Segregation during solidification with spongy deformation of the mushy zone

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Abstract

Mathematical expressions of segregation rates occurring during solidification with spongy deformation of an alloyed mushy zone are derived from classical mass balance analyses. The boundaries of the domain considered for the mass balances deform with the same velocity as the solid phase: the reference frame is attached to the solid phase. The three variables needed to fully describe segregation within this “Lagrangian” approach are the mass of solid in the domain, the volume of the domain and the relative velocity of the liquid with respect to the solid. The main result is a mathematical expression for the local macrosegregation rate. The analysis is further extended to produce an expression for the local microsegregation rate that can be compared with the one proposed by Flemings and Nereo (Trans. AIME 239 (1967) 1449–1461). An additional term thus enters into our expression. This term is proportional to the local strain rate multiplied by the ratio of the volume fraction of solid over the volume fraction of liquid. It is expected to become dominant when the mushy zone is fully developed (large value of the ratio) and when the strain can be transmitted through a coherent solid skeleton that deforms like a sponge. Still, the origin of the deformation remains arbitrary and the derived expressions could be used to quantify segregation due to the thermal contraction of the solid and liquid phases, the shrinkage associated with the phase transformations, and/or the mechanical deformation of the domain. Finally, the expression for the local microsegregation rate is combined with the first law of thermodynamics. The rate of progress of solidification is thus related to the rate of heat extraction, the transport of heat due to the relative liquid flow with respect to the solid, and the enthalpy of dissolution of the solid in the liquid.

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1. Introduction

In cast metals, chemical segregation develops on three scales. Microsegregation develops on the scale of the dendrite, macrosegregations develop on the scale of the entire product, and mesosegregations develop
**Nomenclature**

**Latin symbols**

- $B$: component
- $C_L$: liquid composition [5]
- $D$: domain
- $dS$: surface element
- $dV$: volume element
- $f$: mass fraction (phase)
- $g$: volume fraction
- $J$: diffusion flux density
- $k$: partition coefficient
- $m$: mass
- $n$: normal
- $t$: time
- $V$: volume
- $v$: velocity
- $w$: mass fraction (component)
- $\bar{w}$: average mass fraction (component)

**Greek symbols**

- $\beta$: solidification shrinkage [5]
- $\rho$: density (or mass per unit volume)
- $\Sigma$: surface
- $\Omega$: velocity of boundary
- $\varepsilon$: strain

**Superscripts**

- $\varphi$: phase
- $l$: liquid
- $s$: solid
- $l-s$: liquid relative to solid
- $s/l$: at the solid-liquid interface for the interface and its absolute velocity
- $s/l$: in the solid, at the solid-liquid interface for the chemical composition
- $l/s$: in the liquid, at the solid-liquid interface for the chemical composition

**Subscripts**

- $i$: component
- $e$: outer
- $T$: isotherm
on some intermediate scale: the scale of primary grains for instance. Macrosegregation is the most important one since it is the type of segregation that is far more difficult to reduce subsequently by thermo-mechanical post-treatments. Therefore, the main subject of this work is macrosegregation.

The number of aspects in which macrosegregation manifests itself reveals the variety of the involved phenomena and the complexity of their interactions. Several elementary phenomena often compete to build the final overall segregation pattern in as-cast products. Therefore, modeling macrosegregation, both physically and numerically, is especially useful in order to understand better the fundamental origins of segregation in metals cast under specific conditions. Recent and well-documented reviews of macrosegregation modeling are available in the literature [1–4].

Since Flemings and his co-workers published their pioneer papers on macrosegregation [5–8], the one cause of segregation that has been studied more carefully and thoroughly is the movement of segregated residual liquid with respect to the solid framework of the mushy zone. There are several reasons for the liquid to be entrained deeply into the mushy zone: solidification shrinkage, natural convection, and deformation of the mushy zone. Considerable theoretical and numerical work has become available on macrosegregation due to solidification shrinkage and natural convection. It clearly shows the dependence of the intensity of microsegregation on the relative velocity of the liquid with respect to the solid, \( v_{l-s} \), on its orientation with respect to the temperature gradient, and on the velocity of the isotherms with respect to the solid framework, \( v_T \). On the one hand, this approach is successful for simulating segregation patterns in large ingots, as shown in the most recent review by Beckermann [4]. On the other hand, it is not so easily applicable to situations where the solid skeleton of the mushy zone deforms at the end of solidification because of internal changes or external strains. Such situations are frequent in the most widely used casting process in the world: continuous casting of steel.

Only a few papers deal with modeling segregation during continuous casting of steel [9–16]. Numerical simulation of solidification and segregation in a mushy zone where the solid phase is deforming was carried out for the first time by Miyazawa and Schwerdtfeger in the case of bulging of the solid shell between rolls during continuous casting of steel slabs [10]. These authors chose a fully Eulerian approach to express the mass, solute mass, momentum and energy balances together with a streamline formulation for solving the set of equations. More recently, the same problem of macrosegregation induced by bulging was tackled numerically by Kajitani et al. [16]. They also chose a Eulerian approach. However, they established the fluid flow velocity field by solving the equation describing the pressure field in the liquid instead of using the streamline formulation. These studies contributed interesting theoretical conclusions to the relative effects of solidification shrinkage, bulging, and mechanical soft reduction on the intensity of the central macrosegregation in continuous cast steel slabs. But calculated results seem to be somewhat unexpected: for instance, the prediction that the mechanical soft reduction might increase centerline segregation does not fit industrial experience. The Eulerian formulation, which has advantages with respect to implementation in numerical software, makes it more difficult to compare the various physical situations without new extensive numerical work. Moreover, the Eulerian approach did not produce yet expressions suitable for describing segregation due to deformations of the solid skeleton of the mushy zone that would be directly comparable to those published by Flemings.

The main purpose of this work is to provide general expressions making it possible to describe the build-up of macrosegregation in cast products where the solid skeleton of the mushy zone deforms during solidification. These expressions should be useful to discuss the practical means of decreasing segregation especially in continuous cast steel products.

Predicting the segregation related to solidification implies:

- describing the progress of solidification on the one hand,
- describing the movements of mass in the mushy zone on the other hand.
As far as the description of solidification is concerned, two physical quantities are used in the literature: the mass fraction of solid, \( f_s \), or the volume fraction of solid, \( g_s \). The choice of the mass fraction, \( f_s \), as the main variable for describing the progress of solidification is appropriate when the total mass of the elementary domain, \( D \), in which microsegregation is building up, is constant. This has been the point of view of Gulliver since 1913–1915 [17–19], and that of Scheil since 1942 [20]. The choice of the volume fraction of solid, \( g_s \), is more suited to situations where the physical quantity, which can be considered as constant, is the total volume of the elementary domain \( D \). Flemings and co-workers have made this latter choice popular since 1967 [5–8]. At that time, however, this was not completely explicit, as we shall show later. It is worth emphasizing here that the Flemings approach has been very successful as long as it has been applied to cases where “no solid material enters or leaves the volume element during solidification” [5]. In that sense, Gulliver’s, Scheil’s and Flemings’s approaches to segregation can be qualified as Lagrangian: the elementary domain for establishing the balances was defined on the solid skeleton of the mushy zone, which does not deform. In order to derive more general expressions for the local balances in the case when the solid skeleton of the mushy zone deforms, it has been proposed to keep a Lagrangian approach [21,22]. Therefore, the elementary domain for establishing the balances is built on the solid framework of the mushy zone, sticks to it, and deforms with it. In this new formulation, the natural variable for describing the progress of the solidification is the mass of solid in the domain, \( m_s \).

Concerning the description of the movements of matter in the mushy zone, following Flemings’ initial idea, it is commonly accepted that at least the relative velocity of the liquid with respect to the solid, \( v_{l-s} \), should be introduced. This relative velocity, \( v_{l-s} \), is sufficient only in the case where the solid is rigid and when a Lagrangian approach, referring to the barycentric motion of the solid, is chosen. On the contrary, when the solid deforms, the strain rate of the solid (\( d\varepsilon_{ij}/dt \)), must also be taken into account. As far as the segregation induced by solidification is concerned, only the trace of the strain rate tensor plays a role. This quantity represents the local volume expansion of the solid skeleton:

\[
\frac{d\varepsilon_{11}}{dt} + \frac{d\varepsilon_{22}}{dt} + \frac{d\varepsilon_{33}}{dt} = \frac{1}{V} \frac{\varepsilon DV}{\varepsilon DT} \tag{1}
\]

where the quantity \( V \) represents the volume of the elementary domain \( D \) and operator \((D/DT)\) is related to a quantity defined within the boundary of the domain \( D \), which may deform with time.

