Microscopic Equations of Solidification Process of Multicomponent Alloy*

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The purpose of the present paper is to establish a system of equations which describes the growing process of every crystal in mold.

In the first place, regarding the fact that many crystals of various phases grow and move in the liquid phase during solidification, the conservative equations of mass, heat and momentum have been derived on the phase boundary between liquid and crystals as well as in the phases.

In the second place, the derived equations were discussed from the point of a boundary value problem. Thereafter it has been found that the system requires the equations of the reaction rates and the continuity of temperature on the phase boundary other than conservative equations. Accordingly, the equations of reaction rates have been derived for every component of alloy after Jackson who treated a binary solid solution.

The present system of equations were compared with the various equations used by previous workers on solidification, and it was made clear that almost all of them can be derived by introducing additional assumptions to the present system of equations.

NOMENCLATURE

C : concentration

C_p : specific heat

D_i : diffusion coefficient of component i

h : enthalpy per unit mass

I : unit tensor

J : flux vector (or tensor)

K : thermal conductivity

$k_{o,i}$: equilibrium distribution coefficient of component i

$L^{j/I}$: latent heat that forms phase j from phase I

N : number of phases

n, n' : number of components

n_f : number of unknown variables

n_B : number of necessary boundary conditions

n : unit normal vector of surface (positive direction: toward liquid phase)

p : pressure

$R^{j/I}$: velocity of growth of phase j toward phase I

r : position vector

$\dot{r}$: velocity of movement

S : surface and area

s : surface element vector

T : temperature

t : time

u : displacement vector

V : region and its volume

V : velocity of motion (convection)

X : quantity of conservation, defined for unit volume

μ : viscosity

ρ : density

σ : stress tensor

$\Psi_i^{j/I}$: reaction rate of component i at the interface where phase j forms from phase I

(Superscript) j (=I, II, $\cdots$N) : names of phases

(Subscript) i (=1, 2, $\cdots$n) : names of components

$\circ$: heat

m : momentum

I. INTRODUCTION

The last and presnt centuries have seen succesive studies conducted to analyze alloy solidification processes depending upon the theory of heat transfer[1]~[3].
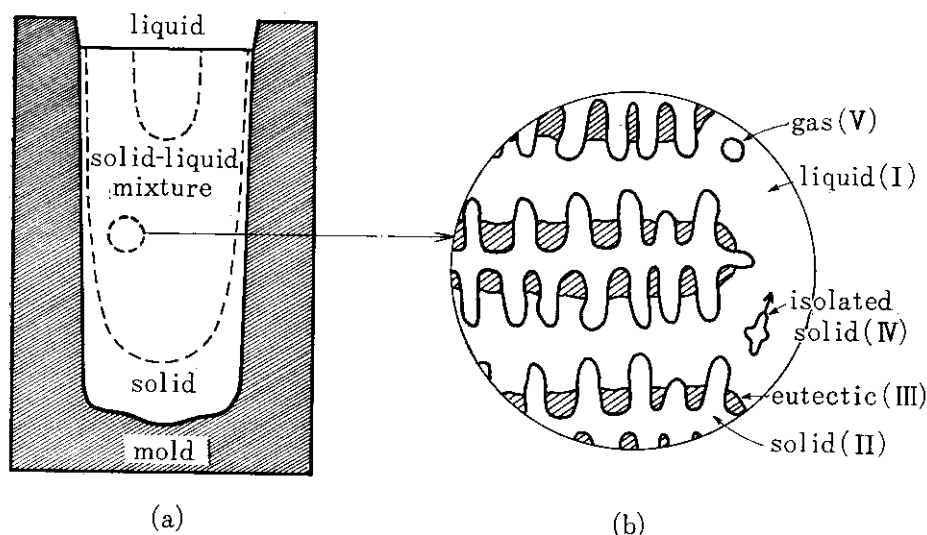
Fig. 1 Schematic representation of solidification process of alloy in a mold

Also, analytical studies based on the theory of mass transfer have been made frequently since the the work by Tiller et al.[4], revealing various features of the solidification of alloys.[5][6] Furthermore, in recent years, analytical investigations have been pursued from the viewpoints of both heat and mass transfer.[7]~[9] Meanwhile, the study of solidification with particular reference to phase diagrams has shifted from the domains of equilibrium solidification toward elucidation of non-equilibrium solidification, with the rates of reaction also taken into concideration.[7][10]

The solidification of an alloy is a process in which a large number of crystals grow simultaneously in a mold. This, however, has not yet been elucidated by any analysis. In addition, the growth of each individual crystal is evidently a reaction process caused by the temperature and concentration around it; however, the mechanism in which the reaction and heat and mass transfer couple with each other has not yet been clearly understood.

