536.421.4:621.56

Research on Heat Conduction with Freezing*
(2nd Report; Freezing of Material Systems
containing Aqua-Solutions)

by Masaru HATTORI**

Kozo KATAYAMA***, Minoru ARAKI†

Kazuo TAKAKUDA†† and Koichiro YAMANO†††

Analytical method for heat conduction with freezing, by using the apparent heat capacity which takes into account the latent heat effect, was applied to freezing of materials containing aqua-solutions. The method was examined with experiments and had its validity established for analyzing the freezing problems of materials not having a fixed freezing point but being in solidification ranges. The method to decide the apparent heat capacity by means of the phase diagram was also shown.

1. Introduction

Characteristics of freezing or melting may be classified into two types. Some materials, such as water or pure metals, have a fixed melting point (type A) and the others have no fixed melting point but a melting range (type B).

Many works have been done to analyze the heat conduction with freezing or melting of type A after Neumann and Stefan. On the other hand, we can find a few literatures concerning the analysis on the freezing problems of type B, although these are associated with many problems of practical importance like the solidification of alloys, foodstuffs, medicine, etc..

In the former report[1], the authors proposed a numerical method of analysis for both types of the freezing problems by defining the apparent heat capacity, $c\rho^*$, in which the latent heat effect is included, and gave the finite difference equation as

$$\int_{T_n^p}^{T_{n+1}^p} c\rho^* dT = \frac{\Delta t}{(\Delta x)^2} \times \left(\int_{T_n^p}^{T_{n+1}^p} \lambda dT + \int_{T_n^p}^{T_{n+1}^p} \lambda dT \right) \dots\dots\dots (1)$$

Fig.1 shows the relation among $c\rho^*$, $c\rho$ and $L\rho$ which is given by

$$\int_{T_1}^{T_2} c\rho^* dT = \int_{T_1}^{T_2} c\rho dT + L\rho \dots\dots\dots (2)$$

The validity of the method on the freezing of type A was established by comparing with an exact solution and the experimental results.

During the solidification of materials of type B, the relation between the latent heat and temperature is not always fixed owing to a change in cooling or freezing rate and effect of solute diffusion. However, for an approximate approach, that relation may be treated as a fixed one which is previously measured and so on.

In this paper, freezing of materials containing aqua-solutions, which have solidification range, is examined. The numerical results of this method are compared with the experimental results to establish the validity of the method for solution of heat conduction with a change of state of type B.

2. Nomenclatures

a :	Thermal diffusivity	[m ² /h]
C :	Concentration	[mol/kg]
$c\rho$:	Heat capacity	[kcal/m ³ °C]
$c\rho^*$:	Apparent heat capacity	[kcal/m ³ °C]
L :	Latent heat	[kcal/kg]
T :	Temperature	[°C]
t :	Time	[h]
Δt :	Time increment	[h]
Δx :	Spatial increment	[m]
λ :	Thermal conductivity	[kcal/mh°C]
ξ :	Solid fraction	[-]
Subscript		
n :	Value at $x=n\Delta x$	
p :	Value when $t=p\Delta t$	

3. Freezing of aqua-solution -I-

Tuna meat was adopted as an example of materials which contain aqua-solution. The latent heat effect was directly measured

* Received 25th May, 1976

** Associate Professor, The Technological University of Nagaoka, Nagaoka, Niigata.

*** Professor, Tokyo Institute of Technology.

† Engineer, Mitsubishi Heavy Industries, Ltd.

†† Assistant, Tokyo Institute of Technology.

††† Student, Kyushu University.

as a part of heat capacity, and the result was used for the analysis of the temperature response of the test experiments.

3-1. Measurement of thermal properties

The thermal conductivity and the heat capacity of the specimen(tuna) were measured by means of the transient comparison method [2]. The probe method was also applied for measuring the thermal conductivity.