Therefore, adding the volume of the elementary domain, \( V \), as a second pertinent variable has been proposed for describing the movements of matter in the mushy zone [21].

In the more general case where the solid skeleton of the mushy zone deforms, in a Eulerian approach, the absolute velocities of both the liquid and the solid, \( v_l \) and \( v_s \), respectively, must be considered. Table 1 summarizes the basis of the description of the physical state of the mushy zone during solidification by different authors, for different physical situations.

The main results of this paper consist in analytical expressions for local micro- and macro-segregation rates, the presentation of which is kept short for clarity. Details of the derivations are given in the appendices. The expression for the local microsegregation rate is combined with the first law of thermodynamics. The rate of progress of solidification is thus related to the rate of heat extraction, the transport of heat due to the relative liquid flow with respect to the solid, and the enthalpy of dissolution of the solid in the liquid. All expressions are compatible with the description of solidification with spongy deformation of the mushy zone.

### 2. Description of the metal during solidification

During solidification, the liquid and the solid phases must be considered separately. The volumes over which the average values of locally defined quantities must be calculated should also be defined carefully.
Table 1
Basis of the description of the physical state of the mushy zone during solidification by different authors, for different physical situations

<table>
<thead>
<tr>
<th>Approach</th>
<th>Physical situation</th>
<th>Movements of liquid</th>
<th>Movements of solid</th>
<th>Progress of solidification</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagrangian</td>
<td>Microsegregation in small castings</td>
<td>0</td>
<td>0</td>
<td>$\rho$</td>
<td>[17–20]</td>
</tr>
<tr>
<td>Macrosegregation in large ingots</td>
<td>$\mathbf{v}^l$</td>
<td>0</td>
<td>$g^s$</td>
<td></td>
<td>[5–8]</td>
</tr>
<tr>
<td>Central segregation in continuous cast steel billets or slabs</td>
<td>$\mathbf{v}^l$</td>
<td>$\mathbf{V}$</td>
<td>$m^r$</td>
<td></td>
<td>[21,22]</td>
</tr>
<tr>
<td>Eulerian</td>
<td>Bulging induced segregation in continuous cast steel slabs</td>
<td>$\mathbf{v}^i$</td>
<td>$\mathbf{v}^s$</td>
<td>$g^s$</td>
<td>[10,16]</td>
</tr>
</tbody>
</table>


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to describe properly the redistribution of solutes during solidification. In the present study, the representative volume domain that is considered, $D$, is made of two single-phase sub-domains, $D^s$ and $D^l$, representing respectively the solid and liquid phases. Fig. 1a outlines the definition of the outer boundary of sub-domain $D^\varphi$, $\Sigma^\varphi$ ($\varphi = l, s$), and the inward normal to a boundary of sub-domain $D^\varphi$, $\mathbf{n}^\varphi$. The inner boundary of the solid and liquid sub-domains corresponds to the solid/liquid interface, $\Sigma^{\varphi l}$.

The average mass fraction of component $B_i$ in the sub-domain $D^\varphi$, $\bar{w}_i^\varphi$, is defined by integrating the proper quantities in this domain:

$$
\bar{w}_i^\varphi = \frac{m_i^\varphi}{m^\varphi} = \frac{\int_{D^\varphi} \rho^\varphi w_i^\varphi dV}{\int_{D^\varphi} \rho^\varphi dV}
$$

(2)

where $m_i^\varphi$ is the mass of component $B_i$ in the sub-domain $D^\varphi$, $m^\varphi$ is the mass of the sub-domain $D^\varphi$, $\rho^\varphi$ is the local mass density of phase $\varphi$ and $w_i^\varphi$ is the local mass fraction of component $B_i$ in phase $\varphi$.

The average mass fraction of component $B_i$ in the entire domain $D$, $\bar{w}_i$, is defined as the ratio of the mass $m_i$ of component $B_i$ distributed in the domain $D$ over the total mass $m$ within $D$:

$$
\bar{w}_i = \frac{m_i}{m} = \frac{\sum_{\varphi} m_i^\varphi}{\sum_{\varphi} m^\varphi} = \frac{\sum_{\varphi} \int_{D^\varphi} \rho^\varphi w_i^\varphi dV}{\sum_{\varphi} \int_{D^\varphi} \rho^\varphi dV}
$$

(3)

2.1. Segregation rates

Macrosegregation corresponds to situations where the average composition of the as-cast metal is different from the nominal composition of the liquid metal. Therefore, we shall focus our attention on the evolution of the average mass fraction of $B_i$ in domain $D$ and we shall define here the “local macrosegregation rate” by the following quantity:

$$
\frac{D\bar{w}_i}{Dt} = \frac{D}{Dt} \left( \frac{m_i}{m} \right) = \frac{1}{m} \left( \frac{Dm_i}{Dt} - \bar{w}_i \frac{Dm}{Dt} \right)
$$

(4)
Please remember that the operator \((D/Dt)\) explicitly states that the boundary of domain \(D\), in which the derived quantity is defined, can deform with time.

Eq. (4) shows that it is necessary to express \((Dm_i/Dt)\) and \((Dm_i/Dt)\) in terms of the variables that are listed in Table 1 (i.e. \(V\), \(m^r\), and \(v^l-s\)) in order to obtain the proper expression for the macrosegregation rate.

As long as the composition of the liquid can be assumed to be homogeneous within domain \(D\) of the mushy zone, the effect of the redistribution of component \(B_i\) between liquid and solid can be characterized by the following quantity, called here the “**local microsegregation rate**”:

\[
\frac{\partial w^l_i}{\partial t}
\]  

(5)
where \( \frac{\partial}{\partial t} \) is the operator that represents the classical partial time derivative of a quantity defined in each point of the sub-domain \( D^i \).

To proceed further, the size and some characteristics of the domain \( D \) must be specified.

2.2. Domains and hypotheses

On the one hand, like the area that must be investigated in the as-cast metal, the size of the domain \( D \) must be larger than the dendrite arm spacing (Hypothesis H1). On the other hand, it must be small enough so that its temperature can be assumed to be uniform (Hypothesis H2). Moreover, the mass fraction of component \( B_i \) in the liquid, \( w_i^l \), is assumed to be uniform throughout the domain (Hypothesis H3). Finally, local chemical equilibrium between liquid and solid is assumed to be achieved along the solid/liquid interface and the effects of curvature of the interface on this equilibrium are neglected (Hypothesis H4). As a consequence of the last three hypotheses (H2–H4), the mass fractions of component \( B_i \) at the solid/liquid interface, in the solid and liquid phases, \( w_{s/l}^i \) and \( w_{l/s}^i \), respectively, are uniform along the interface in the domain. A second consequence is that the densities at the solid/liquid interface of the solid and liquid phases are uniform along the interface in the domain.

The change of the segregation pattern in time can be partly due to the movements of the boundaries of domain \( D \) and to those of sub-domains \( D^j \) and \( D^s \). Fig. 1a and b illustrate the deformations of these domains between time \( t \) and time \( t' \), as well as the velocities of the boundaries \( \Sigma_{c}^e, \Omega_e^c \), the velocity of the solid–liquid interface \( \Sigma_{s/l}^e, \Omega_{s/l}^e \), and the local velocities in each sub-domain \( D^j \) and \( D^s \), \( v^j \) and \( v^s \), respectively.

A few additional assumptions are necessary to specify the velocity fields:

(H5) The velocity of the outer boundary of the solid sub-domain, \( \Omega_e^c \), can be continuously interpolated on the nearby outer boundary of the liquid sub-domain.

(H6) Outer boundaries of domain \( D \) are attached to the solid phase, i.e. to the sub-domain \( D^s \). The sub-domain \( D^s \) forms a solid network that deforms with velocity \( v^s \), leading to the following relation:

\[
\Omega_e^c = v^s \quad \text{along the outer boundary } \Sigma_e^c
\]

(H7) The velocity of the solid, \( v^s \), can be continuously interpolated in the nearby liquid sub-domain. This assumption is illustrated in Fig. 1b and c.

(H8) The density of the solid phase, \( \rho^s \), is uniform in domain \( D \).