Nowadays, castings, ingots, etc. are produced in great quantities. In order to improve the production techniques, analyses have been carried out with the introduction of various models and assumptions. A correct recognition of the process of polycrystal growth and the coupling mechanism of the three things, i. e., heat and mass transfer and phase change reactions, would be fundamental for setting up these models and assumptions.

This paper presents a system of equations called herein "microscopic equations" in view of their function of describing the process in which individual cyrstals grow to form a microscopic structure.

II. THE MODEL OF ALLOY SOLIDIFICATION PROCESSES

Fig. 1 diagrammatically illustrates th process of solidification of an alloy. Generally, as shown in diagram(a), a solid portion, liquid portion and solid-liquid mixture appear in the mold. the solid-liquid mixture is enlarged in diagram(b). As shown in this diagram, in the liquid phase(I) there exist such phases as dendritic solid solutions (II) and eutectics (III), or isolated solids (IV) and gas bubbles (V). They generally move in the liquid phase. Heat and mass transfer takes place both in each phase existing here and across its boundary, and can therefore be subjected to formulation by deriving two separate groups of equations, namely, equations which govern the internal transfer (phase interior equations) and equations which govern the transfer across the boundary (phase boundary equations). In this way, a boundary value problem of multiple regions is set

up by treating as one region the space occupied by each phase in the diagramatic illustration. Since these phases and crystals which form in the solidification process are as small as several μm to several mm in size, the solidification of an alloy can be regarded as a multiregion boundary value problem associated with a very large number of regions.

The boundary, interface of each region, is moved by the motion and growth of the phase. The motion is caused by the stress exerted from the interface, gravity, and other external forces, while the growth is governed by the temperature and concentration produced at the interface as a result of heat and mass transfer. More particularly, the chemical potentials determined by the interfacial temperature and concentration govern the growth. The latent heat and solute let out along with the growth of the boundary, of course, influence the temperature and and concentration fields. This in turn affects the growth rate through the chemical potentials. Solidification proceeds under the condition in which heat and mass transfer and phase change reactions are thus coupled together. Furthermore, the multiregion boundary value problem suggests that the growth of crystal naturally influences the growth of the neighboring crystals, and such succcesive influences advance the over-all solidification of casting.

III. PRINCIPLE AND ASSUMPTIONS USED FOR DERIVATION OF MICROSCOPIC EQUATIONS

The following principle and assumptions are sufficient to derive the system of equations which governs the alloy solidification system discussed in the preceding section, povided that this does not apply to the matters concerning the derivation of the later required equations of phase change reaction rates.

First, we apply the principle of conservation of heat, of mass and of momentum. However, in ordinary solidification, kinetic energy is negligible as compared with thermal energy. So, this paper also takes this standpoint

The assumptions required next are expressions for the fluxes of heat, mass and momentum. It is now assumed that, for heat, Fourie's law,

$$J_0 = K\ grad\ T + \rho h v, \tag{1}$$

holds and that, for the mass of every component as solute, Fick's diffusion law,

$$J_i = -\rho\ D_i grad\ C_i + \rho C_i V, \tag{2}$$

holds. It is also assumed that the flux of momentum can be expressed in the general form

$$J_m = -\sigma + \rho V V \tag{3}$$

where σ is a stress teensor which can be expressed as one of various functions of velocity of motion, displacement, etc. according to the dynamic properties of the phase concerned (Newtonian fluid, elastic subatance, plastic substance, visco-elastico-plastic substance, etc.). For example, liquid, gas, or the like can be regarded substantially as a Newtonian fluid. Then, we have

$$\sigma = \mu\ grad\ V - (\frac{\mu}{3}div V + \rho)\ I. \tag{4}$$

It is also assumed here that the physical values D_i, K, μ, and ρ are all known as functions of temperature concentration pressure, etc.

