Computer Assisted Mechanics and Engineering Sciences, 7: 391–402, 2000.

Modeling of transport phenomena during solidification of binary systems

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(Received September 6, 1999)

The macroscopic equations describing the process of solidification in binary systems are usually introduced via the volume averaging technique. A different approach to obtain these equations, based on the ensemble averaging technique, is proposed in the paper. This technique was used to derive energy and solute conservation equations and the basic constitutive relations appearing in the macroscopic description of the solidification phenomena occurring in the mushy region. In general these relations are non-local and account for non-equilibrium processes. Problem of thermodynamic equilibrium (thermal and chemical) is also discussed. Formulae for enthalpy and porosity of the mushy zone, in the latter case, are given.

1. INTRODUCTION

Solidification problems play an important role in material processing (like casting of steel, non-ferrous alloys, metal-matrix composites) [1, 24], the ground freezing technique, in phase change materials used in thermal energy storage systems, etc. In most of these processes multicomponent solutions are present. These multicomponent solutions undergo solidification over a range of temperatures which causes a solid–liquid mixture to be formed.

The solid–liquid zone, where solidification takes place and known as a mushy region, consists of solid and liquid phases of varying proportions and often makes a substantial part of the whole system [1, 23]. As properties of this system undergo step-wise variation when crossing the phase boundaries, the mushy zone can be treated as a heterogeneous medium. This heterogeneous medium has however some specific, distinct features which are not met in other heterogeneous media like composites, granular or porous media. Within the mushy region proportions of solid and liquid vary in time and space. Thus porosity of the heterogeneous medium is varying from place to place and its determination makes part of the problem [1, 16]. Moreover, transport phenomena occurring in the individual phases and the mutual interactions between solid and liquid are assisted by the phase-change phenomenon with heat generation at the solid–liquid interface. Thus the mushy zone is a heterogeneous medium with local heat sources [9].

Complex microstructure of the mushy region is the main reason for carrying out the analysis on the macroscopic scale, the scale that smoothes out local variation of field variables caused by presence of dendrites or equiaxed crystals formed during the solidification. Thus, before any numerical implementation, a problem of macroscopic modeling of heat and mass transfer phenomena in the mushy region should be addressed. Replacement of the transport phenomena occurring in a two-phase medium with step-wise varying properties (referred as microscopic description) with corresponding transfer phenomena occurring in a single phase continuum with constant or smoothly varying effective properties (macroscopic description) is often known as the homogenization [8]. When carrying out homogenization two basic problems should be answered: (i) how the macroscopic equations look like and (ii) how to determine the effective properties?

Different methods (spectral, variational, volume averaging, ensemble averaging, etc.) were used to obtain macroscopic description of phenomena occuring in heterogeneous media. The volume averaging method and the ensemble averaging are the most common and claim generality of application. It should be however stressed that they are different and, in general, lead to different results.

The macroscopic equations describing the process of solidification are usually introduced via the volume averaging technique [2, 12, 17, 16, 19]. The volume averaging method is based on the concept of a representative elementary volume (REV). Any macroscopic, physical quantities appearing in equations obtained as a result of this method are understood as spatially integrated over the REV and related to the centroid of the REV. Speaking about variation of the macroscopic quantities over distances smaller than dimensions of the REV makes no sense within this approach. Limitations of the volume averaging are realized by some investigators and extensions of this approach are sought which are based on introduction of some weighing functions and using the theory of distributions [18].

A different approach to describe solidification process in the mushy region, based on an ensemble averaging, is proposed in the paper. The ensemble averaging comes from theory of random fields and stochastic processes where it has proved to be useful in finding solution of many problems that appear both in description and understanding of the transport phenomena [3, 4, 13, 14]. The approach is based on the concept of an ensemble of realizations of the microstructure [5, 8, 11, 20] and does not need the notion of the REV. Any macroscopic, physical quantities appearing in the macroscopic equations obtained with this method are understood as statistically mean values (awaited values) defined in any point in the medium. Although the ensemble averaging method has been applied to macroscopically nonhomogeneous media [20], i.e. with effective properties varying, to the author's knowledge it has been not used in solidification problems.

The scope of the paper has been limited to presentation of the solute concentration and the energy equations. In both cases the microscopic constitutive equations in both solid or liquid phase have the same form (Fourier and Fick's laws). The case of the macroscopic momentum equation has been set aside as the microscopic constitutive relations are different in both phases (solid is rigid) [1, 2, 10].

The paper has been organized in the following way. The second section presents basic ideas and definitions associated with the ensemble averaging method. The third section containes derivation of the solute concentration equation and shows how assumption of local, macroscopic equilibrium effects description of the solute transport in the mushy region. The next section discusses the energy equation and limitations in its form introduced by the assumption of local, macroscopic thermal equilibrium. The fifth section presents formulae for the macroscopic enthalpy of the mushy zone when treated as the single phase continuum and derives a formula for the local porosity (liquid fraction) in the mushy zone when both local thermal and chemical equilibrium are valid. Finally the last section gives a brief summary of the main results and suggests problems to be further resolved.

2. FUNDAMENTALS OF THE ENSEMBLE AVERAGING

Let us assume that solidification of the binary mixture occurs in a volume V containing two phases – solid (S) and liquid (L). A set of characteristic points, which may be treated as nucleation sites, are spread all over the considered volume. A nucleation site, when activated, may give rise to a formation of the solid phase. Any spatial distribution of these points is considered to be a different configuration so that an ensemble of configurations is formed. The probability density function associated with the ensemble Ω has been denoted as $p(\Omega)$.

