in Table 4. The H\(_2\)O content in SCN agrees well with the predicted value. On the other hand, H\(_2\)O content in PVA is different from the expected value. The reasons of this discrepancy are uncertain though it may be by vaporization of H\(_2\)O during alloying and filling into the glass cell.

Actually the value of diffusion coefficients of H\(_2\)O in molten SCN and PVA are uncertain. It is necessary to evaluate the change in the calculation when the diffusion coefficient is different. Here, the calculation is made when \(D\) changes from 0.5 to 2.0 times the value used in this study. Then, in SCN–H\(_2\)O system, the results are: \(C_0\): 0.109–0.095 (mass%), \(k\): 0.168–0.047 (–), \(m\): –9.21– –10.5 (K/mass%).

In PVA–H\(_2\)O system, the results are: \(C_0\): 0.0243–0.0211 (mass%), \(k\): 0.18–0.051 (–), \(m\): –16.5– –19.0 (K/mass%). It can be safely concluded that these changes are small enough not to alter the shape of the phase diagram much.

Kaukler and Frazier16) have studied monotectic solidification using SCN–H\(_2\)O alloy system and collected some phase diagrams. Since they are interested in the change of liquidus line, they do not take care about the distribution coefficient and it seems to be zero or quite small. According to their phase diagram, \(m\) is approximately –6.1 K/mass%. In the present study, \(m\) is obtained to be –10.1 K/mass%, which is in the same order. It can be concluded that the present result agrees with the literature data.

4.3 Effect of growth velocity on growth direction

The relationship between the dimensionless growth velocity and the dimensionless growth direction in SCN–H\(_2\)O and PVA–H\(_2\)O alloy systems is studied. Here, planar solid/liquid interface has been observed at 0.75 \(\pi\), therefore \(V_c\) is 0.75 \(\mu m/s\).

In both alloys, after breaking the planar interface, the

### Table 2 Physical parameters of organic substances for calculation.

<table>
<thead>
<tr>
<th>Substance</th>
<th>(M_\text{SCN})</th>
<th>(M_\text{PVA})</th>
<th>(M_\text{H_2O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN</td>
<td>80.1</td>
<td>102.1</td>
<td>18.0</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>3703</td>
<td>2268</td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>5400</td>
<td>1630</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>331.1</td>
<td>308.3</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>8.31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3 Experimental results used for calculation.

<table>
<thead>
<tr>
<th>System</th>
<th>(V_\text{c(SCN)})</th>
<th>(G_\text{SCN})</th>
<th>(T_\text{c(SCN)})</th>
<th>(\Delta T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN–H(_2)O</td>
<td>0.75</td>
<td>5400</td>
<td>331.1</td>
<td>1.0</td>
</tr>
<tr>
<td>PVA–H(_2)O</td>
<td>0.28</td>
<td>1630</td>
<td>308.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

### Table 4 Calculated results of composition and parameters for equilibrium phase diagram.

<table>
<thead>
<tr>
<th>System</th>
<th>(C_0) (mass%)</th>
<th>(k)</th>
<th>(m) (K/mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN–H(_2)O</td>
<td>0.10</td>
<td>0.09</td>
<td>–10.1</td>
</tr>
<tr>
<td>PVA–H(_2)O</td>
<td>0.022</td>
<td>0.10</td>
<td>–18.2</td>
</tr>
</tbody>
</table>
of magnitude. Therefore, it can be concluded that larger than the experimental results, but are in the same order.

\[ V \]

interface (\( k = V \)).

On the other hand, \( \pi' \) slowly increases and gradually approaches unity with increasing growth velocity. The extent of error in predicting \( V_c \) is within 50%. However, this does not lead the large difference in the relationship between \( V/V_c \) and \( \pi' \). \(^5\)

The cell-to-dendrite transitions observed are indicated with dotted lines for both alloys. In the case of SCN–H\(_2\)O alloy, the value of \( V/V_c \) at the transition is 7.8. It is known that \( V_c/k \) is the transition velocity from cellular to dendritic interface (\( V_{tr} \)). \(^10,17,18\) In this case, \( V_{tr}/V_c \) is 11.1, because \( k \) equals to 0.09. In the case of PVA–H\(_2\)O alloy, the value of \( V/V_c \) at the transition is 5.9. The predicted value is 10.0 since \( k = 0.10 \). In both cases, the predicted values are slightly larger than the experimental results, but are in the same order of magnitude. Therefore, it can be concluded that \( V_c/k \) is a good estimation for cell-to-dendrite transition.

### 4.4 Effect of anisotropy of surface energy on the growth direction of solid phase

Relationship between the dimensionless growth velocity and dimensionless growth direction for two alloy systems is shown in Fig. 14. Roughly speaking, \( \pi' \) changes similarly for both alloys, as explained in the previous section. At \( V/V_c = 1 \), solid/liquid interface is planar for both alloys and the solid phase grows along the heat flow direction, \( \pi' = 0 \). In the case of large value of \( V/V_c \), \( \pi' \) approaches unity but does not reach unity in the range of the present study. When \( V/V_c \) is small, \( \pi' \) increases quickly and then increases slowly with increasing \( V/V_c \). In the range of low \( V/V_c \), the change of \( \pi' \) in growth direction is strongly affected by the anisotropy of surface energy. In this range, \( \pi' \) in PVA–H\(_2\)O alloy increases more steeply than does in SCN–H\(_2\)O alloy. A material with higher anisotropy of surface energy will tend to grow in its preferred growth direction even in cellular solid/liquid interface.

### 5. Conclusions

When the solid/liquid interfacial morphology changes from plane, cell and dendrite, the effect of anisotropy of solid/liquid interface energy on the growth direction of solid phase has been investigated experimentally. SCN–H\(_2\)O alloy, which has a low anisotropy, and PVA–H\(_2\)O alloy, which has a strong anisotropy, have been used for in-situ observation of unidirectional solidification. Following points have been derived.

1. Essential parameters of phase diagrams (\( k \) and \( m \)) of SCN–H\(_2\)O alloy system and PVA–H\(_2\)O alloy system have been determined. 
   \( k_{H_2O} \) for SCN–H\(_2\)O is 0.09 and \( k_{H_2O} \) for PVA–H\(_2\)O is 0.10. \( m_{H_2O} \) for SCN–H\(_2\)O is \(-10.1\) (K/mass%) and \( m_{H_2O} \) for PVA–H\(_2\)O is \(-18.2\) (K/mass%).

2. The relationship between the growth velocity and growth direction is common, regardless of the degree of anisotropy. Namely, the growth direction of solid phase changes from heat flow direction to its preferred growth direction with increasing growth velocity.

3. The effect of anisotropy of surface energy on the growth direction of solid phase clearly appears when the solid/liquid interfacial morphology is cellular. In the case of strong anisotropy, the growth direction of solid phase
becomes closer to the preferred growth direction even in the low growth velocity.

(4) In the case of cellular interface, cell tip is asymmetric and is pointed to the preferred growth direction when the anisotropy of surface energy is strong.

REFERENCES