IV. GENERAL CONSERVATIVE PHASE INTERIOR EOUATIONS AND CONSERVATIVE PHASE BOUNDARY EOUATIONS

Conservative equations concerning heat and mass transfer as phase interior equations have already been well known. However, no report has ever disclosed any systematic examination of what types of equations are available as conservative phase boundary equations. With this in mind, we are about to derive conservative phase boundary equations in terms of a general quantity of conservation Xi, covering heat, mass, etc. and its flux Ji. First, as is well konwn, the conservative phase interior epuations may be written in the form[12]

$$\frac{\partial X_i^j}{\partial t} = -div\ J_i^j \tag{5}$$

where i stands for the general quantity, i= 0 for heat, i=1, 2, 3,......n for solvent, stlute 2, solute 3, ... solute n respectively, and i=m for momentum, while the superscript letter j (=I, II, III, ...N) represents phase numbers, and generally j=I for liquid.

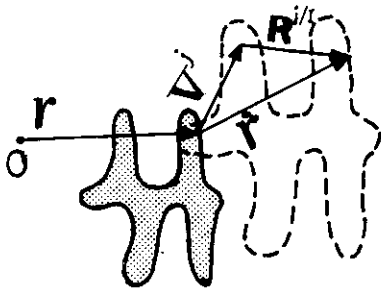Let us now derive the conservative phase boundary equations. For this purpose, we consider a point r

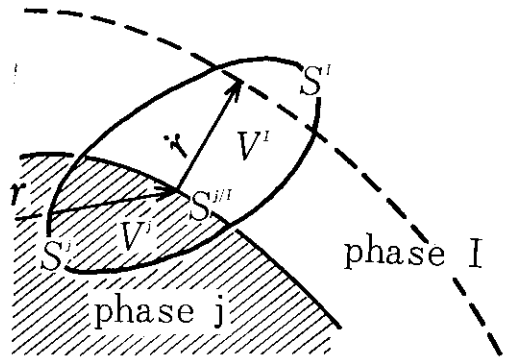**Fig. 2** Movement vector of a crystal in motion and growth.

Fig. 3 Conservation in the vincity of interfacial position **r**.

on the boundary (interface) of a crystal which grows while moving as shown in Fig. 2. The point **r** gets to $r+\dot{r}$ after the lapse of unit time. Since every point on the phase boundary moves in such a manner, the whole phase can be considered to change in shape and position as shown by dotted line in Fig. 2. If the point **r** is growing at a velocity $R^{j/I}$ and moving at V^j, then

$$\dot{r}=R^{j/I}+V^j. \qquad (6)$$

In this case, the principle of conservation can be applied around the point **r** by taking a small zone of space V around the point as shown in Fig. 3. V consists of a portion V^j included in the phase j and a portion V^I included in the phase I. We now denote the boundary of V^j by S^j, the boundary of V^I by S^I, and the boundary portion between the adjoining V^j and V^I by $S^{j/I}$. First, we treat the whole of V in terms of conservation. The increase of the quantity concerned within V in unit time is equal to the sum of incoming flows across the boundary of V. So, we can write,

$$-\frac{\partial}{\partial t}\left(\iiint_{V^j}X_i^j dV+\iiint_{V^I}X_i^I dV\right)=-\left(\iint_{S^j}J_i^j\cdot ds\right.$$
$$\left.+\iint_{S^I}J_i^I\cdot ds\right). \qquad (7)$$

Next, considering the same balance for each of V^I and V^j and applying the formula (5) and the divergence theorem, we obtain

$$-\frac{\partial}{\partial t}\iiint_{V^j}X_i^j dV=\iiint_{V^j}\frac{\partial X_i^j}{\partial t}dV+\iint_{S^{j/I}}X_i^I\dot{r}\cdot ds$$
$$=-\iint_{S^j}J_i^j\cdot ds+\iint_{S^{j/I}}(X_i^j\dot{r}-J_i^j)\cdot ds,$$
$$(8)$$

$$-\frac{\partial}{\partial t}\iiint_{V^I}X_i^I dV-=-\iint_{S^I}J_i^I\cdot ds-\iint_{S^{j/I}}(X_i^I\dot{r}-J_i^I)\cdot ds.$$
$$(9)$$

