Almost all the metallic engineering structural materials are multi-component alloys and most of them undergo a dendritic solidification process under various cooling conditions. During these non-equilibrium solidification processes, not only will certain micro-segregation form inside the dendrite arms, but also several kinds of secondary phases will present interdendritically and/or at the grain boundaries [1]. The types and amounts of the secondary phases may significantly change the mechanical properties of the solidified alloy materials/casting parts both at room and elevated working temperatures [2-3]. Sometimes, even a trace of impurity element may dramatically lower the working temperatures of the solidified parts if the impurity solute forms a eutectic of low melting point (such as S in Fe and Sn in Al) [4]. Therefore, accurate prediction of the solidification path of a multi-component alloy and the amounts of the secondary phases presented under a given solidification condition is critical to understanding and controlling the performances of the solidified alloy materials/parts.

Since the introduction of the CALPHAD method into solidification simulation, the emphasis of solidification modeling work has been converted from binary alloys [5-7] to multi-component alloys [8-11]. Multi-component aluminum alloys represent an important group of commercial light alloys and have been widely used in automotive and aerospace fields due to their light weight, excellent castability and mechanical properties. The computational investigation for multi-component aluminum alloys have been carried out widely, especially in prediction of the solidification paths and micro-segregation behavior [8-11]. However, some of the modeling work assumes a pre-set function for the micro-scale solute profile [5-6], or neglects the back diffusion [7-8]; and most of the models assume the dendrite to be of one morphology, such as spherical, cylindrical, plate-like and so on [5-6, 8-11].

The aim of the present work is to extend the previously proposed multi-length scale model for binary alloys [12-13] to a more general, mixture-averaged multi-component/multi-phase micro-segregation model in a differential form. The models reflect the effects of morphologies of the solidifying phases and solid back diffusion (SBD) on segregation. A commercial Thermo-Calc software package/database was linked to the algorithms via its TQ6-interface for instantaneous determination of the related thermodynamic data of the multi-component alloys. The influences of cooling rates and other parameters on the solidification paths and micro-segregation behavior were numerically investigated by sample calculation of the ternary Al-Cu-Mg alloys. A parallel experimental investigation of Al-Cu-Si alloys solidified under three different cooling conditions were conducted to validate the theoretical model.

**Abstract:** On the basis of a multi-length scale modeling, a mixture-averaged multi-component/multiphase micro-segregation model was proposed without pre-set function for the micro-scale solute profile. The model explains the effect of morphologies of solidifying phases and solid back diffusion (SBD) on segregation, and covers the two limiting solidification cases of Scheil and Lever-rule models. A commercial Thermo-Calc software package/database was linked to the algorithms via its TQ6-interface for instantaneous determination of the related thermodynamic data of the multi-component alloys. The influences of cooling rate and other parameters on the solidification path and micro-segregation behavior were numerically investigated by sample calculation of the ternary Al-Cu-Mg alloys. A parallel experimental investigation on Al-Cu-Si alloys solidified under different cooling conditions was conducted to validate the theoretical model. Reasonable agreements were gained between the predicted solidification paths and the measured results.

**Key words:** solidification path; micro-segregation; multi-component/multi-phase alloys; thermo-Calc

**CLC numbers:** TG146.2’1/TP391

**Document code:** A

**Article ID:** 1672-6421(2012)03-269-06

**Male, born in 1981, Ph.D. candidate. Research interests: simulation of solidification transport phenomenon and calculation of solidification path of multi-component alloys.**

E-mail: zgwhit@163.com

**Received: 2011-05-17; Accepted: 2012-04-21**

**Zhao Guangwei**

(1. School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China; 2. State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, Hunan, China)
1 Multi-component micro-segregation model and algorithm

