Experimental Thermal Conductivity of Ice Crystalline Layer in Layer Melt Crystallization

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Abstract: Measurements of thermal conductivity of ice crystalline layer grown from water-sodium chloride solution by layer crystallization were explored. Interfacial temperature and growth rate of crystalline layer could be measured during the growth of layer. The method was based on heat balance coupled mass balance in growing the layer. The measurements were carried out at layer crystallization conditions such as cooling rate, mixture composition and subcooling degree. The growth rate of ice crystalline layer in water-sodium chloride system was decreased with increasing concentration of sodium chloride, and was proportional to the second power of subcooling degree. The thermal conductivity of crystalline layer was determined by overall heat transfer coefficient and heat transfer coefficients in melt and coolant sides. The overall heat transfer coefficient and the thermal conductivity increased with decreasing the concentration of sodium chloride and the cooling rate.

Keywords: melt crystallization, crystalline layer, thermal conductivity, layer growth rate

Introduction

Melt crystallization is one of the separation techniques applied in large scale separation and ultrapurification of chemicals from multicomponent mixtures, such as close boiling hydrocarbons, isomers, heat sensitive materials, and so on. The use of melt crystallization for separation of the mixtures has increased rapidly in chemical industry since the past few years. In melt crystallization, impurities are recovered in molten form and can be cycled, incinerated, or treated in some other fashion without a solvent removal step. From this point of view, melt crystallization is a clean technology for separation of organics without using a solvent. However, layer melt crystallization is difficult to be analyzed quantitatively in details because heat and mass transfers occur simultaneously during the layer growth [1]. In order to model transport phenomena during layer melt crystallization, the mass, heat and momentum conservation equations were solved numerically [2-4]. Hence at least reasonable estimates of the relevant transport and thermodynamic properties of materials are needed. An attention should be given to the properties required as input data in heat transfer through crystalline layer and crystallization simulation.

In fact, the residual impurity in a solid layer crystallizing from a binary eutectic system is due to the inclusions of the mother melt. It may lower the conductivity coefficient of the crystalline layer. Generally speaking, the thermal conductivity of a solid is particularly sensitive to its detail composition and structure [5,6]. The temperature at which crystalline layer forms would influence the type of crystalline formation and directly affect the thermal conductivity. The thermal conductivity of crystalline layer is affected by the crystal density which depends mainly on inclusion fraction in the crystalline layer [7]. However, it must be a function of some other factors. Therefore, the thermal conductivity of the crystalline layer plays an important role in structuring and affecting rate of crystallization. The previous studies [8,9] on the layer melt crystallization were based on constant thermal conductivity, which is assumed to be the same as that of pure material.

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However, because the interfacial distribution coefficient and inclusion fraction varies with the elapsed time during growth of the crystalline layer, thermal conductivity of crystalline layer cannot be constant. Our recent works showed that the crystalline layer had concentration profiles through the layer [4,10,11]. In addition, the thermal conductivity of water was about 0.2 times lower than that of pure ice.

In this study, method for measuring thermal conductivity of ice crystalline layer was developed. In situ measurement of interfacial temperature and growth rate could be carried out during crystallization. The method was based on energy balance coupled mass balance in growing the layer. The system investigated was water-sodium chloride system. The measurements were carried out for various cooling rates, mixture compositions and subcooling degrees. Some results were compared to those from the previous published data.

**Measurements**

**Methods**

In order to investigate the influence of the three major parameters on layer crystallization (e.g., melt composition, subcooling and cooling rate), a test equipment was built. The schematic diagram of the apparatus set up in this study is shown in Figure 1. The apparatus consists of the layer crystallizer, thermostatic bath, circulators with temperature programming controllers, data acquisition system and image analysis system. The thermostatic bath was composed of a 500 mL vessel containing liquid melt and was equipped with an agitator and an outside jacket. The crystallizer is a cylindrical tube type with a diameter of 26.5 mm and a length of 150 mm. The water-ethylene glycol mixture is used as a coolant. Flow rate of the coolant inside a tube crystallizer was set as 210 cm$^3$/sec. Agitation rate was set to 400 rpm. Copper-constantan thermocouples for the measurement of temperatures were located at three difference positions around the crystallizer; inlet line for the coolant, outlet line for the coolant, and inside of the thermostatic bath. Measurements of the temperature were carried out by amplified trace of signals from the thermocouples, which were monitored with data acquisition system (DT VEE, Data Translation). An image analysis system (Image-Pro Plus, I&G) with a video camera was used in order to measure the thickness variation of crystalline layer with time. The image analyzer was calibrated by actual crystalline layer. A typical example for measuring temperature profile and the thickness variation of crystalline layer with time is shown in Figure 2.