For any moment of time t and any configuration Ω, distribution of the phases is described by the so-called structure (characteristic or phase) function [8]

$$\theta_i = \theta_i(t, \mathbf{x}|\Omega) = \begin{cases} 1 & \text{for } \mathbf{x} \in V_i\,, \\ 0 & \text{for } \mathbf{x} \notin V_i\,, \end{cases}$$

where V_i denotes the volume filled with i-th phase. It is also convenient to introduce a generalized variable defined as

$$f(t, \mathbf{x}|\Omega) = \theta_S(t, \mathbf{x}|\Omega)\, f_S(t, \mathbf{x}|\Omega) + \theta_L(t, \mathbf{x}|\Omega)\, f_L(t, \mathbf{x}|\Omega) \tag{1}$$

which allows to write the governing equations in one, unified way.

Before deriving equations describing macroscopic transport processes it is useful to define two different ensemble averages. The first of them is *the bulk (macroscopic)* average

$$\{f(t,\mathbf{x})\} = \int f(t,\mathbf{x}|\Omega)\, p(\Omega)\, \mathrm{d}\Omega \tag{2}$$

which should be understood as the awaited value in the statistical sense. If function f is taken to be the structure function θ_i then its bulk average is equal to the volume fraction of the i-th phase

$$\{\theta_i(t,\mathbf{x})\} = \varepsilon_i(t,\mathbf{x})\,. \tag{3}$$

The second average is *the phase (intrinsic) average* $\{f\}_i$ defined by the relation

$$\{\theta_i(t,\mathbf{x})\, f(t,\mathbf{x})\} = \varepsilon_i(t,\mathbf{x})\, \{f(t,\mathbf{x})\}_i \tag{4}$$

which gives the mean value of the respective function in the i-th phase.

The bulk averages of the basic thermodynamic variables like temperature T and solute mass concentration C can thus be expressed as

$$\{T(t,\mathbf{x})\} = \varepsilon_S(t,\mathbf{x})\ \{T(t,\mathbf{x})\}_S + \varepsilon_L(t,\mathbf{x})\ \{T(t,\mathbf{x})\}_L\ , \tag{5}$$

$$\{C(t,\mathbf{x})\} = \varepsilon_S(t,\mathbf{x})\ \{C(t,\mathbf{x})\}_S + \varepsilon_L(t,\mathbf{x})\ \{C(t,\mathbf{x})\}_L\ , \tag{6}$$

while the bulk velocity in the medium, when the solid phase is assumed to be stationary, is given by

$$\{\mathbf{w}(t,\mathbf{x})\} = \varepsilon_L(t,\mathbf{x})\ \{\mathbf{w}(t,\mathbf{x})\}_L\ .$$

One of the specific features of the ensemble averaging technique is that the operator of the ensemble averaging commutes with differentiation with respect to $\mathbf{x}$ and t [11]. This occurs by virtue of independence of the probability density function on the space variable and time.

The problem of relation between the ensemble and volume averaging has been discussed in a number of papers [4, 8, 11, 13, 20, 22]. In these cases, where the REV exists, it is possible to compare results coming from these two approaches using *the ergodic theorem* [3, 11, 20]. When the ergodic theorem holds, i.e. when the macroscopic fields, obtained by statistical averaging, are stationary then volume averaged quantities are equal to ensemble averaged. There are many cases when the condition of stationarity does not hold even if the REV can be distinguished in the medium. For instance in the unsteady states of heat transfer (when not whole of the REV is filled with thermal disturbance), near the external boundaries or close to solidus or liquidus lines (where the microscopic properties of the material vary), in places where heat sources or sinks are present or the microstructure of the medium is varying (mushy zone). In all these cases, in order to properly apply the ergodic theorem, one should look for locations where the condition of stationarity holds. These may be, for example surfaces, parallel to solidus or liquidus lines over which spatial integration should be carried out [8, 22].

3. SOLUTE BULK CONCENTRATION EQUATION

Within limits of validity of the Fick's law for solute diffusion the equation describing solute transport in the medium can be written as

$$\partial_t(\rho C) + \nabla \cdot (\mathbf{w}\rho C + \mathbf{j}) = 0. \tag{7}$$

As the concentration C is discontinuous at the phase boundaries it is convenient to use the concept of solubility M defined by the expression

$$M(t,\mathbf{x}|\Omega) = \theta_S(t,\mathbf{x}|\Omega)\kappa + \theta_L(t,\mathbf{x}|\Omega) \tag{8}$$

where κ stands for the partition factor equal to $\kappa = C_S/C_L$ at the interface between the phases. The product of solubility and concentration is continuous across phase boundaries [14]. This allows to write the Fick's law for the solute flux $\mathbf{j}$ in the alternative form

$$\mathbf{j} = -(D/M)\nabla(MC) \tag{9}$$

where

$$D(t,\mathbf{x}|\Omega) = \theta_S(t,\mathbf{x}|\Omega)D_S + \theta_L(t,\mathbf{x}|\Omega)D_L$$

is the solute diffusivity.