As a consequence of assumptions (H5–H7), the variation of the volume of domain \( D \), \( \frac{\text{d}V}{\text{d}t} \), is due to the deformation of the solid and is given by the following expression:

\[
\frac{\text{d}V}{\text{d}t} = -\int_{\Sigma_e^c} \boldsymbol{\Omega}_e^c \cdot \mathbf{n} \, dS - \int_{\Sigma_l^e} \boldsymbol{\Omega}_e^l \cdot \mathbf{n} \, dS = \int_{D^s} \text{div} \, v^s \, dV + \int_{D^j} \text{div} \, v^j \, dV \quad (7)
\]

3. Calculation of the macrosegregation rate

In order to calculate the macrosegregation rate according to Eq. (4), conservation of the total mass and conservation of mass of component \( B_i \) in domain \( D \) must be successively expressed.

The procedure for getting the expression of the rate of change of mass of the overall domain \( D \) in terms of elementary variables, among which the most important ones are \( V \) and \( m^s \), is detailed in Appendix A. The first preliminary result on which the calculation is based is the mass balance for component \( B_i \) in domain \( D \) (Eq. (A.12)). The summation of Eq. (A.12) over all sub-domains \( D^j \) and all compo-
nents \( B \), present in domain \( D \) leads to the expression of the conservation of mass in domain \( D \) (noted (A.18) in Appendix A):

\[
\frac{Dm}{Dt} = \int_{\Sigma_e} \rho'(v^e - \Omega^s_e) \cdot n^e dS + \int_{\Sigma_e} \rho'(v^l - \Omega^l_e) \cdot n^l dS
\]  

(8)

Taking into account hypothesis (H8), a few mathematical operations finally lead to the following expression for the rate of change of mass (noted (A.22) in Appendix A):

\[
\frac{Dm}{Dt} = \rho'(v^e \frac{1}{\rho^e} \frac{d\rho^e}{dt} + v^l \frac{1}{\rho^l} \frac{\partial \rho^l}{\partial t}) + \frac{\rho^s - \rho^l}{\rho^e} \frac{Dm^e}{Dt} + \rho^l \frac{DV}{Dt}
\]  

(9)

The procedure for getting the mass balance for component \( B \) in the domain \( D \) is also detailed in Appendix A (Eqs. (A.14) and seq.). It is summarized here in order to identify the main steps. Once again, the starting point is the mass balance for component \( B \) in each sub-domain \( D^s \) (Eq. (A.12)). The summation over the two sub-domains of domain \( D \) leads to the equation noted (A.17) in Appendix A. On the other hand, the overall mass balance leads to the result noted (A.19) in Appendix A. The combination of Eqs. (A.17) and (A.19) leads to a useful expression for the rate of change of the mass of component \( B \):

\[
\frac{Dm_i}{Dt} = w_i \frac{Dm}{Dt} - \int_{\partial l} \rho'(v^l - v^s) \cdot \nabla w_i dV + \int_{\Sigma_e} \mathbf{J}_i \cdot \mathbf{n}^e dS + \int_{\Sigma_e} \mathbf{J}_i \cdot \mathbf{n}^l dS
\]  

(10)

As a matter of fact, substituting Eq. (10) into Eq. (4) can derive a first interesting expression of the macrosegregation rate. Adding that the gradients of composition (Hypothesis H9) and the velocity of the liquid (Hypothesis H10) are uniform in the domain \( D \), we get:

\[
\frac{D\bar{w}_i}{Dt} = \frac{1}{m} (w_i - \bar{w}_i) \frac{Dm}{Dt} - \frac{1}{m} \rho^s V^l - \nabla \cdot \mathbf{J}_i \cdot \mathbf{n}^l dS + \frac{1}{m} \int_{\Sigma_e} \mathbf{J}_i \cdot \mathbf{n}^e dS + \frac{1}{m} \int_{\Sigma_e} \mathbf{J}_i \cdot \mathbf{n}^l dS
\]  

(11)

The term \((Dm/dt)\) must be broken down into terms of the main variables \( V \) and \( m^e \) to fully understand the reasons for changes of the average composition of domain \( D \).

Substituting Eq. (9) in the (11) for the macrosegregation rate leads to the central result of this work:

\[
\frac{D\bar{w}_i}{Dt} = \frac{1}{m} (w_i - \bar{w}_i) \left[ \rho^l \left( v^l \frac{1}{\rho^l} \frac{d\rho^l}{dt} + v^l \frac{1}{\rho^l} \frac{\partial \rho^l}{\partial t} \right) + \frac{\rho^s - \rho^l}{\rho^e} \frac{Dm^e}{Dt} + \rho^l \frac{DV}{Dt} \right] - \frac{1}{m} \rho^l V^l - \nabla \cdot \mathbf{J}_i \cdot \mathbf{n}^l dS
\]  

(12)

This developed form of the so-called macrosegregation rate is suitable for explicitly calculating the various contributions to macrosegregation that are related to the solidification of a mushy alloy when the solid forms a skeleton that is continuous but spongy.

The first term of the right-hand side of Eq. (12) is proportional to the difference in composition between the liquid and the mush (liquid + solid), \((w_i - \bar{w}_i)\). It is also proportional to the variation of the mass of the domain \( D \), \((Dm/Dt)\). Such variation of mass corresponds to an exchange of liquid between this domain and its neighborhood due to:

- the rate of change in density of both the solid and liquid phases, respectively \((d\rho^l/dt)\) and \((d\rho^s/dt)\),
- the rate of progress of solidification, \((Dm^e/Dt)\),
- the rate of change in volume of the domain \( D \), \((DV/Dt)\), due to the deformation of the solid under various thermo-mechanical forces.
The second term of the right-hand side of Eq. (12) is proportional to the gradient of solute concentration in the liquid within the domain, \( \nabla w_i \). It is proportional also to the average relative velocity of the liquid with respect to the solid, \( \mathbf{v}^l - \mathbf{v}^s \). It corresponds to a liquid flow that circulates through the porous solid skeleton of the mush. Therefore, the relative velocity being considered is dependent somehow on the exchange of mass between the domain and its neighborhood as already mentioned. It must be noted that this term does not include the contributions of the first line.

The two last terms of the right-hand side of Eq. (12) are related to the chemical diffusion in the liquid and in the solid through the outer boundaries of the respective domains. Most of the time, they are negligible.

As a conclusion to this section, we want to emphasize that the first term of the right-hand side of Eq. (12) contains the contribution that can become the far most important one to the macrosegregation rate in specific conditions. Such conditions are frequently encountered during continuous casting of steel. In the center of a thick slab or bloom, at the bottom of the mushy zone, close to the completion of solidification, the longitudinal temperature gradients are small indeed, as are the longitudinal composition gradients. Thus, the second term on the right-hand side of Eq. (12) is small. Moreover, the cooling rate is low. Therefore, the first contributions to the first term are small because \( \rho^s \) and \( \rho^l \) are mainly temperature dependent. Finally, the rate of progress of solidification is negligible. The dominating term is then the one that is related to the variation of the volume of the solid skeleton under various thermo-mechanical forces:

\[
\frac{D\bar{w}_i}{Dt} \approx \frac{\rho^l}{m/V} (w_i^l - \bar{w}_i) \frac{1}{V} \frac{DV}{Dt} \tag{13}
\]

This contribution is all the more important since the solute concentration in residual liquid can be very high at the end of the solidification (i.e. up to eutectic compositions).

Although Eq. (12) is the central result of this work, it is not amenable to comparisons with former expressions since it has no equivalent in the literature. Therefore, we have also expressed the main conclusions of the present work in terms of microsegregation rate.

### 4. Calculation of the microsegregation rate

In order to compare our results with previous work, we derived relationships between the microsegregation rate, as defined by Eq. (5), and variables that describe the progress of solidification and the movements of matter in the mushy zone, as presented in Table 1.