Fig.2 shows a diagram of the measuring apparatus for the transient comparison method. Eleven plates of glass (150 mm × 150 mm × 10 mm, $\sqrt{\lambda c_p} = 20.1 \text{ kcal/m}^2\text{h}^{1/2}\text{°C}$) were used as the reference materials, and the tuna meat was sandwiched between glass plates with a thickness of 10 mm as shown in Fig.2. The specimen was placed in a constant temperature bath and initially kept at uniform temperature.

Temperature responses were measured with copper-constantan thermocouples of 0.1 mm diameter and the heater used was made of grafted carbon paper. The quantity of heat generated from the heater was measured

Fig.1 Apparent heat capacity including latent heat effect

Fig.2 A diagram of thermal properties measuring apparatus

as electric current and voltage.

Measured results of heat capacity are shown in Fig.3 with triangles. The results in solidification range are apparent heat capacities, i.e., these values include the latent heat effect. The principle of this measuring method is based on the solution of linear heat conduction. Hence, if thermal properties depend on the temperature, the measured values of heat capacity should be corrected by taking into account the effect of temperature dependency of thermal properties. Therefore the results were corrected according to the procedures mentioned below.

At first, the values of thermal conductivity and heat capacity and their temperature dependencies are assumed. Temperature responses are calculated on

Fig.3 Heat capacity of tuna

Fig.4 Correction procedures

trial basis by using assumed thermal properties, measured initial temperature and measured heat flux released from the heat source. The trial thermal properties are obtained from calculated temperature responses by the same procedure which determines the thermal properties from the experiment. If both the trial and experimental values of the thermal properties agree, the assumed values are judged to be the thermal properties of the matter at the initial temperature of the experiment. If not, the correction procedures are repeated by changing the assumed values of thermal properties. This correction procedure is shown in Fig.4 schematically.

The corrected values of apparent heat capacity of tuna are shown in Fig.3 with circles. The solid line represents the apparent heat capacity of tuna which is used for the calculation of temperature response of later freezing experiments, and it is plotted by means of the least square method from the corrected heat capacity values.

Near the freezing temperature (-1.2°C)*, the measurement and correction are limited due to the high temperature dependencies of thermal properties; so that apparent heat capacity between -5°C and -1.2°C is assumed as a linear function of temperature, the integrated value of which equals the heat of fusion obtained from the water content of tuna (72.5%).

The apparent heat capacity which is used for calculations of temperature response is as follow;

$$\left. \begin{aligned} c\rho^* &= 776 + 11030/T + 134500/T^2 \\ &\quad (-20^{\circ}\text{C} < T < -5^{\circ}\text{C}) \\ c\rho^* &= 29180 + 5045T \\ &\quad (-5^{\circ}\text{C} < T < -1.2^{\circ}\text{C}) \\ c\rho &= 1000 \quad (-1.2^{\circ}\text{C} < T) \end{aligned} \right\} \dots (3)$$

The measured values of the thermal conductivity are shown in Fig.5 as triangles. The circles in this figure are the thermal conductivity of tuna measured by the probe method. The results of the probe method will be used for calculations of temperature responses of later freezing experiments and they are shown with a solid line in Fig.5.

$$\left. \begin{aligned} \lambda &= 1.26 \quad (-6.29^{\circ}\text{C} > T) \\ \lambda &= 0.1643 \ln(|T| - 1.16) + 0.9925 \\ &\quad (-6.29^{\circ}\text{C} < T < -1.2) \\ \lambda &= 0.464 \quad (-1.2^{\circ}\text{C} < T) \end{aligned} \right\} \dots (4)$$

3-2. Experiment and analysis of freezing

Fig.6 shows a diagram of experimental apparatus used for freezing of tuna.

Specimen (tuna) was closely packed in a container made of acryl resin and polystyrol, and cooling surfaces were made of copper plates. These were sandwiched between two coolers and bolted together.

Temperature responses of specimen were

* Freezing temperature means a temperature at which solidification begins, i.e., it is the first freezing temperature. This temperature was chosen to measure the temperature recovered from super cooling.

measured with c-c thermocouples of 0.1 mm diameter which were placed in the specimen at intervals of five millimeters.