For a control volume (CV) taken from the mushy region in a solidifying multi-component alloy domain, the mixture averaging mass composition for the $n$th solute ($n=1,2,\ldots,N$) can be expressed as follows:\(^\text{[12]}\):

$$\left(\rho C_n\right)_m = \int_0^L \left(\rho_n C_n\right) d\eta + f_n \rho_s C_{n_0} \quad (n=1,2,\ldots,N) \quad (1)$$

where $C_n$ — concentration of the $n$th component
$m$ — mixture-averaged sense
$\rho$ — density
$f_n$ — volume fraction
$S$ — solid phase
$\eta$ — a volume fraction variable
$L$ — liquid phase

In such a solidification case, the CV locates in an open space where the solidification transmissions exist (such as thermal transmission and mass transmission), and the solute mass balances for this mixture CV can be expressed as:

$$\frac{\partial (\rho C_n)}{\partial t} = \nabla \left[ D_n \nabla (f_n \rho_n C_n) \right] + \nabla \left[ D_s \nabla (f_s \rho_s C_s) \right] - \nabla (f_n \rho_n V C_n) \quad (n=1,2,\ldots,N) \quad (2)$$

where the sum of the terms on the right-hand side of Eq. (2) represents the total $n$th solute mass exchange rate between the CV and the surrounding mixture-medium, which is driven by both the convection and diffusions. It is clear that if this mixture CV is isolated from its surroundings while it is cooled down, i.e. in a closed solidification case\(^\text{[12]}\), Eq. (2) then simplifies to:

$$\frac{\partial (\rho C_n)}{\partial t} = 0 \quad (n=1,2,\ldots,N) \quad (3)$$

which is equivalent to

$$\left(\rho C_n\right)_m = \int_0^L \left(\rho_n C_n\right) d\eta + f_n \rho_s C_{n_0} \quad (n=1,2,\ldots,N) \quad (4)$$

where $\rho_{n_0}$ is the original density of the alloy, and $C_{n_0}$ is the original composition of the $n$th component in the alloy. Here, Eq. (4) may represent a general micro-segregation model, taking a differential form but in a mixture-averaged or statistical-average sense. According to the micro/macro-segregation modeling proposed by Xu Daming\(^\text{[12]}\), Eq. (3) can be rewritten as follows for a closed single-phase, say $\alpha$-Al, multi-component solidification:

$$\frac{\partial (\rho C_n)}{\partial t} = \left(\rho C_n\right)_m \frac{\partial \rho_s}{\partial t} + f_n \frac{\partial (\rho_C C_n)}{\partial t} + \frac{\partial (\rho_s C_n)}{\partial t} \quad (n=1,2,\ldots,N) \quad (5)$$

where $\theta_s$ is the solidification shrinkage coefficient, $\beta = \rho_d / \rho_s - 1$.

In this general micro-segregation model of Eq. (5), the unified SBD-parameter $\theta_s$ reflecting any SBD-effects for the $n$th solute can be expressed as:

$$\theta_s = \theta_{s_0} \cdot \theta_n / (1 + \theta_n \cdot \theta_{s_0}) \quad (n=1,2,\ldots,N) \quad (6)$$

where $\theta_n$ is a Fourier diffusion number with geometric modification for the $n$th component, $\theta_{s_0}$ is a non-dimensional parameter for the sensibility of the inter-dendritic liquid concentration variation of the $n$th component to SBD, and * means at an interface.

The non-dimensional parameters of $\theta_n$ and $\theta_s$ can be written accordingly as:

$$\theta_{s_0} = \frac{D_n(T) / R_s}{S} \cdot A_{\alpha sN} \quad (n=1,2,\ldots,N) \quad (7)$$

where $D_n$ is diffusion coefficient for the $(n)$th component, $R_s$ is solidification rate, $R_s = \delta f / \partial t$, and

$$\theta_n = \frac{(1 + \beta) \lambda_s}{f_s} \cdot f_{s*} \quad (n=1,2,\ldots,N) \quad (8)$$

where $\beta$ is the solidification shrinkage coefficient, $\beta = \rho_d / \rho_s - 1$.