A homogeneous mixture of water and sodium chloride was prepared and a total of about 200 mL was charged into the bath. The solution was heated above its saturation temperature and then a desired melt temper-
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![Figure 2](image)

**Heat Transfer Coefficient**

The heat transfer coefficient in melt side has been evaluated in the operating conditions corresponding to the constancy of the layer thickness. At such conditions, the convection heat flux is equal to heat transfer across the layer and the convection coefficient is easily determined by the heat balance steady-state equation when the layer stops to grow.

$$h_0 = \frac{Q_{\infty}}{A_\infty(T_i^* - T_m)}$$  (1)

Where $Q_{\infty}$ and $A_\infty$ mean the heat quantity of coolant and the surface area when the growth of crystal stops, respectively. $T_i^*$ is equilibrium interfacial temperature for the melt concentration. $T_m$ is melt temperature. From the experiments, a value of the heat transfer coefficient in melt side is 563 W/m²K.

For heat transfer of coolant in tube, the Reynolds number and the Prantl number were 35700 and 209, respectively. Heat transfer coefficient in tube can be calculated from the following relation [12].

$$h_i = 0.026 \frac{k_c}{d_i} N_{Re}^{0.8} N_{Pr}^{1/3}$$  (2)

Where $k_c$ and $d_i$ are thermal conductivity of coolant and inside diameter of the tube, respectively. It was found that heat transfer coefficient inside crystallizer tube was 10332 W/m²K.

**Experimental Thermal Conductivity**

The heat transfer rate of coolant $Q_c$ can be described as:

$$Q_c = m_c C_p (T_{co} - T_{cl})$$  (3)

Where $m_c$, $C_p$, $T_{cl}$ and $T_{co}$ mean the flow rate of coolant, heat capacity of coolant, inlet temperature and outlet temperature of coolant, respectively.

The overall heat transfer coefficient $U$ is defined by LMTD and the surface area of crystalline layer $A$.

$$U = \frac{Q_c}{A \cdot LMTD}$$  (4)

Where, LMTD is logarithm mean temperature difference between coolant and melt.

$$LMTD = \frac{T_{co} - T_{cl}}{\ln \frac{T_m - T_{cl}}{T_m - T_{co}}}$$  (5)

where $T_m$ is temperature of the melt, which is kept constant during the growth. The surface area can be calculated from the measured layer thickness.

$$A = \pi(L_w + 2L_c)H$$  (6)

Where $L_w$, $L_c$ and $H$ is thickness of crystallizer wall, thickness of crystalline layer and the height of crystalline layer, respectively.

Thermal conductivity of crystalline layer can be described as:

$$k_{cl} = L \left( \frac{1}{U} - \frac{1}{h_i} - \frac{L_{\infty}}{k_w}, \frac{1}{h_o} \right)^{-1}$$  (7)

Where, $k_w$ is thermal conductivity of crystalline layer. The subscripts c, o, w and cl represent coolant side, melt side, crystallizer wall and crystalline layer. Eventually, thermal conductivity of the layer $k_{cl}$ is calculated by measured parameters like $L_c$, $U$, $h_i$ and $h_o$, and known parameters like $L_w$ and $k_w$.

**Results and Discussion**

**Growth Rate of Crystalline Layer**

In melt crystallization, crystal growth rate is determined by heat transfer rate. The thickness of crystalline layer formed on cold surface of crystallizer depends on crystal growth rate and is expressed as a function of time in growing the layer. The crystal growth rate $v$ is defined as variation of layer thickness $\Delta L$ for time interval at $\Delta t$. 
Figure 3. Plot of the crystal growth rate versus the subcooling degree \( \Delta T \) for the various feed compositions at cooling rates of 0.1 K/min and 2.5 K/min.

\[
\nu = \frac{\Delta L}{\Delta t}
\]  

(8)

The growth rate of crystalline layer at time \( t \), \( \nu_t \) is evaluated from slope in plot of the crystalline layer thickness versus the elapsed time.

\[
\nu_t = \frac{L_{t+1} - L_{t-1}}{t_{t+1} - t_{t-1}}
\]  

(9)

It is assumed that the sensible heat change in the solid and melt is negligible. And then, the rate of crystallization can be obtained from a heat balance, as follows:

\[
\lambda \rho_c \nu = U(T_m - T_c) - h_c(T_m - T_i)
\]  

(10)

Where \( \lambda \), \( T_i \), \( T_c \) and \( T_m \) are latent heat of crystallization, the S-L interfacial temperature, cooling temperature and melted liquid temperature, respectively. The temperature of the S-L interface, \( T_i \) was evaluated from Equation 10 using the measurement parameters \( \nu \), \( U \) and \( h_c \), operating parameters \( T_m \) and \( T_c \), and physical properties \( \lambda \) and \( \rho_c \).

The crystal growth rate was expressed as a function of subcooling degree [4]. The subcooling degree means temperature difference between the melt and the crystal surface.

Figure 3 shows the relationship between the crystal growth rate \( \nu \) and the subcooling degree \( \Delta T \) for the various feed compositions at cooling rates of 0.1 K/min and 2.5 K/min. As a result, the crystal growth rate for mixture of water - sodium chloride was proportional to 2.0 power of subcooling degree, as follows:

\[
\nu = 3.7 \times 10^{-6}(T_m - T_i)^2
\]  

(11)

The dependence of growth rate on subcooling rate is of the first power in case of a pure compound and the first to the second power for impure mixtures [4,13].