The ensemble averaging of the solute concentration, Eq. (7), leads to

$$\partial_t\{\rho C\} + \nabla\cdot\{\mathbf{w}\rho C + \mathbf{j}\} = 0. \tag{10}$$

In order to find the final, macroscopic form of the solute concentration equation the ensemble averages appearing in the above equation should be expressed as a function of the bulk concentration $\{C\}$. This can be achieved if relation between microscopic concentration C and its bulk value is known. The solute concentration is written as

$$C = P_{\mathrm{eq}}\{C\} + C' \tag{11}$$

where P_{eq} stands for phase equilibrium function and C' denotes a fluctuation. The formal relation between C and $\{C\}$ can be derived, in a manner identical to presented in [8], using the Green function theory, and the final expression can be given in the following form,

$$(MC) = \{MC\} + \int_0^t\!\!\int_V \varphi_C\cdot\nabla'\{MC\}\,\mathrm{d}V'\mathrm{d}\tau + \int_0^t\!\!\int_V \psi_C\,\partial_\tau\{MC\}\,\mathrm{d}V'\mathrm{d}\tau. \tag{12}$$

The functions φ_C and ψ_C satisfy the following integro-differential equations:

$$\begin{aligned}\varphi_C = {}&\int_0^t\!\!\int_V \nabla G\cdot\left[(\mathbf{w}\rho)'\varphi_C - D'(\mathbf{1}\delta_t\delta_\mathbf{x} + \nabla\varphi_C) - \{(\mathbf{w}\rho)'\varphi_C - D'(\mathbf{1}\delta_t\delta_\mathbf{x} + \nabla\varphi_C)\}\right]\mathrm{d}V'\mathrm{d}\tau\\ &-\int_0^t\!\!\int_V G\left[(\mathbf{w}\rho)'\delta_t\delta_\mathbf{x} + \rho'(\partial_\tau\varphi_C + \varphi_C\delta_\tau) - \{(\mathbf{w}\rho)'\delta_t\delta_\mathbf{x} + \rho'(\partial_\tau\varphi_C + \varphi_C\delta_\tau)\}\right]\mathrm{d}V'\mathrm{d}\tau,\end{aligned} \tag{13}$$

$$\begin{aligned}\psi_C = {}&\int_0^t\!\!\int_V \nabla G\cdot\left[(\mathbf{w}\rho)'\psi_C - D'\nabla\psi_C) - \{(\mathbf{w}\rho)'\psi_C - D'\nabla\psi_C)\}\right]\mathrm{d}V'\mathrm{d}\tau\\ &-\int_0^t\!\!\int_V G\left[\rho'(\partial_\tau\psi_C + \psi_C\delta_\tau + \delta_\tau\delta_\mathbf{x}) - \{\rho'(\partial_\tau\psi_C + \psi_C\delta_\tau + \delta_t\delta_\mathbf{x})\}\right]\mathrm{d}V'\mathrm{d}\tau,\end{aligned} \tag{14}$$

where:

$$(\mathbf{w}\rho)' = \mathbf{w}\rho/M - \mathbf{w}_r\rho_r\,, \qquad D' = D/M - D_r\,, \qquad \rho' = \rho/M - \rho_r\,.$$

The subscript r, in the above definitions, denotes certain reference quantity associated with the Green function G while δ_t and $\delta_\mathbf{x}$ stand for Dirac pseudofunction.

Using Eqs. (11) and (12), and the assumption $\{MC\} = \mathrm{const}$, it is possible to obtain the following expression for the equilibrium function

$$P_{\mathrm{eq}}(t,\mathbf{x}|\Omega) = \theta_S(t,\mathbf{x}|\Omega)\,\frac{\kappa}{\varepsilon_L + \kappa\varepsilon_S} + \theta_L(t,\mathbf{x}|\Omega)\,\frac{1}{\varepsilon_L + \kappa\varepsilon_S}\,. \tag{15}$$

Substituting Eq. (12) into the ensemble averaged terms appearing in Eq. (10) allows to write the latter in the following form,

$$\{\mathbf{w}\rho C + \mathbf{j}\} = \{\mathbf{w}\}(\rho P_{\mathrm{eq}})_L\{C\} - \int_0^t\!\!\int_V D_{\mathrm{ef}}\cdot\nabla'\{C\}\,\mathrm{d}V'\mathrm{d}\tau - \int_0^t\!\!\int_V \nu_{C\mathrm{ef}}\,\partial_\tau\{C\}\,\mathrm{d}V'\mathrm{d}\tau\,, \tag{16}$$

$$\{\rho C\} \qquad = \{MP_{\mathrm{eq}}\}\left[\{\rho/M\}\{C\} + \int_0^t\!\!\int_V \zeta_{\mathrm{ef}}\cdot\nabla'\{C\}\,\mathrm{d}V'\mathrm{d}\tau + \int_0^t\!\!\int_V \mu_{\mathrm{ef}}\,\partial_\tau\{C\}\,\mathrm{d}V'\mathrm{d}\tau\right], \tag{17}$$

where

$$\begin{aligned} D_{\mathrm{ef}} &= \{DP_{\mathrm{eq}}(\mathbf{1}\delta_{\mathrm{x}}\delta_t + \nabla\varphi_C)\} - (\rho/M)_L\{MP_{\mathrm{eq}}\}\{\theta_L\mathbf{w}\varphi_C\}, \\ \nu_{C\mathrm{ef}} &= \{DP_{\mathrm{eq}}\nabla\psi_C\} - (\rho/M)_L\{MP_{\mathrm{eq}}\}\{\theta_L\mathbf{w}\psi_C\}, \\ \zeta_{\mathrm{ef}} &= \{\rho/M\varphi_C\}, \\ \mu_{\mathrm{ef}} &= \{\rho/M\psi_C\}. \end{aligned} \tag{18}$$

The relation between the considered averaged terms and the bulk concentration, given by Eqs. (16) and (17), are thus nonlocal. The nonlocality denotes that the macroscopic solute flux in the considered point in the medium depends not only on the macroscopic solute concentration in the same point and moment of time but on the macroscopic concentration distribution in the whole medium both in the considered moment of time as well as that existing in the past [8, 14]. The terms in Eqs. (16) and (17) that contain time derivative of $\partial_t\{C\}$ are connected with relaxation phenomena of the bulk solute flux $\{\mathbf{j}\}$ and the bulk volumetric concentration $\{\rho C\}$. It should also be noted that some part of the advective solute flux is dispersed on the macroscopic scale and on the level of the macroscopic description the fluid velocity enters diffusive terms. Symbols D_{ef} ν_{ef}, ζ_{ef}, μ_{ef}, stand for the effective properties of the mushy zone which, according to Eq. (18), can be determined from knowledge of microscopic properties of solid and fluid and microstructure of the mushy zone hidden in the microstructure functions φ_C, ψ_C.