The $A_{\alpha sN}$ in Eq. (7) represents a basic geometry-unit vector and $\zeta$ is a normalized weighting vector corresponding to the basic geometry-unit $A_{\alpha sN}$\(^\text{[12]}\). By properly designing of the $f_s$-dependent $\zeta$-vector, the term of $\zeta A_{\alpha sN}$ may reasonably reflect the influences of the morphology of any complex solidifying phase on formation of the micro-segregation.

In the derivation of the multi-component micro-segregation model of Eqs. (4) to (7), the following assumptions are also made: (1) local thermodynamic keeps equilibrium at the solid/liquid interface of the growing dendrites; (2) no pore forms in the multi-component solidification process, i.e., the geometry continuity of $\sum_{n=1}^{N} f_n^* + f_1 = 1$, where $M$ is the number of phases totally solidified; (3) the redistribution of the $n$th-solute in the inter-dendritic melt is uniform due to the high ratio of $D_n / D_s > 10^4$ ($n=1,2,\ldots,N$) at least for a metallic-base alloy system; (4) the cross-diffusion effects are negligible (i.e. the off-diagonal diffusion coefficients are all negligibly small).

It is well known that, during the solidification process of an alloy, the complicated multi-phases solidification may constantly occur even for a binary system, e.g. in the Ti-Al binary system. In present study, the emphasis is placed on the modeling and algorithms for solidification paths and micro-segregation in a ternary eutectic system, Al-Cu-Mg system. In a ternary eutectic solidification process of a commercial aluminum alloy, the primary phase to solidify is usually $\alpha$-Al solution. Then some two-phase eutectic follows and attaches to the primary phase; and due to the limited solid-diffusion of the substitute alloying elements in the commercial alloys some three-phase eutectic will usually also form; see the illustration in Fig. 1. Now taking a typical ternary eutectic solidification path, i.e., $0<f_{3E}<f_{2E}+f_{1E}$, as an example, the corresponding liquid concentrations $C_n^* (n=1, 2)$ for each of solidification stages can be calculated by using of

Fig. 1: Schematic microstructure consisting of $\alpha$-dendrite, two-phase eutectic ($\alpha+\beta$) and ternary eutectic ($\alpha+\beta+\gamma$) in a later solidification stage of ternary eutectic alloy
the following equations.

In the stage of the single-solution solidification, e.g. $\alpha$-Al, $0 \leq f_{s(1E)}^{*} < f_{S(2E)}^{*}$, which is an extension version that derived for a binary dendritic solidification with an arbitrary solid back diffusion (SBD) effect by Xu Daming et al. \cite{11};

$$C_{n}^{i+1} = \frac{[(f_{i} \rho_{s}^{i} f_{i} - f_{i}^{*} \rho_{s}^{i} \rho_{s}^{i})] C_{n}^{i}}{(f_{i} \rho_{s}^{i})^{t+1} + (\Delta f_{s}^{i} + \Phi_{n}^{i} f_{i}^{*} \rho_{s}^{i})^{t+1}} \quad (n = 1, 2) \quad (9)$$

where

$$2E \rightarrow (\alpha + \beta) \text{ eutectic}$$

$$C_{n}^{i+1} = \frac{[(f_{i} \rho_{s}^{i} f_{i} - f_{i}^{*} \rho_{s}^{i} \rho_{s}^{i})] C_{n}^{i}}{(f_{i} \rho_{s}^{i} f_{i} - f_{i}^{*} \rho_{s}^{i} \rho_{s}^{i})^{t+1} + (\Delta f_{s}^{i} + \Phi_{n}^{i} f_{i}^{*} \rho_{s}^{i})^{t+1}} \quad (n = 1, 2) \quad (10)$$

Note that for a two-phase eutectic solidification in a ternary system, only one of the concentrations, $C_{n}^{i+1}$, is independent; because there exists a $(\alpha + \beta)$-tough in the ternary phase diagram space for the two-phase eutectic reaction.