The sum of the left sides of the expressions (8) and (9) is the left side of the expression (7). Substituting and rearranging, therefore, we have

$$\iint_{S^{j/I}}\{J_i^j-J_i^I-(X_i^j-X_i^I)\ \dot{r}\}\cdot ds=0. \qquad (10)$$

The volume of V taken around the point **r** can arbitrally be reduced. Eventually we have

$$\{J_i^j-J_i^I-(X_i^j-X_i^I)\ \dot{r}\}\cdot n=0. \qquad (11)$$

This is the wanted set of general conservative phase boundary epuations. The positive sense of the vector direction is toward phase I from phase j.

V. MICROSCOPIC EOUATIONS OF HEAT AND MASS TRANSFER

The microscopic equations can be obtained by substituting concrete conservation quantiies of heat, mass and mnmentum into the general conservative equations of the foregoing section. That is, as quantities corresponding to the quantity of conservation X_i^j, $\rho^j h^j$, $\rho^j C_i^j$ and $\rho^j v^j$ are taken for heat,, mass

Table 1 Derived equations of heat and mass transfer for
microscopic solidification of n-component-alloy.

conservation	phase interior equations	phase boundary equations
heat	$\rho^j\,C_p^j\dfrac{\partial T^j}{\partial t}=div\,K^j\,\text{grad }T^j$ $-\rho^j\,C_p\,V^j\cdot\text{grad }T^j \quad (1)$	$\{K^j\,\text{grad }T^j-K^I\,\text{grad }T^I$ $-\rho^j\,L^{j/I}R^{j/I}\}\cdot\boldsymbol{n}=0 \qquad (5)$
mass (i=2~n)	$\dfrac{\partial}{\partial t}(\rho^j\,C_i^j)=div(\rho^j\,D_i^j\,\text{grad }C_i^j$ $-\rho^j\,C_i^j\,V^j) \qquad (2)$	$\{-\rho^j\,D_i^j\,\text{grad }C_i^j+\rho^I\,D_i^I\,\text{grad }C_i^I-(\rho^j\,C_i^j$ $-\rho^I\,C_i^I)\,R^{j/I}-\rho^I\,C_i^I(V^I-V^j)\}\cdot\boldsymbol{n}=0\;(6)$
mass (total)	$\dfrac{\partial\rho^j}{\partial t}=-div\,(\rho^j V^j) \qquad (3)$	$\{(\rho^I-\rho^j)\,R^{j/I}-\rho^I\,(V^I-V^j)\}\cdot\boldsymbol{n}=0 \quad (7)$
momentum	$\rho^j\dfrac{\partial V^j}{\partial t}=div\,\boldsymbol{\sigma}^j-(\rho^j V^j\cdot\text{grad})\,V^j$ $+\rho^j K^j \qquad (4)$	$\{-\boldsymbol{\sigma}^j+\boldsymbol{\sigma}^I-\dfrac{\rho^j}{\rho^I}(\rho^j-\rho_I)\,R^{j/I}R^{j/I}\}$ $\cdot\boldsymbol{n}=0 \qquad (8)$

and momentum, respectively. Also, we apply the relations (1) – (3) to J_i^j. Upon substitution into the equations (5) and (11) and rearrangement, we can derive the system of equations shown in Table 1, using the following and other relations.

$$\frac{\partial h^j}{\partial T}=C_p^j, \qquad \text{definition of specific heat}$$

$$\sum_{i=1}^{n}C_i^j=1, \qquad \text{definition of concentration}$$

$$\sum_{i=1}^{n}D_i^j\,grad\,C_i^j=0 \qquad \text{defnition of diffusion}$$

$$L^{j/I}=h^j-h^I, \qquad \text{difinition of latent heat}$$

(12)

The equations (1) and (2) in Table 1 correspond to the well known equation of heat conduction with convection and that of diffusion respectively, while the equations (3) and (4) correspond to the equation of continuity and that of motion in hydrodynamics, both being also well known. In the expression (4), external force K^j such as gravity is also involved. Of the phase boundary equations, those represented by (5) and (6) have so far been frequently used in solidification analyses. The expression (7), which has also been used in certain cases, governs the convection due to solidification shrinkage. The expression (8) is not found in the earlier literature. This formula expresses that, if there is a density difference between two phases, different stresses act on the phase boundary during growth.