Many length-scales are usually observed in the mushy region. There are connected with details of microstructure of the considered medium and with variation of the solute macroscopic concentration distribution. The specific feature of the non-local form of the consitutive relations given above and in the subsequent Section 4 is that they take into account all of the mentioned scales and no scale order analysis is necessary.

Nonlocal phenomena describe locally non-equilibrium processes. Non-equilibrium process in case of solute transport denotes that, on the macroscopic level, the solute is exchanged between the phases. One of the ways to approximately account for chemical non-equilibrium is the so called diffusion model that relates the intrinsic solute concentration in solid and liquid (or the bulk solute concentration and the intrinsic solute concentration in the liquid). This kind of a model, that is often additionally adopted in literature bears postulative character [12, 19, 23]. Another way of accounting for chemical non-equilibrium is, the so called, two-equation (two-fluid) model [1] in which averaging, in the mushy zone, is carried out separately for each phase and exchange of the solute between phases taken into account on the macroscopic level.

3.1. Local chemical equilibrium

As previously mentioned, for solute transport many lengthscales can be observed in the mushy zone. It is possible, in some cases to make order of magnitude analysis and simplify the constitutive relations given in Eqs. (16) and (17). This can be done by carring out expansions of the microstructure functions φ_C, ψ_C in the growing powers of the characteristic microdimension ℓ. This microdimension is understood as the largest from length-scales describing local microstructure of the mushy zone (e.g. primary dendrite spacing). Retaining of the lowest order terms in these expansions leads to the approximation of local chemical equilibrium in the mushy zone.

In order to discuss the problem in more detail let us calculate phase averages applying definition (4) to expression (12). This leads to the following formula

$$\{MC\}_i = \{MC\} + \underbrace{\int_0^t\!\!\int_V \{\varphi_C\}_i \cdot \nabla'\{MC\}\,\mathrm{d}V'\mathrm{d}\tau + \int_0^t\!\!\int_V \{\psi_C\}_i\,\partial_\tau\{MC\}\,\mathrm{d}V'\mathrm{d}\tau}_{\text{non-equilibrium part}} \tag{19}$$

If in the above expression $\{\varphi_C\}_i = 0$ and $\{\psi_C\}_i = 0$, then the local chemical equilibrium holds. It follows from eq.(19) that the phase concentrations are then related to the bulk concentration by the relations

$$\{C\}_S = \frac{\kappa}{(\varepsilon_L + \kappa \quad \varepsilon_S)}\{C\}, \qquad \{C\}_L = \frac{1}{(\varepsilon_L + \kappa \quad \varepsilon_S)}\{C\}. \tag{20}$$

In order to find how the constitutive relations in this case look like it is convenient to expand function $\varphi_C(t,\mathbf{x};\tau,\mathbf{y}|\Omega)$ (and ψ_C) in an infinite series versus growing powers of the microdimension ℓ:

$$\varphi_C(t,\mathbf{x};\tau,\mathbf{y}|\Omega) = \varphi_{C0}(t,\mathbf{x}|\Omega)\,\delta(t,\tau)\,\delta(\mathbf{x},\mathbf{y}) + \ell\varphi_{C1}(t,\mathbf{x}|\Omega)\,\delta(t,\tau)\,\nabla\delta(\mathbf{x},\mathbf{y}) + O(l^2).$$

This kind of expansion, when introduced into Eq. (12), allows to carry out order of magnitude analysis between scales characterizing microstructure of the mushy zone and scales characterizing solute transport in the medium. Retaining the first right-hand side term in the above expansion corresponds to an assumption that gradients (and time derivatives) of the bulk concentration are slowly spatially (or temporally) varying, i.e., scales associated with these variations are much greater than the microdimension ℓ. In fact this assumption is equivalent to assumption of the well separation of a spectrum of lengthscales describing the microstructure of the mushy zone and a spectrum of length scales describing variation of the macroscopic concentration and temperature fields.

Noting properties of functions φ_C and ψ_C, deduced from Eqs. (13) and (14), the microscopic concentration, in the case of chemical equilibrium, varies according to the formula:

$$MC(t,\mathbf{x}|\Omega) = \{MP_{\text{eq}}(t,\mathbf{x})\}\left[\{C(t,\mathbf{x})\} + \varphi_{C0}(t,\mathbf{x}|\Omega)\cdot\nabla\{C(t,\mathbf{x})\}\right] \tag{21}$$

and the relations for the ensemble averaged terms, appearing in the conservation Eq. (10), can be simplified to the local form

$$\{\mathbf{w}\rho C + \mathbf{j}\} = \{\mathbf{w}\}(\rho P_{\text{eq}})_L\{C\} - D_{\text{ef}}\ \nabla\{C\}, \tag{22}$$

$$\{\rho C\} \qquad = \{\rho P_{\text{eq}}\}\{C\}. \tag{23}$$

Chemical equilibrium process is thus local, i.e. the macroscopic solute flux at the considered point depends solely on gradient of the macroscopic concentration calculated in the same location and in the same moment of time – Eqs. (22) and (23). Then, on the macroscopic level, there is no exchange of solute between solid and fluid phases.