Before starting the experiments, flow rate of coolant (ethylene-glycol 40% solution) was controlled to establish equilibrium between surface temperatures. Freezing experiments were carried out after confirming that the temperature of specimen is uniform.

Experimental results of temperature responses at the cooling surface ($x=0$), $x=10$ mm, $x=20$ mm and $x=30$ mm are plotted in Fig.7 as circles. Lines in the figure are calculated results. The measured temperature of cooling surface was used as boundary condition for the finite difference calculation.

The solid lines in Fig.7 show the calculated results using the value of apparent heat capacity decided by eq.(3) and thermal conductivity as in eq.(4). Considering that the values of thermal properties used for this calculation may include some errors, because these are measured results under high temperature dependencies and the assumed apparent heat capacity, the analysis is found to be characterizing the freezing of solution fairly well.

A trial calculation was done on the assumption that the measured thermal conductivity, which is given as in eq.(4), has an error of about $\pm 5\%$. Assumed thermal

Fig.5 Thermal conductivity of tuna

Fig.6 A diagram of experimental apparatus of freezing tuna

conductivity is shown in Fig.5 with a dashed line and it is given as follows;

$$\left. \begin{aligned} \lambda &= 1.21 \quad (T < -5.7^\circ\text{C}) \\ \lambda &= 0.1577 \ln(|T| - 1.16) + 0.9716 \quad (-5.7 < T < 1.2) \\ \lambda &= 0.464 \quad (-1.2 < T) \end{aligned} \right\} \dots (5)$$

The result of trial calculation of temperature response is shown in Fig.7 with dashed lines and these agree well with experimental results.

The Chain lines in Fig.7 show the other trial calculation result. In the second trial, apparent heat capacity was decided on an assumption that the relation between concentration of solution and depression of freezing point is governed by Raoult's law. That is, the depression of freezing point ΔT is proportional to molar concentration of solute.

$$\Delta T = \frac{n}{N} \frac{RT_0^2}{H} \dots (6)$$

where n and N are mols of solute and solvent respectively, H is the latent heat of solvent (kcal/kmol), T_0 is the freezing temperature of solvent ($^\circ\text{K}$) and R is the gas constant (kcal/kmol $^\circ\text{K}$).

Since only the solvent freezes in solidification of aqua-solution, the solid fraction against temperature is expressed as

$$\xi = 1 - T_f/T \dots (7)$$

The apparent heat capacity in the region below freezing temperature ($T_f = -1.2^\circ\text{C}$) is then written as

$$cp^* = 613 + 434.4/T + 69170/T^2 \dots (8)$$

In this calculation, the value of eq.(5) was adopted as thermal conductivity of tuna.

From these results shown in Fig.7, it may be said that the finite difference method presented with eq.(1) is one of the valid method for analyzing heat conduction with freezing of type B, if thermal conductivity and apparent heat capacity are previously known.

Fig.7 Measured and calculated results of temperature response

In addition, the temperature dependencies of latent heat effect and thermal conductivity affect remarkably the analytical result, so that an accurate measurement of thermal properties taking account of the latent heat effect near the freezing point will be desirable for analyzing the heat conduction with solidification of alloys or foodstuffs.

4. Freezing of aqua-solution -II-

In solidification of alloys or solutions, a flat liquid-solid interface does not exist but there is a coexisting region of solid and liquid (solid-liquid region) between the solid region and the liquid region. The concentration of solution in solid-liquid region increases due to the solute being driven out with a progress of freezing of solvent, and the freezing point of solution depresses. Here, we tried to analyze the heat conduction with freezing of type B by a quasi-equilibrium approach assuming the solidification to progress at the liquidus temperature of phase-diagram [$T=f(C)$ in Fig.8].

In the following experiments, temperature responses in the sands having the pores saturated with glucose solution are compared with analytical results.