In the system of equations listed in Table 1, unknown variables to be solved as functions of time and position are T^j, C_i^j (i=2~n), V^j, $\boldsymbol{\sigma}^j$ and $R^{j/I}$.

VI. PHASE BOUNDARY EQUATIONS TO BE ADDED

Let us examine the conditions under which the unknown variables of the system of equations in Table 1 can be determined as the solution of the multiregion boundary value problem of N regions (j =I~N).

First, as to the phase interior equations (1)–(4), the number of the independent equations coincides with that of the unknown variables. In this sense, there are sufficient conditions for determining the solution. What matters, however, is the relation between the number of the phase boundary equations and that of the independent variables, and the equations (5)—(8) given only by the conservation relations cannot provide a sufficient number of boundary conditions. So, we now examine how many phase boundary equations are lacking and how they should be given.

For example, the analysis of the solidification of a pure metal as a Stefan problem employs, in addition to the formula (5) in Table 1, two independent phase boundary conditions as $T^j=T^I=$ melting point.[13] Also, in the analysis of the solidification of a solid solution as a diffusion problem, as Tiller et al.[4] did, we assume the growth velocity $R^{j/I}$ is known (this assumption uncouples heat transfer from mass transfer) and add phase boundary equations of the type

$C_i^j/C_i^I = k_o$, i (equilibrium distribution coefficients). More such examples induce the following general statement:

If the boundary between two phases for which there holds such a system of second order differential equations as the equations (1) and (2) in Table 1 has n_f unknown variables in all, the number of independent boundary equations required to solve this boundary value problem is given by

$$n_B = \begin{cases} n_f: \text{ when the boundary growth velocity} \\ \quad \text{ is known} \\ n_f+1: \text{ when the boundary growth velo-} \\ \quad \text{ city is unknown.} \end{cases} \tag{13}$$

We now assume that a solid solution of n components grow from a liquid phase of the n components. Then, for the phase boundary, the unknown variables included in the equations (1) and (2) in Table 1 are T^j, T^I, C_i^j (i=2~n), and C_i^I (i=2~n), their total number being 2n (on the assumption that, in this case, V^j and V^I are independently determined by the system of equations (3), (4), (7) and (8)). Therefore, a general system in which the growth velocity is unknown requires (2n+1) phase boundary equations. The equations (5) and (6), however, give only n conditions. The remaining conditions must be givn by something other than the principle of conservation.

Baker et al.[14] regard the continuity of temperature at the phase boundary as a basic condition. This is also a condition employed in all analyses of Stefan problems which have been carried out up to the present, and may be written as

$$T^j = T^I. \tag{14}$$

The number of the remaining phase bounbary conditions is $(2n+1)-n-1=n$.

We now presuppose that these conditions should be given by equations of reaction rates. Jackson regards the reaction of solidification of a n-component solid solution as the assemblage of independent phase change reactions of individual n components.[15] The derivation of concrete equations of reaction rates from this standpoint will be achieved in another paper.

However, we here assume that, from this stand-

point, we have derived the mass of component i subjected to phase change per unit area of the phase boundary in unit time, $\Psi_i^{j/I}$. Then, it must be emphasized that this is related to the amount of mass transfer as follows:

$$\Psi_i^{j/I}(C_i^j, C_i^I, T^j) = \{\rho^j C_i^j R^{j/I} + D_i^j \rho^j \text{ grad } C_i^j\} \cdot n \tag{15}$$
$$(i=1 \sim n)$$

The n relations represented by this expression (15) are the wanted phase boundary equations. The right side of the formula (15) can be obtain by calculation on the premise that, in Fig. 3, the amount of phase change is the difference between the mass increase in V^j in unit time and the amount of efflux from the boundary S^j of V^j. The left-side reaction rate expression generally becomes a function of the temperature on the phase boundary and the concentrations of both phases.