The effective diffusivity D_{ef}, appearing in Eq. (22), is defined by the expression

$$D_{\text{ef}} = \{DP_{\text{eq}}(1 + \nabla\varphi_{C0})\} - \underbrace{(\rho/M)_L\,\{MP_{\text{eq}}\}\,\{\theta_L\mathbf{w}\varphi_{C0}\}}_{\text{solute dispersion}} \tag{24}$$

and still contains term responsible for solute dispersion in the medium associated with advection by the fluid in the mushy zone. The respective integro-differential equation for the function φ_{C0} can be easily derived from Eq. (13) and reads

$$\varphi_{C0} = \int_V \nabla G^*\cdot\left[(\mathbf{w}\rho)'\varphi_{C0} - D'(1 + \nabla\varphi_{C0}) - \{(\mathbf{w}\rho)'\varphi_{C0} - D'(1 + \nabla\varphi_{C0})\}\right]\mathrm{d}V'$$
$$- \int_V G^*\left[(\mathbf{w}\rho)' - \{(\mathbf{w}\rho)'\}\right]\mathrm{d}V'.$$

It should be underlined that differential form corresponding to the above equation can also be derived [7, 8].

It is worth to say at the end of this section that it may be proved, see [6], that equations and the effective properties for the two-equation model [1] can be obtained by retaining the term of order ℓ^2 in expansion following Eq. (20). According to the classification introduced by Kunin [15] the two-equation model describes weakly nonlocal phenomena.

4. ENERGY EQUATION

Assuming a constant pressure process and using definition of the generalized enthalpy, the energy conservation equation can be written as

$$\partial_t(\rho h) + \nabla \cdot (\mathbf{w}\rho h + \mathbf{q}) = 0 \tag{25}$$

where the heat flux vector obeys the Fourier law

$$\mathbf{q}(t,\mathbf{x}|\Omega) = -k(t,\mathbf{x}|\Omega)\,\nabla T(t,\mathbf{x}|\Omega) \tag{26}$$

and k stands for the generalized thermal conductivity

$$k(t,\mathbf{x}|\Omega) = \theta_S(t,\mathbf{x}|\Omega)k_S + \theta_L(t,\mathbf{x}|\Omega)k_L\,.$$

The ensemble averaging of the energy conservation equation leads to the following expression

$$\partial_t\{\rho h\} + \nabla \cdot \{\mathbf{w}\rho h + \mathbf{q}\} = 0 \tag{27}$$

In order to derive the final macroscopic form of the energy equation the ensemble averages appearing in the above equation should be expressed as a function of the bulk temperature $\{T\}$ and the bulk concentration $\{C\}$. This can be achieved if relation between microscopic concentration T and its bulk value is known. The latter relation can be derived by transforming Eqs. (25) and (26) into the form

$$k_r\nabla^2 T - \rho_r c_r(\mathbf{w}_r \cdot \nabla T + \partial_t T) = \nabla \cdot [(\mathbf{w}\rho h - \rho_r c_r \mathbf{w}_r T) - k'\nabla T] + \partial_t(\rho h - \rho_r c_r T) \tag{28}$$

where $k' = k - k_r$. The subscript r denotes a reference quantity, which should be generally configuration independent. Using the Green function theory in a manner identical to presented in [9] an expression for the microscopic temperature is obtained. The generalized enthalpy in Eq. (28), being function of temperature T and activity MC, has been subsequently linearized with respect to the bulk variables $\{T\}$ and $\{MC\}$

$$\begin{aligned}\rho h(t,\mathbf{x},T,MC|\Omega) &= \rho h^o(t,\mathbf{x},\{T\},\{MC\}|\Omega) + \partial_T\rho h^o(t,\mathbf{x},\{T\},\{MC\}|\Omega)\,(T-\{T\})\\ &\quad + \partial_{MC}\rho h^o(t,\mathbf{x},\{T\},\{MC\}|\Omega)\,(MC-\{MC\})\end{aligned} \tag{28'}$$

and the final form of relation between the microscopic and the bulk variables presented in the form

$$\begin{aligned}T &= \{T\} + S + \int_0^t\int_V \varphi_T \cdot \nabla'\{T\}\,\mathrm{d}V'\mathrm{d}\tau\\ &\quad + \left[\int_0^t\int_V \varphi_{TC}\cdot\nabla'\{MC\}\,\mathrm{d}V'\mathrm{d}\tau + \int_0^t\int_V \psi_{TC}\,\partial_\tau\{MC\}\,\mathrm{d}V'\mathrm{d}\tau\right]\end{aligned} \tag{29}$$

where functions S and φ_T satisfy the following equations:

$$\begin{aligned}S &= -\int_0^t\int_V \nabla G\cdot[k'\nabla S - \mathbf{w}\partial_T(\rho h^o)S + \mathbf{w}_r\rho_r c_r S - \mathbf{w}(\rho h^o)\\ &\qquad - \{k'\nabla S - \mathbf{w}\partial_T(\rho h^o)S + \mathbf{w}_r\rho_r c_r S - \mathbf{w}(\rho h^o)\}]\,\mathrm{d}V'\mathrm{d}\tau\\ &\quad - \int_0^t\int_V G\,\partial_\tau[\partial_T(\rho h^o)S + \rho_r c_r S + (\rho h^o) - \{\partial_T(\rho h^o)S + \rho_r c_r S + (\rho h^o)\}]\,\mathrm{d}V'\mathrm{d}\tau\,,\end{aligned} \tag{30}$$