4-1. Analysis using phase-diagram

Following assumptions are made to formulate a finite difference equation which

Fig.8 A model of phase diagram

Fig.9 Coexistence region of solid and liquid phases

prescribes the temperature all over the solid, solid-liquid and liquid regions.

(1) Solidification progresses at the liquidus temperature on the phase diagram.

(2) Though the concentration of solution in the solid-liquid region increases with progress of solidification (as shown in Fig.9 conceptionally), the solute does not diffuse from one to another element (element means subdivided area for the finite difference calculations).

(3) Volume change due to solidification is ignored.

(4) Solution is an ideal one so that generation or absorption of heat due to the change in concentration is ignored.

A finite difference equation is formulated as follows by means of energy balance at n -th element in solid-liquid region (Fig.9) during time interval Δt .

$$\int_{T_n^p}^{T_{n+1}^p} c\rho dT + L\rho(\xi_{n+1}^p - \xi_n^p) = \frac{\Delta t}{(\Delta x)^2} \left(\int_{T_n^p}^{T_{n+1}^p} \lambda dT + \int_{T_n^p}^{T_{n+1}^p} \lambda dT \right) \quad (9)$$

where ξ_n^p is a fraction of solidified part of the n -th element at time $t = p\Delta t$.

Since the first term of the left hand side of eq.(9) does not contain the latent heat, the heat capacity $c\rho$ in the integral may be substituted by the value of heat capacity against temperature T_n^p [3]. Then the value of heat capacity in solid-liquid region can easily be obtained from the heat capacity of solid and liquid states and the solid fraction ξ_n^p .

The relation between solid fraction and solute concentration is obtained from the above assumptions and a liquidus line of the phase-diagram which gives the relation between freezing temperature and concentration;

$$T_{n+1}^p = f(c_{n+1}^p) \quad (10)$$

$$\xi_{n+1}^p = (1 - c_{fw}) / (1 - c_f / c_{n+1}^p) \quad (11)$$

where C_f and C_{fw} are initial concentrations of solution expressed by molar and weight concentrations respectively.

The left hand side of eq.(9) is essentially the same as the apparent heat capacity $c\rho^*$ given in eq.(2)

$$\int_{T_n^p}^{T_{n+1}^p} c\rho^* dT = \int_{T_n^p}^{T_{n+1}^p} c\rho dT + (\xi_{n+1}^p - \xi_n^p) L\rho \quad (12)$$

The temperature T_{n+1}^p , concentration c_{n+1}^p and solid fraction ξ_{n+1}^p can be obtained from eqs.(9)~(11).

4-2. Thermal properties of glucose solution

The thermal conductivity, heat of fusion and freezing point vs. concentration relation of glucose solution were measured. Specific heat and density are referred to International Critical Table.

Thermal conductivity of glucose solution was measured by the probe method. Fig.10 shows a schematic diagram of measuring apparatus of the probe method. A platinum wire of 50 μ m diameter and 50 mm length was used as a probe and placed at the center of a double glass tube of inner

diameter 15 mm.

A Wheatstone bridge and X-Y recorder were used to measure and record the change of electrical resistance of platinum wire. Maximum rises in temperature were limited to less than 0.2°C in solid-liquid state and 0.5°C in liquid state. The thermal conductivities of glucose solution between five and thirty weight percent are shown in Fig.11. Confirmation was made that influences of nonlinearities of thermal properties due to the latent heat effect are negligible on the measured results.

Fig.10 A diagram of the probe method

Fig.11 Thermal conductivity of glucose solutions

Fig.12 Phase-diagram of glucose solution measured

Freezing temperature vs. solute concentration relation was measured by Beckmann's thermometer. The result T - C relation

$$T = -1.84C - 0.092C^2 - 0.0076C^3$$

is plotted with a solid line in Fig.12 as the phase-diagram of glucose solution, where C is expressed with molarity mol/kg.

The quantity of heat of fusion *versus* initial concentration is shown in Fig.13. The dashed line in Fig.13 shows an assumed value taking account of quantity of solvent (water), and circles and a solid line show the measured result of latent heat of fusion using a differential scanning calorimeter.