Next, we consider the case in which a solid solution of n' (n'<n) components forms from a n-component liquid phase. The number of unknown variables is $n_f = n+n'$, and the equations (5) and (6) in Table 1 give n boundary conditions. (The equations (6) are made to hold by placing $C_i^j = 0$ for the components unrelated with the solid solution.) The equation (14) holds as it is. So, the remaining number is $(n+n'+1)-n-1=n'$. If, therefore, equations of the from (15) are given for n' components $(i=1\sim n')$, they make up sufficient conditions. In short, in the case of the formation of a solution of less components, no special consideration is required in the application of the derived equations.

Next, we consider the case in which n'-component compounds form from a n-component liquid phase. Since the concentration of the compound phase is fixed, the equations (2) in Table 1 are unnecessary, and the unknown variables are T^j, T^I and C_i^I (i= 2~n); thus, $n_f = n+1$. In this case also, the equations (5) and (6) in Table 1 and the equation (14) in the text hold as they are. Accordingly, the number of the remaining boundary equations is $(n+1+1)-n-1=1$. In short, the reaction of conpound formation requires one equation of reaction rate. This rate equation can be determined as follows, by considering that the formula (15) holds for a rate-determin-

Table 2 Microscopic equations for pure metals

	phase interior equations	phase boundary equations
conservation of heat	$\rho^j C_p^j \dfrac{\partial T^j}{\partial t} = div \; K^j \; grad \; T^j$ $- \rho^j C_p^j V^j \cdot grad \; T^j$ (1)	$\{K^j \; grad \; T^j - K^I \; grad \; T^I$ $- \rho^j \; L^{j/I} R^{j/I}\} \cdot n = 0$ (4)
conservation of mass	$\dfrac{\partial \rho^j}{\partial t} = - div(\rho^j V^j)$ (2)	$\{(\rho^I - \rho^j)R^{j/I} - \rho^I (V^j$ $- V^I)\} \cdot n = 0$ (5)
conservation of momentum	$\rho^j \dfrac{\partial V^j}{\partial t} = div \; \sigma^j - (\rho^j V^j \cdot grad) V^j$ $+ \rho^j K^j$ (3)	$\{-\sigma^j + \sigma^I - \dfrac{\rho^j}{\rho^I}(\rho^j - \rho^I)R^{j/I}R^{j/I}\}$ $\cdot n = 0$ (6)
kinetic or thermodynamical requirement		$T^j = T^I$ (7) $\Psi^{j/I} = \rho^j R^{j/I} \cdot n$ (8)

ing component among the n' components.

Since C_i^I are fixed for compounds, the expression (15) reduces to

$$\frac{\Psi^{j/I}}{C_i^j} = \rho^j R^{j/I} \cdot n \qquad (16)$$

We now assume that $\Psi_i^{j/I}$ of each component is a quantity determined independently of the other components by reaction kinetics. Then, the left side of the formula (16) should have different values for the individual components, whereas the right side has a fixed value irrespective of each component. This can be reasonably explained by considering that only $\Psi_i^{j/I}$ of a certain rate-determining component is determined independently by reaction kinetics, while the reaction rates $\Psi_i^{j/I}$ of the other components lower, following that of the rate-determining component.

It is therefore necessary to examine which component is the rate-determining. To do so, we first obtain, for all components, the values of $\Psi_i^{j/I}$ which are kinetically determined, and subsequently compare the resulting values of $\Psi_i^{j/I} / C_i^j$. Then, the component having the smallest absolute value is the rate-determining one. In short, in the case of the formation of compounds, the formula (15) applied to the thus found rate-determining component becomes the phase boundary equation.

VII. DISCUSSION

A system of equations has thus been established

to describe the process of growth of polycrystals of an alloy in a mold. The growth reaction expression $\Psi_i^{j/I}$ included in the equation system will be expressed in concrete forms in another paper.