$$\begin{aligned}\varphi_T &= -\int_0^t\int_V \nabla G\cdot[k'(\mathbf{1}\delta_t\delta_\mathbf{x} + \nabla\varphi_T) - \mathbf{w}\partial_T(\rho h^o)\varphi_T + \mathbf{w}_r\rho_r c_r\varphi_T\\ &\qquad - \{k'(\mathbf{1}\delta_t\delta_\mathbf{x} + \nabla\varphi_T) - \mathbf{w}\partial_T(\rho h^o)\varphi_T + \mathbf{w}_r\rho_r c_r\varphi_T\}]\,\mathrm{d}V'\mathrm{d}\tau\\ &\quad - \int_0^t\int_V G\,\partial_\tau[\partial_T(\rho h^o)\varphi_T - \rho_r c_r\varphi_T - \{\partial_T(\rho h^o)\varphi_T - \rho_r c_r\varphi_T\}]\,\mathrm{d}V'\mathrm{d}\tau\,.\end{aligned} \tag{31}$$

The function φ_{TC} can be determined from the expression

$$\begin{aligned}\varphi_{TC} = &\int_0^t\int_V \nabla G\cdot\left[\mathbf{w}\partial_{MC}(\rho h^o)\varphi_C - \{\mathbf{w}\partial_{MC}(\rho h^o)\varphi_C\}\right]\mathrm{d}V'\mathrm{d}\tau \\ &-\int_0^t\int_V G\,\partial_\tau\left[\partial_{MC}(\rho h^o)\varphi_C - \{\partial_{MC}(\rho h^o)\varphi_C\}\right]\mathrm{d}V'\mathrm{d}\tau\end{aligned} \tag{32}$$

where φ_C can be found from Eq. (13). The function ψ_{TC}, appearing in Eq. (29), can be calculated from expression identical to Eq. (32) with ψ_C substituted for φ_C.

Relations between the ensemble averaged terms and the bulk temperature and concentration, Eq. (27), can then be easily obtained using Eqs. (26), (28) and (29). The procedure leads to the following expressions

$$\begin{aligned}\{\mathbf{w}\rho h + \mathbf{q}\} = &\{\mathbf{w}\}(\rho h^o)_L - \int_0^t\int_V k_{\mathrm{ef}}\cdot\nabla'\{T\}\,\mathrm{d}V'\mathrm{d}\tau \\ &-\left[\int_0^t\int_V D_{T\mathrm{ef}}\cdot\nabla'\{C\}\,\mathrm{d}V'\mathrm{d}\tau - \int_0^t\int_V \nu_{T\mathrm{ef}}\,\partial_\tau\{C\}\,\mathrm{d}V'\mathrm{d}\tau\right] + \mathbf{q}_{HS}\,,\end{aligned} \tag{33}$$

$$\begin{aligned}\{\rho h\} \quad &= \{\rho h^o\} + h_{HS} + \int_0^t\int_V \chi_{T\mathrm{ef}}\cdot\nabla'\{T\}\,\mathrm{d}V'\mathrm{d}\tau \\ &+\left[\int_0^t\int_V \chi_{C\mathrm{ef}}\cdot\nabla'\{C\}\,\mathrm{d}V'\mathrm{d}\tau + \int_0^t\int_V \mu_{C\mathrm{ef}}\,\partial_\tau\{C\}\,\mathrm{d}V'\mathrm{d}\tau\right],\end{aligned} \tag{34}$$

where

$$\begin{aligned}k_{\mathrm{ef}} \;&= \{k(\mathbf{1}\delta_{\mathrm{x}}\delta_t + \nabla\varphi_T)\} - \varepsilon_L\,\partial_T(\rho h^o)_L\,\{\mathbf{w}\varphi_T\}_L\,, \\ D_{T\mathrm{ef}} &= \{MP_{\mathrm{eq}}\}\left[\{k\nabla\varphi_{TC}\} - \partial_T(\rho h^o)_L\,\{\theta_L\mathbf{w}\varphi_{TC}\} - \partial_{MC}(\rho h^o)_L\,\{\theta_L\mathbf{w}\varphi_C\}\right], \\ \nu_{T\mathrm{ef}} &= \{MP_{\mathrm{eq}}\}\left[\{k\nabla\psi_{TC}\} - \partial_T(\rho h^o)_L\,\{\theta_L\mathbf{w}\psi_{TC}\} - \partial_{MC}(\rho h^o)_L\,\{\theta_L\mathbf{w}\psi_C\}\right], \\ \chi_{T\mathrm{ef}} &= \{\partial_T(\rho h^o)\varphi_T\}\,, \\ \chi_{C\mathrm{ef}} &= \{MP_{\mathrm{eq}}\}\left[\{\partial_T(\rho h^o)\varphi_{TC}\} - \{\partial_{MC}(\rho h^o)\varphi_C\}\right], \\ \mu_{C\mathrm{ef}} &= \{MP_{\mathrm{eq}}\}\left[\{\partial_T(\rho h^o)\psi_{TC}\} - \{\partial_{MC}(\rho h^o)\psi_C\}\right], \\ \mathbf{q}_{HS} &= \{k\nabla S\} - \partial_T(\rho h^o)_L\,\{\theta_L\mathbf{w}S\}\,, \\ h_{HS} &= \{\partial_T(\rho h^o)\,S\}\,.\end{aligned} \tag{35}$$