We derived a first expression for the conservation of mass of component \( B_i \) by combining Eqs. (9) and (10), leading to:

\[
\frac{Dm_i}{Dt} = \rho^l w_i^l \left( \nabla \cdot \frac{1}{\rho^s} \frac{d\rho^l}{dt} + \nabla \cdot \frac{1}{\rho^s} \frac{d\rho^l}{dt} \right) + w_i \frac{\rho^s - \rho^l}{\rho^s} \frac{Dm^s}{Dt} + \rho^l w_i^l \frac{DV}{Dt} - \int \nabla \rho^l (\mathbf{v}^l - \mathbf{v}^s) \cdot \nabla w_j dV \tag{14}
\]

\[
+ \int_{\Sigma_e} \mathbf{J}_i \cdot \mathbf{n} dS + \int_{\Sigma_i} \mathbf{J}_i \cdot \mathbf{n} dS
\]

We then derived a second expression for the conservation of mass of component \( B_i \) that contains explicitly the microsegregation rate (Appendix A, Eqs. (A.23) and seq.). This equation is referred to as Eq. (A.30) in Appendix A:

\[
\frac{Dm_i}{Dt} = \rho^l w_i^l \left( \nabla \cdot \frac{1}{\rho^s} \frac{d\rho^l}{dt} + \nabla \cdot \frac{1}{\rho^s} \frac{d\rho^l}{dt} \right) + \frac{\rho^s w_i^s - \rho^l w^s}{\rho^s} \frac{Dm^s}{Dt} + \rho^l w_i^l \frac{DV}{Dt} - \int \nabla \cdot \mathbf{J}_i dV + \rho^l \frac{\partial w_i^l}{\partial t} \mathbf{v}^l \tag{15}
\]

Combining Eqs. (14) and (15) yields the following final result:
\[
\frac{\partial w_i^l}{\partial t} = \frac{1}{\rho^s V_s} (w_i^{l/s} - w_i^{s/l}) \frac{Dm^e}{Dt} - v^{l-s} \text{grad} w_i^l - \frac{1}{\rho^s V_s} \int_{Z_i} \mathbf{J}_s^l \cdot \mathbf{n} \, dS + \frac{1}{\rho^s V_s} \int_{Z_i} \mathbf{J}_l^s \cdot \mathbf{n} \, dS
\]  

(16)

Eq. (16) shows that microsegregation that builds up in a solidifying mushy zone can evolve because of four different elementary phenomena:

- The first term on its right-hand side is proportional to the rate of change of the mass of solid, \( (Dm^e/\partial t) \). It is thus directly related to the progress of solidification. It is also proportional to the difference in composition between solid and liquid across the solid/liquid interface, \( (w_i^{l/s} - w_i^{s/l}) \).
- The second term on the right-hand side of Eq. (16) is proportional to the gradient of solute concentration in the liquid within the domain, \( \text{grad} w_i^l \). It is proportional also to the average relative velocity of the liquid with respect to the solid, \( v^{l-s} \). This term became popular following the work of Flemings’ group in the sixties [5–8].
- The third term on the right-hand side of Eq. (16) is related to the back diffusion flux in the solid phase, \( \mathbf{J}_s^l \), from the solid–liquid interface.
- The fourth term accounts for the effects of the diffusion flux in the liquid phase, \( \mathbf{J}_l^s \), through the outer boundary of the liquid domain.

It is interesting to note that the rate of variation of the total volume, \( (Dv/\partial t) \), does not appear explicitly in Eq. (16) of the microsegregation rate. This result is related to our choice of the variables for describing the progress of solidification. The situation may be different with other variables, as we shall see in the following.

As a matter of fact, these results must now be compared to those of Flemings and Nereo, as published in the 1967 reference paper [5]. These authors insisted on the relationship between the quantity \( (\partial w^l_i/\partial t) \), called here: microsegregation rate, and the rate of progress of solidification. With the original notations, the central result is Eq. (14) of Ref. [5]:

\[
\frac{\partial C_L}{\partial t} = \frac{1 - k}{1 - \beta} \frac{\partial g_L}{\partial t} - \mathbf{v} \cdot \nabla C_L
\]  

(17a)

where \( k \) is the partition ratio, \( \beta \) is the solidification shrinkage that is defined by the quantity \( \rho^s - \rho^l / \rho^s \), \( \mathbf{v} \) is the “local velocity of interdendritic liquid relative to solid” and \( C_L \) is the “liquid composition within the volume element”.

The former equation was derived under a few conditions that will be recalled later. With the notations of this work, it should be rewritten as follows:

\[
\frac{\partial w_i^l}{\partial t} = \frac{\rho^s}{\rho^l} (1 - k_i^{l/s}) \frac{w_i^l}{1 - g_i} \frac{Dg^s}{\partial t} - v^{l-s} \text{grad} w_i^l
\]  

(17b)

where \( k_i^{l/s} \) is the partition ratio of component \( B_i \) between the solid and liquid phases. It must be compared to Eq. (16) of this work. Therefore, the rate of change of solid mass entering Eq. (16) must be expressed in terms of volume fraction of solid. The definition of the volume fraction leads directly to the following expression between \( (Dg^s/\partial t) \), \( (Dm^e/\partial t) \) and \( (Dv/\partial t) \):

\[
\frac{Dm^e}{\partial t} = \rho^s V_s \frac{Dg^s}{\partial t} + \rho^s g^s \frac{DV}{\partial t} + g^s V \frac{d \rho^e}{\partial t}
\]  

(18)

By substituting Eq. (18) in Eq. (16), a new general expression of the microsegregation rate is obtained in terms of volume fraction of solid, volume of the domain, and relative velocity of the liquid:
\[ \frac{\partial w_i}{\partial t} = \rho^s \frac{1}{\rho^l 1-g^s} (w_l^{i/s} - w_i) \frac{Dg^s}{Dt} - \mathbf{v}^{l-s} \cdot \nabla w_i + \rho^s \frac{g^s}{\rho^l 1-g^s} (w_l^{i/s} - w_i^g) \left[ \frac{1}{V} \frac{DV}{Dt} + \frac{1}{\rho^s} \frac{d\rho^s}{dt} \right] \] (19a)

\[ - \frac{1}{1-g^s} \frac{1}{\rho^l V} \int_{\Sigma_{\text{ls}}} \mathbf{J}_l \cdot \mathbf{n} dS \quad \text{and} \quad - \frac{1}{1-g^s} \frac{1}{\rho^l V} \int_{\Sigma_{\text{ls}}} \mathbf{J}_l \cdot \mathbf{n} dS \]

These hypotheses are: no exchange of mass by diffusion between the domain and its surroundings and no change with time of the density of solid. Under these conditions, Eq. (19a) becomes:

\[ \frac{\partial w_i}{\partial t} = \rho^s \frac{1}{\rho^l 1-g^s} (w_l^{i/s} - w_i) \frac{Dg^s}{Dt} - \mathbf{v}^{l-s} \cdot \nabla w_i + \rho^s \frac{g^s}{\rho^l 1-g^s} (w_l^{i/s} - w_i^g) \frac{1}{V} \frac{DV}{Dt} \] (19b)

The main difference between this last result (19b) of this work and Flemings and Nereo’s Eq. (17b) is the presence of a new term that is associated with the volume change of domain D:

\[ \frac{\rho^s}{\rho^l (1-g^s)} (w_l^{i/s} - w_i^g) \frac{1}{V} \frac{DV}{Dt} \] (20)

It may be noted that this term is all the more important when solidification is nearly completed. Then, indeed, the factor \([g^s(1-g^s)]\) tends to infinity when the solid fraction \(g^s\) tends to unity.

In this analysis, each specific situation of solidification is defined by a history of the progress of solidification, a history of the deformation of the growing solid, and a history of the hydrodynamics of the residual liquid. These histories are characterized, respectively, by the quantities \((Dm^s/Dt)\), \((DV/Dt)\) and \(v^{l-s}\). Since the main cause of solidification remains heat extraction, we must complete our analysis by studying the link between the imposed heat transfer and the progress of solidification.

5. Heat extraction and solidification

To relate the intensity of heat extraction and the rate of progress of solidification, the first law of thermodynamics applied to the domain D must be expressed. This domain is a multicomponent, polyphasic and open system (Appendix B). It is assumed that the only work to be considered is the mechanical work exerted by the external pressure on the system and on the liquid that enters or leaves the domain D. Moreover, it is reasonable to consider that the pressure is uniform and constant. Finally, we get:

\[ \frac{D}{Dt} \int_D \rho h dV = \sum_i \int_{\Sigma_{\text{li}}} \rho h_i (\mathbf{v}_i - \mathbf{\Omega}_i) \cdot \mathbf{n} dS + \frac{DQ}{Dt} \] (21)

where \(h\) represents the enthalpy per unit mass, \(h_i\) is the partial massic enthalpy of component \(B_i\) in the liquid phase and \(Q\) the heat exchanged with the surroundings.

Eq. (21) accounts for the fact that the boundaries of the domain stick to the solid (Hypotheses H5 and H6) and that solid-state diffusion is negligible, as assumed by Flemings and Nereo. Under such a condition that solid-state diffusion is negligible, calculations detailed in Appendix B lead to the following expression for the energy balance:

\[ -\Delta h \frac{Dm^s}{Dt} + \left( m^s \left( \sum_i w_l^{i/s} \frac{\partial h_i^s}{\partial t} \right) + m^l \left( \sum_i w_l^{i/s} \frac{\partial h_i^l}{\partial t} \right) \right) + m^l v^{l-s} \left( \sum_i w_l^{i/s} \nabla h_i^l \right) + \int_{D'} \sum_i (\mathbf{J}_l \cdot \nabla h_i^l) dV \] (22)
where $\Delta h$ represents the enthalpy of dissolution per unit mass of a solid, the composition of which is $w_i$, into a liquid, the composition of which is $w_i'.