In the process of the three-phase $(\alpha + \beta + \gamma)$ eutectic solidification ($f_{S(2E/3E)}^{*} \leq f_{s}^{*} \leq 1.0$), the liquid concentrations for both the solutes 1 and 2 have to keep constant according to Gibbs phase rule:

$$C_{n}^{i+1} = C_{n(1E)} \quad (n = 1, 2) \quad (11)$$

In Eqs. (9) to (11), the $f_{S(2E)}^{*}$ and $f_{S(2E/3E)}^{*}$ are the critical solid-fractions during the solidification transitions of $f_{S(1E)}^{*}$, $f_{S(2E)}^{*}$, and $f_{S(2E/3E)}^{*}$, respectively. The parameters related to the SBD in two-phase eutectic solidification process, as required in Eq. (10), are calculated using the following expressions:

$$\Phi_{a(2E)}^{*} = \theta_{a(2E)} \varphi_{a(2E)}/(1 + \theta_{a(2E)} \varphi_{a(2E)}) \quad (n = 1, 2) \quad (12)$$

where, the unified SBD-parameter $\Phi_{a}$ takes the same expression forms as in Eq. (12). To easy understand the changing tendency of micro-segregation with each possible influential parameter, an analytical expression model is often a preferential choice for a computationally efficient multi-length scale solidification modeling. However, it also should be pointed out that, because Eq. (17) is only an approximate solution to Eq. (5) (primarily due to taking the $\Phi_{a}$ parameter as a constant in the integration process), the obtained analytical micro-segregation model of Eq. (17) would give a less accurate description than the differential model of Eqs. (9) to (16) for the same solidification problem.

There are seven possible types of solidification path combinations that may occur in a ternary eutectic solidification system, i.e. $0 \leq f_{S(1E)}^{*} \leq f_{S(1E)}^{*} + 1.0$, $0 \leq f_{S(1E)}^{*} - f_{S(2E)}^{*} \leq 1.0$, $0 \leq f_{S(1E)}^{*} - f_{S(2E)}^{*} \leq 1.0$, $0 \leq f_{S(1E)}^{*} - f_{S(2E)}^{*} \leq 1.0$, $0 \leq f_{S(1E)}^{*} - f_{S(2E)}^{*} \leq 1.0$ and $0 \leq f_{S(1E)}^{*} - f_{S(2E)}^{*} \leq 1.0$. A completely numerical computation algorithm and program should be able to treat all these possible solidification cases. The entire algorithm in this paper is basically the same as that reported by Zhao Guangwei et al. \cite{14} for the analytical micro-segregation model but there are some differences. In the present algorithms, the solid-fraction, $f_{s}$, for all solidified phases is taken as the control variable for the entire solidification process of a given alloy. Compared with that uses different control variables in different solidification stages, this is more convenient when the micro-segregation model is coupled with macro-scale transport simulation. Another key issue in a multi-component/multi-phase solidification computation is the reliability of liquid-solid phase-change thermodynamic data and the way to access them. These thermodynamic data include the liquidus surface/mono-variant curves, multi-composition-dependent partition coefficients, etc. In the present modeling, these data are directly obtained from a ThermoCalc software package/database via its TQ6-interface in the computation processes.

2 Sample calculations for Al-Cu-Mg alloys

To investigate the feasibility of the proposed model, the Eqs. (9) to (16) and the algorithm were coupled with the ThermoCalc/
databases and the computational performances and sample calculations were carried out on an Al-1.0Cu-6.3Mg (in wt.% and same hereinafter) alloy system. The program is coded using FORTRAN90 language and directly coupled with a commercial Thermo-Calc (version-R) and COST2-database package via its TQ6-Interface. The data/functions used for the other related properties of the investigated ternary aluminum alloy systems in this paper are listed in Table 1.