It should be noted that both relations, Eqs. (33) and (34), are nonlocal. They also show that the bulk heat flux and the bulk enthalpy depend not only on the macroscopic temperature but also on the macroscopic concentration. This follows from dependence of enthalpy on the solute concentration, Eqs. (43) and (44). The nonlocality denotes that the macroscopic heat flux and enthalpy in the considered point in the medium depends not only on the macroscopic temperature and solute concentration in the same point and moment of time but on the macroscopic temperature and solute concentration distributions in the whole medium both in the considered moment of time as well as that existing in the past [8, 14]. Moreover, some of the energy, due to tortuous path followed by liquid phase in the mushy region, is dispersed and enters diffusive terms. The latter conclusion is justified by presence of fluid velocity in the expressions for the effective properties: k_{ef}, $D_{T\mathrm{ef}}$ and $\nu_{T\mathrm{ef}}$. The term $\mathbf{q}_{HS}$, appearing in Eq. (33), arises due to presence of temperature-dependent local heat sources at the solid–liquid interface. These heat sources, that are associated with phase change, locally deform temperature fields and cause additional transport of heat [4].

4.1. Local thermal equilibrium

Similarly to the local chemical equilibrium, the problem of local thermal equilibrium may be discussed. If eq.(29) is multiplied by the structure function for each phase and ensemble averaged then the following expression for the phase temperature is received

$$\{T\}_i = \{T\} + \{S\}_i + \int_0^t \int_V \{\varphi_T\}_i \cdot \nabla'\{T\}\,\mathrm{d}V'\mathrm{d}\tau + \underbrace{\left[\int_0^t \int_V \{\varphi_{TC}\}_i \cdot \nabla'\{MC\}\,\mathrm{d}V'\mathrm{d}\tau + \int_0^t \int_V \{\psi_{TC}\}_i\,\partial_\tau\{MC\}\,\mathrm{d}V'\mathrm{d}\tau\right]}_{\text{non-equilibrium part}} \tag{36}$$

In the case of the local thermal equilibrium the phase temperatures should be the same and equal to the bulk temperature. It can then be concluded that all terms on the right-hand side, starting from the second one, should be negligible. In order to analyze the problem it is convenient to expand each of the functions φ_T, φ_{TC}, ψ_{TC} and φ_C, ψ_C in a series given in the previous section where the local chemical equilibrium has been discussed. The expansions are valid for the case when the bulk temperature and concentration are slowly spatially (or temporally) varying in respect to ℓ. In this case the microscopic temperature varies according to the formula

$$T(t,\mathbf{x}|\Omega) = \{T(t,\mathbf{x})\} + S(t,\mathbf{x}|\Omega) + \varphi_{T0}(t,\mathbf{x}|\Omega)\cdot\nabla\{T(t,\mathbf{x})\} + \varphi_{TC0}(t,\mathbf{x}|\Omega)\cdot\nabla\{MC(t,\mathbf{x})\} \tag{37}$$

and the relations for the ensemble averaged terms, appearing in the conservation equation (27), can be simplified to the local form

$$\{\mathbf{w}\rho h + \mathbf{q}\} = \{\mathbf{w}\}(\rho h^o)_L - k_{\mathrm{ef}}\cdot\nabla\{T\} - D_{T\mathrm{ef}}\cdot\nabla\{C\}, \tag{38}$$

$$\{\rho h\} = \{\rho h^o\}. \tag{39}$$

The effective thermal conductivity k_{ef} is then defined by

$$k_{\mathrm{ef}} = \{k(\mathbf{1} + \nabla\varphi_{T0})\} - \varepsilon_L\,\underbrace{\partial_T(\rho h^o)_L\{\mathbf{w}\varphi_{T0}\}_L}_{\text{thermal dispersion}} \tag{40}$$

while the Dufour coefficient by the expression

$$D_{T\mathrm{ef}} = \{MP_{\mathrm{eq}}\}\left[\{k\nabla\varphi_{TC0}\} - \varepsilon_L\,\partial_T(\rho h^o)_L\{\mathbf{w}\varphi_{TC0}\}_L - \varepsilon_L\,\partial_{MC}(\rho h^o)_L\{\mathbf{w}\varphi_{C0}\}_L\right]. \tag{41}$$

The respective integro-differential equations for the functions φ_{T0}, φ_{TC0} can be easily derived from Eqs. (31) and (32).

5. FORMULAE FOR ENTHALPY AND POROSITY OF THE MUSHY ZONE IN CASE OF THERMODYNAMIC EQUILIBRIUM

In order to close the set of equations, that were discussed in the last two sections, it is necessary to present expressions for the bulk enthalpy $\{\rho h^o\}$ and the enthalpy $(\rho h^o)_L$ of the liquid phase and the volume fraction of the liquid phase ε_L. The bulk enthalpy can, using Eqs. (1) and (4), be related to the volume fractions and the phase enthalpies by the formula

$$\{\rho h^o\} = \varepsilon_S(t,\mathbf{x})\,\rho_S h_S(\{T\},\{C\}) + \varepsilon_L(t,\mathbf{x})\,\rho_L h_L(\{T\},\{C\}). \tag{42}$$

The phase enthalpies, as potentials, can be evaluated, in relation to a certain reference state $(T_r,\ 0)$ of temperature and concentration, in a different way. In the case of the liquid enthalpy $(\rho h^o)_L = \rho_L h_L(\{T\},\{C\})$ it is advisable not to cross the two-phase (mushy) region when carrying out calculations as enthalpy in this region depends on the composition and the liquid fraction is