In general, the partial massic enthalpy of component $B_i$ in the phase $\varphi$, $h_i^\varphi$, depends on the temperature and the composition of the phase. For ideal solutions, it depends only on temperature.

Under the restriction that the partial massic enthalpies depend only on temperature and under the assumption that the fourth term on the left-hand side of Eq. (22) is negligible because it is the product of two small terms, we get:

$$\Delta h \frac{Dm^s}{Dt} + (m^i c_p^\varphi + m^s c_p^\varphi) \frac{dT}{Dt} + m^i c_p^\varphi v^{l-s} \cdot \text{grad } T = \frac{DQ}{Dt}$$  \hspace{1cm} (23)

where $c_p^\varphi$ represents the heat capacity per unit mass at constant pressure of phase $\varphi$ and $m^\varphi$ the mass of phase $\varphi$ in the domain $D$, ($\varphi = l, s$).

The expression (23) of the energy balance provides a relationship between the rate of heat extraction, $(\frac{DQ}{Dt})$, the rate of progress of solidification, $(\frac{Dm^s}{Dt})$, the rate of cooling, $(\frac{\partial T}{\partial t})$, and the scalar product $(v^{l-s} \cdot \text{grad } T)$.

In other respects, it is possible to combine the expressions (16) of the microsegregation rate of each component in order to obtain another relationship between $(\frac{Dm^s}{Dt})$, $(\frac{\partial T}{\partial t})$, and $(v^{l-s} \cdot \text{grad } T)$. As a matter of fact, according to hypotheses (H2–H4), it is possible to link the temperature and the liquid composition locally in the mushy zone because local chemical equilibrium is achieved between liquid and solid across the solid/liquid interface. We can write:

$$\text{grad } T = \sum_i m_i \text{grad } w_i^l$$  \hspace{1cm} (24a)

$$\frac{\partial T}{\partial t} = \sum_i m_i \frac{\partial w_i^l}{\partial t}$$  \hspace{1cm} (24b)

where $m_i$ is the slope of the liquidus surface related to component $B_i$. In other words, $m_i = \frac{\partial T_{Li}}{\partial w_i^l}$ where $T_{Li}$ is the liquidus temperature related to the local composition of the liquid in the mushy zone.

In the case when there is “no exchange of mass by diffusion between the domain and its surroundings”, multiplying Eq. (16) by $m_i$ for each component $B_i$ and adding term to term all the resulting equations for all components leads to the following equation:

$$\frac{\partial T}{\partial t} = \frac{1}{\rho V} \left( \sum_i m_i (w_i^{l/s} - w_i^{s/l}) \right) \frac{Dm^s}{Dt} - v^{l-s} \cdot \text{grad } T$$  \hspace{1cm} (25)

Transforming Eq. (25) leads to the following relationship between the rate of progress of solidification and the rate of cooling of the liquid in its own Lagrangian frame:

$$\frac{Dm^s}{Dt} = \frac{m^i}{\sum_i \{ -m_i (w_i^{l/s} - w_i^{s/l}) \} } \left( -\frac{dT}{dt} \right)^1$$  \hspace{1cm} (26)

where $(-\frac{dT}{dt})^1$ is the rate of cooling of the liquid in its own Lagrangian frame:

$$\left( -\frac{dT}{dt} \right)^1 = - \frac{\partial T}{\partial t} - v^{l-s} \cdot \text{grad } T = -(v^{l-s} - v_T) \cdot \text{grad } T$$  \hspace{1cm} (27)

with $v_T$ the velocity of the local isotherm $T$ in the reference frame of the solid.

Since the denominator on the right-hand side of Eq. (26) is usually positive, the sign of the quantity...
(27) gives the sign of \( \frac{Dm_s}{Dt} \). It is positive when the velocity of the liquid is smaller than the velocity of the isotherms in the direction of the temperature gradient. It is negative in the case when liquid moves quicker than the isotherms in this direction. In the latter situation, the solid of the mushy zone can remelt locally although the metal cools down. This result generalizes the conclusions of Mehrabian et al. [8] about the possibility of local remelting in the case of the solidification of a multicomponent alloy with spongy deformation of the mushy zone.

6. Conclusion

This work offers general relationships making it possible to describe the building-up of macrosegregation in cast products where the solid skeleton of the mushy zone deforms during solidification. These equations are useful for devising practical means for decreasing segregation, especially in continuous cast steel products.

In order to derive such general expressions, a Lagrangian approach has been proposed where the elementary domain for establishing the balances is built on the solid framework of the mushy zone, sticks to it, and deforms with it. In this formulation, the natural variable for describing the progress of solidification is the mass of solid in the domain, \( m_s \). Moreover, adding the volume of the elementary domain, \( V \), has been proposed as a second pertinent variable for describing the movements of matter in the mushy zone. The first variable related to mass movements remains the relative velocity of the liquid with respect to the solid: \( v_{ls} \), as in Flemings’ analysis.

Attention has been focused on the evolution of the average mass fraction of component \( B_i \) in the domain \( D \) that has been termed “local macrosegregation rate”. The explicit Eq. (12) of the so-called macrosegregation rate is shown to be suitable for comparing respective individual contributions to macrosegregation during solidification of a mushy alloy, when the solid forms a skeleton that is continuous but spongy.

The first contribution is proportional to the composition difference between the liquid and the mush. It is also proportional to the mass variation of domain \( D \). This variation of mass corresponds to an exchange of liquid between domain \( D \) and its neighborhood due to different causes:

- the changes in densities of both the solid and liquid phases due mainly to temperature variations,
- the progress of solidification,
- the volume change of domain \( D \) due to deformation of the solid.

The second contribution to the macrosegregation rate is proportional to the gradient of solute concentration in the liquid within the domain. It is proportional also to the average relative velocity of the liquid with respect to the solid. It corresponds to a liquid flow that circulates through the porous solid skeleton of the mush. It is related to the term that became popular following the work of Flemings’ group on macrosegregation in the sixties. It must be noted that this well-known latter contribution does not include the former one, which may also happen to be the most important of both.

As a matter of fact, the first effect, that is the main novelty of this work, contains a term that can become the far most important cause of macrosegregation during continuous casting of steel. In the center of a thick steel slab or bloom, at the bottom of the mushy zone, close to the completion of solidification, the longitudinal temperature gradients are small indeed, as are the longitudinal composition gradients. The dominating term is then the one that is related to the variation of the volume of the solid skeleton under various thermo-mechanical forces.

In order to compare the present contribution with former work, we have derived expression (16) between the local microsegregation rate, as defined by the rate of change of the liquid composition, and variables that describe the progress of solidification and the movements of mass in the mushy zone. From this
viewpoint, the main result of this work (Eq. (19b)) differs from Flemings’ well-known equation by the presence of a new term that is proportional to the rate of volume change of the domain during solidification.

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Appendix A. Mass balances at different scales

A.1. Local expressions of the mass balances

A.1.1. Local mass balances in the volumes

In the absence of a term of mass production in volume, the continuity equation for the component $B_i$ in the sub-domain $D_\phi$ can be written as follows in a first given reference frame:

$$\frac{\partial (\rho w_i \rho v_i)}{\partial t} + \text{div}(\rho w_i v_i v_i) = 0$$

where $v_i$ is the velocity of the component $B_i$ in the sub-domain $D_\phi$ with respect to the given frame.

The summation of the former equation over all the components present in the domain $D_\phi$ leads to a first expression of the overall continuity equation in the phase $\phi$:

$$\frac{\partial \rho_\phi}{\partial t} + \text{div}(\rho_\phi v_\phi) = 0$$

(A.2)

To derive Eq. (A.2) from Eq. (A.1), the definition of the barycentric velocity of the sub-domain $D_\phi$, $v_\phi$, must be recalled:

$$v_\phi = \sum_i w_i \phi_i$$

(A.3)

and it must be noted that:

$$\sum_i w_i = 1$$

(A.4)

Let us now introduce the relationship between two different operators that differ from each other by the reference frame. Please note $\phi^I$ the first reference frame and $\phi^2$ the second one:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_\phi^2 - v_\phi^1 \text{grad}$$

(A.5)

where $v_\phi^2 - v_\phi^1$ is the relative velocity of the second frame $\phi^2$ with respect to the first one, $\phi^I$, $(\partial/\partial t)$ the derivation operator in the reference frame $\phi^I$, and $d/dt$ the derivation operator in the reference frame $\phi^2$.