First, we examine by this equation system how heat and mass transfer and phase change reactions are coupled. We begin by rewriting the equation system for a pure metal ($n=1$). Then we have the equations shown in Table 2. In this equation system, the unknown variables to be solved are T^j, T^I, V^j, V^I, σ^j, σ^I, and $R^{j/I}$, none of which can be solved independently of the others. If, however, we let $\rho^j = \rho^I$, the phase boundary formula (5) can be rewritten as $V^I = V^j$, thus having no relation to $R^{j/I}$. Then, the equations (2), (3), (5) and (6) in Table 2 constitute a equation system for determining V^j, V^I, σ^j, and σ^I (or pressure p), while the remaining equations (1), (4), (7) and (8) make up another equation system for determining T^j, T^I and $R^{j/I}$. That is, the mass transfer system is uncoupled from the heat transfer system. This means in terms of physics that since there is no density difference, there occurs no convection due to solidification shrinkage, with the velocity determined regardless of solidification. The temperature distribution is influenced by convection velocity according to the formula (1) in Table 1. However, V can be treated as a known value, so that we do not say that they are coupled.

Next, we turn to a binary solid solution ($n=2$). The microscopic equations which hold in this case are the equations in Table 2, the equations (2) and

(6) in Table 1, and the equation (15) ($i=2$) in the text. In this system of equations, all are coupled. However, if the densiry can be assumed to have no relation to temperature or concentration and we can let $\rho^I = \rho^j$, then there is an independent equation system for the velocity just as in the case of a pure metal. In the remaining equation system, the temperature, concentrations and growth velocity are coupled. By solving this system, the interfacial temperature, concentrations and growth velocity can be determined at the same time. It is therefore also possible to ascertain by calculation how the relation between the temperature and concentrations deviates from the equilibrium phase diagram. The details of the calculation will be presented in a separate report. We here examine how earlier analytic methods have accomplished the required uncoupling.

Except for one case[7], no mass transfer analysis has been made with a system of equations including those of reaction rates. The previous analyses have taken the viwpoint that, for the interfacial temperature and concentrations, the relations between equilibrium temperature and concentrations on the phase diagram,

$$C_2^j / C_2^I = k_{o,2} : \text{equilibrim distribution coefficient} \quad (17)$$

$$C_2^I = C_2^j(\Psi) : \text{concentration on liquidus line} \quad (18)$$

hold. If we ignore the formula (15) and take the relations (17) and (18), the number of the boundary conditions surely meets the formula (13), so that we can obtain the solution. Nevertheless, we cannot avoid the physical contradiction that the interface is growing under the equilibrium conditions On the other hand, if we use the formula (13), $\Psi_i^{j/I}$becomes zero when the relations (17) and (18) hold. Hence the expression (15) reduces to

$$\{ C_i^j R^{j/I} + D_i^j \text{ grad } C_i^j \} \cdot n = 0 \quad (19)$$

Adding up to n ($i=1 \sim n$), according to the definitions (12), we obtain

$$R^{j/I} \cdot n = 0. \quad (20)$$

The growth velocity of the interface thus becomes zero automatically.

There has been no reported case of analyzing the solidification process of a solid solution of three or more component. If, however, we try to make such analysis without using any reaction rate equations, there arises the need for setting up three or more independent boundary conditions instead of the set of equations (15). These conditions are difficult to derive from the phase diagram in the same manner as in the case of the binary system. That is, the method which has so far been used for the binary system is difficult to apply extensively to the system of thrree or more components, and the handling of the formula (15) derived herein seems natural.

VIII CONCLUSION

(1) As evidenced above, the process of solidification of an alloy composed of multicomponent multiphase polycrystals can be formulated as a multiregion bouudary value problem in which heat and mass transfer and the phase change reaction are multually coupled.

(2) The system of equations derived herein describes the process of formation of a microstructure of alloy by solidification, and can be applied not only to solidification processes including the formation of solid solutions but also to those involving the formation of compounds.

(3) We can derive the equation system used in previous analytical works, by introducing additional assumptions into the present system of microscopic equations.

Concrete forms of the reaction rate exression included in the system of microscopic equations derived herein will be reported in a separate paper. The details of an analysis of solidification phenomena with the use of this equation system will also be separately reported.

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