Table 1: Physical properties for Al-Cu-Si and Al-Cu-Mg alloys used in the present calculations

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Expressions and values</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid diffusion coefficient of Cu in α</td>
<td>$D_{Cu}^\alpha = 4.8 \times 10^4 \text{EXP}(-16069/T)$ [m²/s]</td>
<td>[9]</td>
</tr>
<tr>
<td>Solid diffusion coefficient of Si in α</td>
<td>$D_{Si}^\alpha = 2.02 \times 10^6 \text{EXP}(-16069/T)$ [m²/s]</td>
<td>[9]</td>
</tr>
<tr>
<td>Solid diffusion coefficient of Mg in α</td>
<td>$D_{Mg}^\alpha = 6.23 \times 10^5 \text{EXP}(-13831/T)$ [m²/s]</td>
<td>[9]</td>
</tr>
<tr>
<td>Density of α-phase</td>
<td>$\rho_\alpha = 2.7 \times 10^3$ [kg/m³]</td>
<td>[10]</td>
</tr>
<tr>
<td>Density of θ-phase</td>
<td>$\rho_\beta = 4.34 \times 10^3$ [kg/m³]</td>
<td>[15]</td>
</tr>
<tr>
<td>Density of Si-phase</td>
<td>$\rho_\gamma = 2.33 \times 10^3$ [kg/m³]</td>
<td>[10]</td>
</tr>
<tr>
<td>Solidification shrinkage of α-phase</td>
<td>$\rho_s = 0.043$</td>
<td></td>
</tr>
</tbody>
</table>

The morphologies of solidifying phases, solid back diffusion (SBD) effects on segregation and the cooling rates can be considered in the parameter $\phi_n$ in Eq. (6). This parameter represents the extent of the SBD effect, which can significantly influence the calculation results of solidification path [12, 14]. Figure 2 shows the calculated solidification paths of the Al-1.0Cu-6.3Mg alloy under the six assumed conditions with different values of parameter $\phi_n$. It can be seen from Fig. 2(a) that the solidification paths and $T_f$ curves of the Lever-rule conditions $\phi_{Mg}=\phi_{Cu}=0$, $\phi_{Mg}=\phi_{Cu}=1$, and $\phi_{Mg}=\phi_{Cu}=0.5$ are all same as $L\rightarrow L$ but with different final compositions due to the different extent of the SBD effect, while the solidification path in condition $\phi_{Mg}=\phi_{Cu}=0.35$ is $L\rightarrow L+\alpha+S$ with 1.27% [see Fig. 2(b)] of the volume fraction formed as binary eutectic. For the condition of $\phi_{Mg}=\phi_{Cu}=0.20$, it can also be seen from Figs. 2(a) and 2(b), the solidification path reaches the binary trough of $L+\alpha+T$ at 469.21 °C and ends with 7.76% of the volume fraction formed as binary eutectic. The solidification path of the Scheil condition $\phi_{Mg}=\phi_{Cu}=0$ is $L\rightarrow L+\alpha+S$, which reaches the binary trough of $L+\alpha+T$ at 469.98 °C and reaches the ternary eutectic point with 8.50% and 2.55% of the volume fraction formed as binary eutectic and ternary eutectic, respectively. It can be seen that the influence of parameter $\phi_n$ on the solidification path is obvious and all the calculation results of the assumed conditions are between the limit conditions of the Lever-rule and the Scheil model. The higher the parameter $\phi_n$, the closer the calculated solidification path is to the Lever-rule, in which the SBD is infinite.

Another group of sample calculations gives the solidification paths [Fig. 3(a)] and $T_f$ curves [Fig. 3(b)] calculated using the differential micro-segregation model of Eqs. (9) to (16) for Al-10.5Cu-2.5Mg alloy at two different assumed solidification rates ($R$). It can be seen from Fig. 3(a) that under the assumption of a higher solidification rate, the solidification path experiences three stages of $L+\alpha\rightarrow L+\alpha+\theta\rightarrow L+\alpha+\theta+S$, and the volume fractions of binary and ternary eutectic are 8.87% and 18.00%, respectively. The solidification path for the lower solidification rate ends in the binary eutectic solidification at 503.65 °C and with 19.02% of the volume fraction formed as binary eutectic. From the above sample calculation results shown in Figs. 2 and 3, one may believe that the proposed differential micro-segregation model/algorithm can give reasonable descriptions for the solidification path and micro-segregation behavior.