The diffusion flux of the component $B_i$ in the sub-domain $D_\phi$, $J_i^\phi$, should also be introduced:

$$J_i^\phi = \rho_\phi w_i (v_i^\phi - v_\phi)$$

(A.6)

After the development of the divergence term in Eq. (A.1) and combination with the Eqs. (A.2), (A.5)
and (A.6), the continuity Eq. (A.1) can be rewritten as follows in the Lagrangian frame of the barycentric movement of the phase $\varphi$:

$$\rho^\varphi \frac{dw^\varphi}{dt} + \text{div}\ J^\varphi = 0$$  \hspace{1cm} (A.7)

Similarly, it is possible to rewrite the overall continuity equation in developing $\text{div}(\rho^\varphi v^\varphi)$ and using the definition (A.5) of the total derivation:

$$\frac{d\rho^\varphi}{dt} + \rho^\varphi \text{div} v^\varphi = 0$$  \hspace{1cm} (A.8)

### A.1.2. Local mass balances at the solid/liquid interface

In the absence of a term of interfacial mass production, without any adsorption or desorption at the solid/liquid interface $\Sigma_{s/l}$, the continuity equation for the component $B_i$ along the solid–liquid interface $\Sigma_{s/l}$ can be written as follows:

$$\rho^s w^s_i (v^s_i - \Omega^{s_i}) \cdot n^s + \rho^l w^l_i (v^l_i - \Omega^{s_l}) \cdot n^l = 0$$  \hspace{1cm} (A.9)

The summation of the former equation over all the components that are present in the vicinity of the interface in conjunction with Eqs. (A.3) and (A.4) leads to the overall continuity equation across this interface:

$$\rho^s (v^s - \Omega^{s_i}) \cdot n^s + \rho^l (v^l - \Omega^{s_l}) \cdot n^l = 0$$  \hspace{1cm} (A.10)

### A.2. Time derivative of the integral of an additive volumetric quantity over a deforming domain

The time derivative of the integral of an additive quantity related to a component $B_k, f_k$, over a domain $D^\alpha$ which deforms arbitrarily with time can be written as follows [23]:

$$\frac{D}{Dt} \int_{D^\alpha} \rho f_k dV = \int_{\Sigma^\alpha} \rho f_k (v_k - \Omega^\alpha) \cdot n^\alpha dS + \int_{D^\alpha} A_k dV$$  \hspace{1cm} (A.11)

where $\rho_k$ is the local density of the component $B_k$ in phase $\alpha$, $f_k$ the additive quantity per unit mass of component $B_k$ in phase $\alpha$, $\Omega^\alpha$ the velocity of the boundary of the domain $D^\alpha$, noted $\Sigma^\alpha$, $v_k$ the absolute velocity of the component $B_k$, velocity that is defined at each point of phase $\alpha$, $n^\alpha$ the normal unit vector to the interface $\Sigma^\alpha$ directed toward the inward of the domain $D^\alpha$, and $A_k$ the production term of the quantity $f_k$ in the volume of phase $\alpha$: $A_k = \rho_k (df_k/dt)$.

### A.3. Expressions of mass conservation at the scale of the domains

#### A.3.1. Conservation of mass for the component $B_i$ in the sub-domain $D_\varphi$ ($\varphi = s, l$)

The nature of the domain $D^\varphi$ should now be specified. It can be either the solid or the liquid sub-domain. By identifying the additive quantity per unit mass in Eq. (A.11) with the mass fraction of component $B_i$, $w^\varphi_i$, and in the absence of a production term of $w^\varphi_i$ in volume, the conservation of mass of component $B_i$ in the sub-domain $D^\varphi, m^\varphi_i$, can be written:

$$\frac{Dm^\varphi_i}{Dt} = \frac{D}{Dt} \int_{D^\varphi} \rho w^\varphi_i dV = \int_{\Sigma^\varphi} \rho w^\varphi_i (v^\varphi_i - \Omega^{\varphi_i}) \cdot n^\varphi dS + \int_{\Sigma^{s/l}} \rho w^\varphi_i (v^\varphi_i - \Omega^{s_l}) \cdot n^\varphi dS$$  \hspace{1cm} (A.12)
A.3.2. Conservation of mass in the sub-domain $D_i$

Taking into account Eqs. (A.3) and (A.4), the summation of Eq. (A.12) over all components $B_i$ that are present in the sub-domain $D_i$ leads to the expression of the conservation of the mass in this sub-domain:

$$\frac{Dm_i}{Dt} = \int_{\Sigma_i^e} \rho^e(v^e - \Omega^e_i) \cdot n^e dS + \int_{\Sigma_i^{s/l}} \rho^e(v^e - \Omega^{s/l}_i) \cdot n^e dS$$

(A.13)

A.3.3. Conservation of mass for the component $B_i$ in the domain $D$

The summation over all sub-domains $D_i$ of the conservation Eq. (A.12) leads to the expression of the conservation of the mass of the component $B_i$ in the domain $D$, $m_i$:

$$\frac{Dm_i}{Dt} = \int_{\Sigma_i^e} \rho^e w_i^e(v^e_i - \Omega^e_i) \cdot n^e dS + \int_{\Sigma_i^{s/l}} \rho^e w_i^e(v^e_i - \Omega^{s/l}_i) \cdot n^e dS$$

(A.14a)

$$+ \int_{\Sigma_i^{s/l}} \rho^s w_i^s(v^s_i - \Omega^{s/l}_i) \cdot n^s dS + \int_{\Sigma_i^e} \rho^s w_i^s(v^s_i - \Omega^s_i) \cdot n^s dS$$

The sum of the third and fourth terms of the right-hand side of Eq. (A.14a) cancels according to (A.9). One gets:

$$\frac{Dm_i}{Dt} = \int_{\Sigma_i^e} \rho^e w_i^e(v^e_i - \Omega^e_i) \cdot n^e dS + \int_{\Sigma_i^{s/l}} \rho^e w_i^e(v^e_i - \Omega^{s/l}_i) \cdot n^e dS$$

(A.14b)

Eqs. (A.14b) and (A.6) can be combined in order to differentiate the contributions due to convection and diffusion in each sub-domain:

$$\frac{Dm_i}{Dt} = \int_{\Sigma_i^e} \rho^e w_i^e(v^e_i - \Omega^e_i) \cdot n^e dS + \int_{\Sigma_i^{s/l}} \rho^e w_i^e(v^e_i - \Omega^{s/l}_i) \cdot n^e dS + \int_{\Sigma_i^e} J_i^e \cdot n^e dS + \int_{\Sigma_i^{s/l}} J_i^{s/l} \cdot n^{s/l} dS$$

(A.15a)

The first term of the right-hand side of Eq. (A.15a) cancels because of the hypothesis (H6). Eq. (A.15a) can then be transformed further by using (H5–H7):

$$\frac{Dm_i}{Dt} = \int_{\Sigma_i^e} \rho^e w_i^e(v^e - v^e_i) \cdot n^e dS + \int_{\Sigma_i^{s/l}} J_i^e \cdot n^s dS + \int_{\Sigma_i^{s/l}} J_i^{s/l} \cdot n^{s/l} dS$$

(A.15b)

By adding and subtracting the integral of $(\rho^e w_i^e(v^e - v^e_i) \cdot n^e)$ over the surface of the solid/liquid interface $\Sigma^{s/l}$, a surface integral along $\Sigma^{s/l}$ is obtained. It is then transformed into a volume integral thanks to Ostrogradsky’s theorem. The use of the theorem of the divergence leads to the following expression:

$$\frac{Dm_i}{Dt} = -\int_{D_i} \rho^e w_i^e(v^e - v^e_i) \cdot \nabla w_i^e dV - \int_{D_i} \rho^e v^e_i \cdot \nabla w_i^e dV - \int_{\Sigma^{s/l}} \rho^e w_i^e(v^e - v^e_i) \cdot n^e dS$$

(A.16)

$$+ \int_{\Sigma_i^e} J_i^e \cdot n^e dS + \int_{\Sigma_i^{s/l}} J_i^{s/l} \cdot n^{s/l} dS$$

According to hypothesis (H3), it is possible to rewrite Eq. (A.16) by extracting $w_i^e$ from the first and third integrals in the right-hand side:
\[
\frac{\text{D}m}{\text{D}t} = -w_l \int_{D_l} \text{div}[\rho'(v^l - v^s)]dV - \int_{D_l} \rho'(v^l - v^s) \text{grad} w_l dV - w_l \int_{\Sigma^{s/l}} \rho'(v^l - v^s) \cdot n^l dS + \int_{\Sigma^{s/l}} J^l \cdot n^l dS
\]  
(A.17)

+ \int_{\Sigma^{s/l}} J^l \cdot n^l dS

A.3.4. Conservation of the total mass in the domain \(D\)

The summation of Eq. (A.12) over all sub-domains \(D^p\) and all components \(B_i\) present in the domain \(D\) leads to the expression of the conservation of the total mass in the domain \(D\), \(m\):

\[
\frac{\text{D}m}{\text{D}t} = \int_{D} \rho'(v^l - \Omega^l) \cdot n^l dS + \int_{D} \rho'(v^l - \Omega^l) \cdot n^l dS
\]  
(A.18)

To derive Eq. (A.18), a summation of Eq. (A.14b) for all components \(B_i\) can be used as a start, followed by Eqs. (A.3) and (A.4).