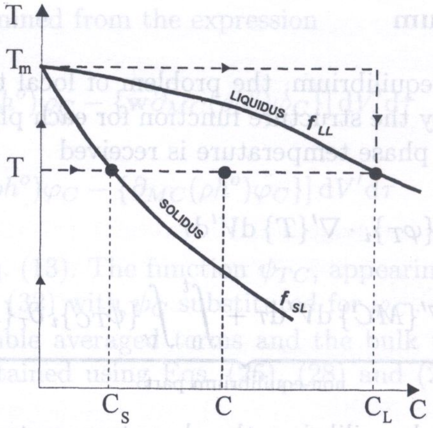

Fig. 1. A scheme of phase diagram

not *a priori* known. Instead it is convenient to follow the way presented in the accompanying figure (Fig. 1). The phase enthalpies can then be expressed as

$$\rho_S h_S(\{T\},\{C\}) = \int_{T_r}^{\{T\}} \rho_S c_S(T,0)\,\mathrm{d}T + \int_0^{\{C\}_S} \rho_S h_{Sp}(\{T\},C)\,\mathrm{d}C\,, \tag{43}$$

$$\rho_L h_L(\{T\},\{C\}) = \int_{T_r}^{T_m} \rho_S c_S(T,0)\,\mathrm{d}T + \rho_S L(T_m)$$

$$+ \int_0^{\{C\}_L} \rho_L h_{Lp}(T_m,C)\,\mathrm{d}C + \int_{T_m}^{\{T\}} \rho_L c_L(T,\{C\}_L)\,\mathrm{d}T\,, \tag{44}$$

where c_S, c_L denote specific heats, while T_m and $L(T_m)$ are the freezing temperature and the latent heat of freezing of the pure solvent, respectively. Symbols h_{Sp} and h_{Lp} stand for the partial derivatives of enthalpy in respect to the solute concentration.

The phase concentrations are related to the bulk concentration by relations of Eq. (20) which can be used to find the volume fractions of the phases in the mushy region

$$\varepsilon_L(t,\mathbf{x}) = 1 - \varepsilon_S(t,\mathbf{x}) = \frac{\{C\} - f_{SL}^{-1}(\{T\})}{f_{LL}^{-1}(\{T\}) - f_{SL}^{-1}(\{T\})} = \varepsilon_L(\{T\},\{C\})\,. \tag{45}$$

Here f_{SL}^{-1} and f_{LL}^{-1} stand for the inverse functions describing solidus and liquidus line (Fig. 1), respectively.

It should be noted that, according to Eq. (45), the phase volume fractions are dependent solely on the bulk temperature and concentration and when introduced, together with Eqs. (43) and (44), into Eq. (42) allow to express the bulk volumetric enthalpy only as a function of $\{T\}$ and $\{C\}$. An alternative to this analytical procedure is to adopt an empirical relation between temperature and concentration for the binary mixture in question [21].

6. CONCLUDING REMARKS

The method, presented in the paper, gives an alternative to the volume averaging approach when used in formulation of transport equations valid in the mushy zone for the phenomenon of solidification of binary mixtures. The method is based on the technique of ensemble averaging. The macroscopic quantities, obtained with this technique, have different physical interpretation than obtained by the technique of volume averaging.

The paper shows that form of the constitutive relations between macroscopic variables needs not to be postulated but can be formally derived from respective microscopic relations irrespective of the assumptions as to the length-scales influencing the process. These relations are generally nonlocal. Nonlocal aspects of transport processes in the mushy zone were not presented till now in literature. The nonlocality is associated with the non-equilibrium processes occurring in the mushy zone. Thus to model macroscopic non-equlibrium process of solute transfer in the mushy zone it is not necessary to adopt additional models of diffusion in the solid phase which often bear postulative character. If the spectrum of scales, associated with microstructure of the mushy zone, is well separated from the spectrum of scales, associated with spatial distributions and time variation of macroscopic solute concentration (temperature), it is possible to obtain simplified, local form of the constitutive relations which resemble the known Fick's or Fourier laws valid for homogeneous media. The latter relations describe equilibrium processes within the mushy zone.

The consitutive relations contain effective properties of the mushy zone, responsible for heat and solute transport. The expressions (18) and (35) give definitions of the effective properties for the nonlocal (non-equilibrium) case of the constitutive relations while Eqs. (24), (40) and (41) respective expression for the local (equilibrium) case. All these expressions show how these effective properties can be calculated from functions φ_C, ψ_C, φ_T, φ_{TC}, ψ_{TC} describing microstructure of the mushy zone and from knowledge of the microscopic properties of solid and liquid phase in the mushy zone like: diffusivities D_S, D_L; density ρ_S, ρ_L; solubility M_S, M_L; thermal conductivities k_S, k_L and enthalpies h_S, h_L. The effective properties of the mushy zone, given by the discussed definitions, should be understood as statistically awaited values. The strategy for determination of these properties is thus following: for the known microstructure of the mushy zone solve equations for the microstructure functions like (13), (14), (30), (31), (32) and use definitions (18), (35), (24), (40), (41) to calculate the effective properties. This has been previously done for some composite and porous media and the results are presented in [7] and [8]. It should be noted that symbol of the ensemble averaging appearing on the right-hand side of these definitions may be replaced, in situation when the ergodic theorem holds, by spatial averaging over some volumes or over some surfaces (eg., paralel to the solidus or liquidus lines).

Role of some terms in the transport phenomena, that appear in the macroscopic constitutive relations (like dispersion, interaction of phase change and heat flow, etc.), should be carefully estimated. The terms which correspond to other phenomena (e.g., heat transport enhancement due to presence of heat sources at the interface or cross effects like the Dufour one) should also be addressed in more detail. The model presented in the paper can be used to analyze influence of the local non-equilibrium phenomena on the solidification process by retaining further terms in the expansion as discussed in the section devoted to chemical equilibrium.

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