3 Experimental validation

To further investigate the feasibility of the model/algorithm, a solidification experiment using Al-4.61Cu-0.92Si ternary alloy was carried out. The experimental details were similar to those described by Zhao Guangwei et al. [14]. To create widely different cooling rates for the investigated alloys, the melts were cast into three moulds with the same inner specimen dimensions but made of different materials: graphite, sodium silicate sand, and alumina-silicate-fiber felt (a thermal insulating material). In the pouring...
and solidification processes, the cooling curves for each mould specimen were simultaneously measured using calibrated K-type thermocouples. High-resolution BSE images of microstructures of the solidified aluminum alloy specimens were captured by a Hitachi S-4700 Scanning Electron Microscope (SEM). The images were used for measurements of the amounts (fractions) of secondary-phases using a quantitative image analysis program (Image-Pro Plus 6.0). The typical microstructures for the solidified alloy specimens are dendritic as shown in Figs. 4(a) to 4(c) for the graphite mould, sand mould and the insulated mould, respectively. The experimental results are summarized in Table 2 and will be used in the later calculation.

Figures 5(a) and (b) show the calculated solidification paths and T-f_s curves for Al-4.61Cu-0.92Si alloy using the experimental parameters listed in Table 2. It can be seen that the calculated solidification paths for the alloy with different molds, i.e. L+\alpha \rightarrow L+\alpha+\theta \rightarrow L+\alpha+\theta+Si, are the same as the experimental results. From the T-f_s curves shown in Fig. 5(b), such phenomena can be predicted that the more rapid the solidification rate, the greater the amount of the secondary phase will form.
As Al and Si are neighboring elements, the BSE-image brightness contrast between the α-Al and Si-phases is very low and it is difficult for them to be accurately distinguished by the analysis software. Therefore, in the present experimental investigation, the fractions for the α-Al in all primary, binary and ternary phases, as well as the Si-phases in the ternary eutectics are counted together as a combination phase of (α+Si). The corresponding comparisons between the calculated amounts of (α+Si) phase by the present differential micro-segregation model and the analytical model \(^{[14]}\), and the measured results for the experimental Al-4.61Cu-0.92Si specimens solidified in different moulds are given in Fig. 6. The calculated results also indicate that, although both the differential and analytical models may offer reasonable descriptions for the micro-segregation behavior and solidification paths, the predictions from the differential one are more reliable, which is supported by the experimental data.

(2) Solidification experiment of Al-4.61Cu-0.92Si ternary alloys was carried out using three different moulds which gave different cooling rates varying over a range of three orders of magnitude. Reasonably good agreement between the predicted solidification paths and the measured results further indicate the accuracy of the differential model and algorithm, and the comparison between the calculation results for the differential model and analytical model indicate that the solidification path predictions from the differential model are more reliable.

References


4 Conclusions

Based on a previous multi-length scale modeling approach, a mixture-averaged multi-component/multiphase micro-segregation model in differential form was proposed without pre-set function for the micro-scale solute profile. A commercial Thermo-Calc software package/database is linked to the algorithms via its TQ6-interface for instantaneous determination of the related thermodynamic data at each calculation time step. Through sample calculations and experimental validation, the following conclusions can be made:

(1) Sample calculations of the solidification paths for Al-Cu-Mg alloys with different \( \phi \), parameters (a unified parameter reflecting the SBD-effect on the \( n \)th component) and cooling rates validate the feasibility of the model/algorithm. The calculation results also indicate that the solidification path of an alloy can be greatly influenced by the solidification conditions.