Eq. (A.18) can then be transformed by using hypotheses (H5–H7) and by adding and subtracting the integral of \((\rho'(v^l - v^s) \cdot n^l)\) over the surface of the solid/liquid interface \(\Sigma^{s/l}\):

\[
\frac{\text{D}m}{\text{D}t} = -\int_{D} \text{div}[\rho'(v^l - v^s)]dV - \int_{\Sigma^{s/l}} \rho'(v^l - v^s) \cdot n^l dS
\]  
(A.19)

The following calculations are necessary in order to develop the expression of the rate of change of the mass \(A.19\) in terms of elementary variables, amongst which the most important ones are \(V\) and \(m^p\).

According to hypotheses (H2–H4) and to Eq. (10), the first term of the right-hand side of Eq. (A.19) can be transformed as follows:

\[
- \int_{D} \text{div}[\rho'(v^l - v^s)]dV = - \int_{D} \text{div}(\rho'v^l) dV + \int_{D} \text{div}(\rho'v^s) dV = -V \text{div}(\rho'v^l) + \rho' \int_{D} \text{div} v^l dV =
\]  
(A.20a)

\[-V \text{div}(\rho'v^l) + \rho' \left( \frac{DV}{Dt} - \int_{D} \text{div} v^l dV \right)\]

The expressions (A.2) and (A.8) of the local continuity in volume are useful for transforming the first and third terms of the right-hand side of Eq. (A.20a). We get:

\[- \int_{D} \text{div}[\rho'(v^l - v^s)]dV = V \frac{\partial \rho^l}{\partial t} + \rho^l \frac{DV}{Dt} + \rho^l \int_{D} \frac{1}{\rho^l} \frac{d\rho^p}{dt} dV\]  
(A.20b)

Taking into account hypothesis (H8) according to which the density of the solid phase is uniform in the domain, we finally get:

\[- \int_{D} \text{div}[\rho'(v^l - v^s)]dV = V \frac{\partial \rho^l}{\partial t} + \rho^l \frac{DV}{Dt} + V^s \rho^l \frac{d\rho^p}{\partial t}\]  
(A.20c)

The second term of the right-hand side of Eq. (A.19) is related to what happens along the solid/liquid interface. The addition and the subtraction of the integral over the solid/liquid interface \(\Sigma^{s/l}\) of the quantity \((\rho'\Omega^{s/l} \cdot n^l)\) are first carried out:

\[
\int_{\Sigma^{s/l}} \rho'(v^l - v^s) \cdot n^l dS = \int_{\Sigma^{s/l}} \rho'(v^l - \Omega^{s/l}) \cdot n^l dS - \int_{\Sigma^{s/l}} \rho'(v^l - \Omega^{s/l}) \cdot n^l dS
\]  
(A.21a)
The overall continuity equation across the solid/liquid interface (A.10) is injected in Eq. (A.21a).

\[
\int_{\Sigma^{vl}} \rho^l (v^l - v^s) \cdot n^s dS = \left( \frac{\rho^l}{\rho^s} - 1 \right) \int_{\Sigma^{vl}} \rho^s (v^s - \Omega^{st}) \cdot n^s dS = \left( \frac{\rho^l}{\rho^s} - 1 \right) \frac{Dm^s}{Dt} \tag{A.21b}
\]

Finally, by taking into account Eqs. (A.20c) and (A.21b), Eq. (A.19) becomes:

\[
\frac{Dm}{Dt} = \rho^l \left( v^s + \frac{1}{\rho^s} \frac{D\rho^l}{Dt} \right) + \frac{\rho^s - \rho^l}{\rho^s} \frac{Dm^s}{Dt} + \rho^l \frac{DV}{Dt} \tag{A.22}
\]

A.3.5. Second expression for the conservation of mass for the component \(B_i\) in the domain \(D\)

Let us start again from Eqs. (A.14) and combine it with Eq. (A.6) in order to differentiate the contributions due to convection and diffusion in each sub-domain of the domain \(D\). If hypotheses (H5–H7) are taken into account, we get:

\[
\frac{Dm}{Dt} = \int_{\Sigma^{vl}} \rho^l w^l (v^l - v^s) \cdot n^l dS + \int_{\Sigma^{vl}} \left[ \rho^s w^s (v^s - \Omega^{st}) \cdot n^s + \rho^s w^l (v^l - \Omega^{st}) \cdot n^l \right] dS + \int_{\Sigma^c} J^l \cdot n^s dS \tag{A.23}
\]

\[
+ \int_{\Sigma^{vl}} J^l \cdot n^l dS + \int_{\Sigma^c} J^l \cdot n^l dS \tag{A.24}
\]

On one hand, the sum of the four surface integrals related to the diffusion fluxes can be transformed into two volume integrals. On the other hand, by adding and subtracting the integral of \((\rho^l w^l (v^l - v^s) \cdot n^l)\) over the surface of the solid/liquid interface \(\Sigma_{vl}\), it is possible to let the integral of \((\rho^l w^l (v^l - v^s) \cdot n^l)\) appear over the overall surface of the boundary \(\Sigma^l\). Then, it is useful to transform this surface integral into a volume integral. After developing this new integral, we finally get:

\[
\frac{Dm}{Dt} = \int_{D^l} \text{div} (\rho^l w^l v^l) dV - \int_{D^l} \text{div} (\rho^l w^l v^s) dV + \int_{\Sigma^{vl}} (\rho^s w^l - \rho^l w^l) (v^s - \Omega^{st}) \cdot n^l dS - \int_{D^s} \text{div} J^l dV \tag{A.25}
\]

\[
- \int_{D^l} \text{div} J^l dV
\]

The two first terms of the right-hand side of Eq. (A.24) can be transformed, thanks to the theorem of the divergence. Moreover, the use of the overall continuity Eq. (A.2) to the liquid domain leads to:

\[
- \int_{D^l} \text{div} (\rho^l w^l v^l) dV + \int_{D^l} \text{div} (\rho^l w^l v^s) dV = \int_{D^l} w^l \frac{\partial \rho^l}{\partial t} dV + \int_{D^l} w^l \text{div} (\rho^l v^s) dV - \int_{D^l} \rho^l (v^l - v^s) \text{grad} \ w^l dV \tag{A.26}
\]

The last term of the right-hand side of Eq. (A.24) can be transformed by using Eqs. (A.5) and (A.7) applied to the liquid:

\[
\int_{D^l} \text{div} J^l dV = - \int_{D^l} \rho^l \frac{\partial w^l}{\partial t} dV = - \int_{D^l} \rho^l \left( \frac{\partial w^l}{\partial t} + (v^l - v^s) \text{grad} \ w^l \right) dV \tag{A.27}
\]

By combining Eqs. (A.25) and (A.26), Eq. (A.24) can be rewritten as follows:
\[
\frac{Dm_i}{Dt} = \int_{D^i} w_i \frac{\partial \rho_i}{\partial t} dV + \int_{D^i} w_i \text{div}(\rho_i \mathbf{v}_i) dV + \int_{\partial D^i} \rho_i \frac{\partial \mathbf{w}_i}{\partial t} \cdot d\mathbf{S} + \int_{\partial D^i} (\rho_i \mathbf{w}_i - \rho_i \mathbf{w}_{i}^{\text{ref}})(\mathbf{v}_i - \mathbf{\Omega}_i^{\text{ref}}) \cdot \mathbf{n} dS - \int_{D^i} \text{div} \mathbf{J}_i dV
\]  
(A.27)