4-3. Experiments and analysis of solidification

Toyoura sand bed saturated with glucose solution was used for the solidification experiments in order to prevent a convective flow of solution caused by temperature and concentration differences.

Thermal conductivity of sand saturated with solution is given by the following equation[4],

$$\lambda = \frac{a\lambda_s\lambda_i}{\lambda_i(1-d) + \lambda_s d} + b\lambda_i + c\lambda_s \quad \dots\dots\dots(13)$$

where $a=1-c$, $b=\lambda_{\text{vacuum}}/\lambda_s \approx 0$, $c=\phi-0.03$, $d=(1-\phi)/a$ and ϕ is porosity of sand bed ($\phi=0.37$). Thermal conductivity of sand bed in vacuo, λ_{vacuum} , may be ignored in this case because the saturant is liquid. The thermal conductivity of glucose solution is shown in Table and Fig.11 as solid lines, which smoothen the measured results. Thermal conductivity of sand particle is referred to authors' report[5], $\lambda_s = 4.3$ kcal/mh°C.

Fig.14 shows a diagram of the experimental apparatus. A cubic container, (a

Thermal conductivity of glucose solutions

Conc.	Temperature [°C]	Thermal conductivity [kcal/mh°C]
10%	~-4.0	$\lambda_0 = 1.64$
	-4.0 ~ -2.0	$\lambda_0 = -1.40 - 0.10T - 0.010T^2$
	-2.0 ~ -1.15	$\lambda_0 = -5.625 - 7.689T - 2.048T^2$
	-1.15 ~	$\lambda_0 = 0.50$
20%	~-7.0	$\lambda_0 = 1.45$
	-7.0 ~ -4.0	$\lambda_0 = 1.077 - 0.10T - 0.006667T^2$
	-4.0 ~ -2.58	$\lambda_0 = -11.17 - 7.023T - 0.9718T^2$
	-2.58 ~	$\lambda_0 = 0.48$

Fig.13 Latent heat of glucose solution

side of 150 mm), holding the sand bed was made of acryl resin, and a 2 mm thick copper plate was used as a cooling plate to make the surface temperature uniform. Thermocouples, (c-c, 0.2 mmφ), were arranged as shown in Fig.14, and temperature responses were measured and recorded with a digital voltmeter at intervals of one minute. The container was placed on a cooler and was cooled by dry ice ethanol coolant.

The experimental results of freezing of 10 and 20 weight percent glucose solu-

Fig.14 A diagram of experimental apparatus

Fig.15 Measured and calculated temperature response (10% solution)

Fig.16 Measured and calculated temperature response (20% solution)

tions are shown in Figs.15 and 16 with circles. The solid lines show the numerical results using the latent heat value plotted with the dashes line in Fig.13, and chain lines do the results using the latent heat measured by the differential scanning calorimeter (solid line in Fig.13).

These numerical and experimental results show that the method proposed in this section is valid for the analysis of the heat conduction with freezing of materials which have a solidification range.

5. Conclusion

For the freezing of materials having a solidification range, an analytical method using the apparent heat capacity, in which the latent heat effect is included, is proposed and examined. In the analyses, the apparent heat capacity was measured in two ways; one is the direct measurement and the

other uses a phase-diagram.

The proposed method is shown to be valid to analyze the heat conduction with a change of state of materials which have no fixed melting point but a solidification range.

References

- [1] Katayama, K. and Hattori, M., Bull. of the Japan Soc. Mech. Engr., 18, 115 (1975), 41.
- [2] Katayama, K. and Okada, M., Bull. of the Japan Soc. Mech. Engr., 12, 54 (1969), 1439.
- [3] Katayama, K. et al., Bull. of the Japan Soc. Mech. Engr., 15, 89 (1972), 1394.
- [4] Woodside, W. and Messmer, J.H., J. of Appl. Phys., 32, 9 (1961), 1688.
- [5] Katayama, K. et al., ASHRAE J., 15, 4 (1973), 56.