The crystal growth rate decreases with increasing the crystalline layer thickness during the growth. It means that thermal conductive resistance of crystalline layer increases with increasing the crystalline layer thickness due to increase in thermal resistance of crystalline layer.

**Thermal Conductivity of Crystalline Layer**

The temperature of coolant and melt sides, and thickness of crystalline layer were measured directly during the growth of the layer. The overall heat transfer rate Q, was obtained from the heat balance of coolant side by Equation 3. The overall heat transfer coefficient U was calculated from the heat balance of coolant side by Equation 4, with logarithm mean temperature difference between coolant and melt, and LMTD by Equation 5.

Figure 4 shows variation of the thermal conductivity of the ice crystalline layer with the elapsed time. The layer crystallizations were carried out for three different mixtures at cooling rate of 2.5 K/min. The thermal conductivity of the ice crystalline layer increases with time and is constant after about 200 s even though crystalline layer continues to be grown. It suggests that most of impurity inclusions is entrapped in the crystalline layer at the beginning of crystallization due to high constitutional supercooling. Higher feed composition yields compact crystalline layers with high thermal conductivities. The crystalline layer is developing a compact structure, such that the inclusion fraction is low. In a low feed composition, structure of crystalline layer...
is needle-like, it is therefore easy to entrap the inclusions during the growth [4].

Figures 5 and 6 show the effect of cooling rate on the overall heat transfer coefficient $U$ and the thermal conductivity $k_c$ during the growth from 3 wt% sodium chloride solution, respectively. The overall heat transfer coefficient and the thermal conductivity of crystalline layer decreases with increasing the cooling rate [14]. Thus, the growth rate increases linearly with increasing cooling rate. Higher cooling rate yields higher growth rate. The cooling rate affects structure of crystalline layer and impurity inclusions in the layer; that is, high cooling

Figure 5. Effect of cooling rate on the overall heat transfer coefficient U during the growth from 3 wt% sodium chloride solution.

Figure 7. Effect of feed composition on the overall heat transfer coefficient $U$ at cooling rates of 0.1 K/min and 2.5 K/min.

Figure 6. Effect of cooling rate on the thermal conductivity $k_c$ during the growth from 3 wt% sodium chloride solution.

Figure 8. Effect of feed composition on the thermal conductivity $k_c$ at cooling rates of 0.1 K/min and 2.5 K/min.

rates yield high impurity inclusions amounts in the layer due to high crystal growth rates. The values of the thermal conductivity were found to be 1.75, 1.41 and 1.20 at cooling rates of 0.1, 1 and 5 K/min, respectively.

Figures 7 and 8 show the effect of feed composition on the overall heat transfer coefficient $U$ and the thermal conductivity $k_c$, respectively, at cooling rate of 0.1 K/min and 2.5 K/min. The overall heat transfer coefficient and the thermal conductivity of crystalline layer decreases with increasing concentration of sodium chloride. It means that the impurity inclusions trapped in ice crystal during layer growth increases with increasing concen-
tration of sodium chloride [15].

**Conclusions**

The method for measuring thermal conductivity of ice crystalline layer was explored during the growth. Interfacial temperature and growth rate of crystalline layer can be measured. In order to evaluation of the overall heat transfer rate, the temperatures of coolant and melt, the growth rate and the thickness of crystalline layer were used. The overall heat transfer coefficient was calculated from the overall heat transfer rate. The thermal conductivity of crystalline layer was determined by overall heat transfer coefficient and heat transfer coefficient of melt and coolant. The overall heat transfer coefficient in crystallization and thermal conductivity of crystalline layer determined by the method increase with decreasing concentration of sodium chloride and cooling rate.

**Nomenclature**

- \( C_p \)  specific heat (J/kg K)
- \( d \)  diameter of crystallizer (m)
- \( h \)  heat transfer coefficient (W/m\(^2\)K)
- \( H \)  height of the layer (m)
- \( k \)  thermal conductivity (W/mK)
- \( \text{LMTD} \)  logarithm mean temperature difference
- \( L_w \)  thickness of crystallizer wall (m)
- \( L_t \)  thickness of crystalline layer (m)
- \( m_c \)  mass flow of coolant (kg/s)
- \( Q \)  heat flux (W/m\(^2\))
- \( t \)  time (s)
- \( \Delta t \)  time interval (s)
- \( T \)  Temperature (K)
- \( U \)  overall heat transfer coefficient (W/m\(^2\)K)
- \( v \)  crystal growth rate (m/s)
- \( \text{co} \)  outlet of coolant
- \( \text{ci} \)  inlet of coolant
- \( \text{cl} \)  crystalline layer
- \( i \)  S-L interface
- \( m \)  melt
- \( s \)  solid
- \( \rho \)  density (density)
- \( \lambda \)  latent heat of crystallization (J/kg)

**Subscripts**

- \( c \)  coolant side

**References**