According to hypotheses (H2–H4), the temperature and the liquid composition are homogeneous in the domain. Therefore, the liquid density is homogeneous too. Therefore, it is possible to extract \( w_i \rho_i \) from the integral in the second term of the right-hand side of Eq. (A.27). Finally, using Eq. (10), Eq. (A.8) applied to the solid, and the assumption that the density of the solid phase depends only on the temperature make it possible to rewrite the second term of the right-hand side of Eq. (A.27) as follows:

\[
\int_{D^i} w_i \text{div}(\rho_i \mathbf{v}_i) dV = w_i \rho_i \int_{D^i} \text{div} \mathbf{v}_i dV = w_i \rho_i \left( \frac{DV}{Dt} + \mathbf{v} \cdot \frac{1}{\rho_i} \frac{d\rho_i}{dt} \right)
\]  
(A.28)

Taking into account hypotheses (H5–H7), the expression of the conservation of mass (A.13) applied to the solid sub-domain leads to:

\[
\frac{Dm^s}{Dt} = \int_{\Sigma^s} \rho^s (\mathbf{v}^s - \mathbf{\Omega}^s) \cdot \mathbf{n} dS = \int_{\Sigma^s} \rho^s (\mathbf{v}^s - \mathbf{\Omega}^{\text{ref}}) \cdot \mathbf{n} dS
\]  
(A.29)

Finally, by combining Eqs. (A.27)–(A.29), and by taking into account the fact that the liquid composition, the liquid density, and the solid density are homogeneous in the domain, we get:

\[
\frac{Dm_i}{Dt} = \rho_i \mathbf{w}_i \left( \mathbf{v}_i \cdot \frac{1}{\rho_i} \frac{d\rho_i}{dt} + \mathbf{v} \cdot \frac{1}{\rho_i} \frac{d\rho_i}{dt} \right) + \frac{\rho_i \mathbf{w}_i^s - \rho_i \mathbf{w}_{i}^{\text{ref}}}{\rho^s} \frac{Dm^s}{Dt} + \rho_i \mathbf{w}_i \frac{DV}{Dt} - \int_{D^i} \text{div} \mathbf{J}_i dV + \rho_i \frac{\partial \mathbf{w}_i}{\partial t} \cdot \mathbf{v}_i
\]  
(A.30)

Appendix B. First law of thermodynamics

The expression of the first law of thermodynamics for a multicomponent, polyphasic and open system defined by domain \( D \) is given by:

\[
\frac{D}{Dt} \int_D \rho e dV = \sum_i \int_{\Sigma^i} \rho_i e_i^l (\mathbf{v}_i - \mathbf{\Omega}_i^l) \cdot \mathbf{n} dS + \frac{DW}{Dt} + \frac{DQ}{Dt}
\]  
(A.31a)

where \( e \) represents the internal energy per unit mass, \( e_i^l \) is the partial massic internal energy of the component \( B_i \) in the liquid phase, \( W \) is the work of forces that are exerted on the system and \( Q \) is the heat exchanged with the surroundings.

Eq. (A.31a) accounts for the fact that the boundaries of the domain stick to the solid and that the solid-state diffusion is negligible. The only work to be considered is the mechanical work exerted by the external pressure on the system and on the liquid that enters or leaves the domain \( D \). The pressure can be considered uniform and constant. Therefore, the first principle can be rewritten as follows:

\[
\frac{D}{Dt} \int_D \rho h dV = \sum_i \int_{\Sigma^i} \rho_i h_i^l (\mathbf{v}_i - \mathbf{\Omega}_i^l) \cdot \mathbf{n} dS + \frac{DQ}{Dt}
\]  
(A.31b)

The left-hand side of Eq. (A.31b) must be broken down as follows:

\[
\frac{D}{Dt} \int_D \rho h dV = \frac{D}{Dt} \sum_i \int_{D^i} \rho_i h_i dV + \frac{D}{Dt} \sum_i \int_{D^i} \rho_i h_i dV
\]
Using Eq. (A.11) for each component in each sub-domain, and taking into account the hypotheses (H5–H7), we get:

\[
\frac{D}{Dt} \sum_i \int_{V_i} \rho_i^s \frac{dh_i^s}{dt} dV = \sum_i \int_{\Sigma_i} \rho_i^s (v_i^s - \Omega_i^{vd}) \cdot n^s d\Sigma + \sum_i \int_{V_i} \rho_i^s \frac{dH_i^s}{dt} dV
\]

\[
\frac{D}{Dt} \sum_i \int_{V_i} \rho_i^l \frac{dh_i^l}{dt} dV = \sum_i \int_{\Sigma_i} \rho_i^l (v_i^l - v^s) \cdot n^l d\Sigma + \sum_i \int_{V_i} \rho_i^l \frac{dH_i^l}{dt} dV
\]

It must be recalled that the operator \( \frac{dV}{d_t} \) \((\varphi = s, l)\) corresponds to a derivation in the frame related to the movement of the component \( B_i \) in the phase \( \varphi \). According to (A.5) it is possible to write:

\[
\frac{dh_i^s}{dt} = \frac{\partial h_i^s}{\partial t} + (v_i^s - v^s) \cdot \text{grad } h_i^s
\]

\[
\frac{dh_i^l}{dt} = \frac{\partial h_i^l}{\partial t} + (v_i^l - v^s) \cdot \text{grad } h_i^l
\]

where \( \frac{\partial}{\partial t} \) is the time derivative in the frame of the solid skeleton of the domain.

Following Flemings’ hypothesis, solid-state diffusion is negligible. We can thus write:

\[
\rho_i^s \frac{dH_i^s}{dt} = \rho_i^s \frac{\partial h_i^s}{\partial t}
\]

In the liquid phase, according to Eq. (A.6), we can write:

\[
\rho_i^l \frac{dH_i^l}{dt} = \rho_i^l \frac{\partial h_i^l}{\partial t} + \rho_i^l w_i^l (v_i^l - v^s) \cdot \text{grad } h_i^l + J_i \cdot \text{grad } h_i^l
\]

Eq. (A.31b) can be rewritten as follows:

\[
\sum_i \int_{\Sigma_i} [\rho_i^s (v_i^s - \Omega_i^{vd}) \cdot n^s + \rho_i^l (v_i^l - \Omega_i^{vd}) \cdot n^l] d\Sigma + \sum_i \int_{V_i} \rho_i^s \frac{\partial h_i^s}{\partial t} dV + \sum_i \int_{V_i} \rho_i^l \frac{\partial h_i^l}{\partial t} dV
\]

\[
+ \rho_i^l \left( \sum_i w_i^l \text{grad } h_i^l \right) \cdot v_i^l - \sum_i \int_{V_i} J_i \cdot \text{grad } h_i^l dV = \frac{dQ}{dt}
\]

Thanks to the continuity Eq. (A.9), the first integral of the left-hand side of Eq. (A.32) can be simplified as follows:

\[
\int_{\Sigma_i} \sum_i [\rho_i^s (v_i^s - \Omega_i^{vd}) \cdot n^s (h_i^s - h_i^l)] d\Sigma = \left\{ \sum_i w_i^{sl} (h_i^s - h_i^l) \right\} \int_{\Sigma_i} \rho_i^l (v_i^l - \Omega_i^{vd}) \cdot n^l d\Sigma = -\Delta h \frac{D m^s}{Dt}
\]

where \( \Delta h \) is the enthalpy of dissolution per unit mass of the solid of composition \( w_i^{sl} \) in the liquid of composition \( w_i^{ls} \), respectively.

Finally, the energy balance reduces to:

\[
-\Delta h \frac{D m^s}{Dt} + \left\{ m_i \left( \sum_i w_i^l \frac{\partial h_i^l}{\partial t} \right) \right\} + m_i v_i^l - \left( \sum_i w_i^l \text{grad } h_i^l \right) + \int_{V_i} \sum_i (J_i \cdot \text{grad } h_i^l) dV = \frac{dQ}{dt}
\]

(A.33)
References

Erratum to “Segregation during solidification with spongy deformation of the mushy zone” [Acta Materialia 51 (2003) 5263–5283] ✤, ✤ ✤

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The publishers regret that Eq. (1) was printed incorrectly. The correct equation is shown below:

\[
\frac{d\varepsilon_{11}}{dt} + \frac{d\varepsilon_{22}}{dt} + \frac{d\varepsilon_{33}}{dt} = \frac{1}{V} \frac{D}{Dr}. \tag{1}
\]