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## BACK-DIFFUSION IN CRYSTAL GROWTH. PERITECTICS

## DYFUZJA WSTECZNA WE WZROŚCIE KRYSZTAŁU. PERYTEKTYKI

A model for the solute micro-segregation/redistribution is delivered. The description is associated with solidification of the peritectic alloys. The peritectic transformation is treated as the phenomenon which modifies the solute redistribution profile resulting from both partitioning and back-diffusion. The relationship allowing for the amount of peritectic phase calculation is also formulated.

*Keywords:* micro-segregation; redistribution; peritectic reaction

Proponowany jest model mikrosegregacji/redystrybucji składnika stopowego. Opis ten dotyczy krystalizacji stopów perytektycznych. Transformacja perytektyczna jest traktowana jako zjawisko, które modyfikuje profil redystrybucji składnika wynikający z rozdziału i dyfuzji wstecznej. Sformułowane jest także równanie, które pozwala wyznaczyć ilość fazy perytektycznej.

## Notation

$D_S$	– coefficient of diffusion into the solid, [m <sup>2</sup> /s]	$N_{i-1}$	– point on <i>liquidus</i> line at which the peritectic transformation occurs, [mole fr.]
$k_i$	– equilibrium partition ratio for <i>i</i> -th solidification range, [mole fr./mole fr.]	$\bar{N}_S$	– average solute concentration within the solid, [mole fr.]
$k_i^0$	– first component of the $k_i$ – partition ratio, [mole fr./mole fr.]	$q$	– number of solidification ranges in a given phase diagram,
$k_i^L$	– second component of the $k_i^L$ – partition ratio, [mole fr./mole fr.]	$R_i$	– half the space of primary phase, [m]
$l_i^0$	– amount of the liquid at the beginning of the <i>i</i> -th solidification range, [dimensionless]	$R_i^{\max}$	– half the space of: primary phase + peritectic phase, [m]
$L_0$	– amount of the liquid at the beginning of solidification; $L_0 = 1$ , [dimensionless]	$R_i^{\min}$	– half the space of primary phase which remains after peritectic reaction, [m]
$N_i^B$	– current solute redistribution in the solid for the <i>i</i> -th range, [mole fr.]	$t_i^f$	– local solidification time for the <i>i</i> -th solidification range, [s]
$N_i^L$	– current solute concentration in the liquid for the <i>i</i> -th range, [mole fr.]	$t_i^p$	– local peritectic transformation time for the <i>i</i> -th solidification range, [s]
$N_i^S$	– current solute concentration at the <i>s/l</i> interface for the <i>i</i> -th range, [mole fr.]	$T$	– temperature, [K]
$N_0$	– nominal solute concentration of a studied alloy or $N_{i-1}$ for $i = 1$ , [mole fr.]	$x$	– current amount of a growing crystal; $x \in [0, 1]$ , [dimensionless]
$N_i$	– solute concentration at the end of the <i>i</i> -th solidification range, also point on liquidus line at which peritectic transformation occurs, [mole fr.]	$x_i$	– amount of primary phase which takes part in peritectic reaction, [dimensionless]
		$x_i^0$	– amount of the crystal at a given stage of solidification when solidification is arrested within the <i>i</i> -th solidification range, [dimensionless]
		$x_i^{\max}$	– amount of: peritectic phase + primary phase after peritectic reaction, [dimensionless]

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- $x_i^{\min}$  – amount of remaining primary phase after peritectic reaction, [dimensionless]  
 $X^0$  – amount of a growing crystal at a given solidification stage, [dimensionless]  
 $\alpha_i^D$  – back-diffusion parameter for the primary phase formation, [dimensionless]  
 $\alpha_i^P$  – back-diffusion parameter for the peritectic phase formation, [dimensionless]  
 $\beta_i^{ex}$  – coefficient of the extent of redistribution, [dimensionless]  
 $\beta_i^{in}$  – coefficient of the intensity of redistribution, [dimensionless]

## Introduction

Most castings show some evidences of a fine-scale solute redistribution. This compositional inhomogeneity can be revealed as a solute concentration gradient on a micro-scale, and additionally, it can result in the formation of a second phase. The inhomogeneity is additionally perturbed when solidification is accompanied by peritectic transformations or peritectic and eutectic transformations which appear during solidification sequentially.

The current model provides the definitions for the **solidification path**, **s/l interface path** and **redistribution path** in the case of solidification of an alloy which comes from the multi-peritectic phase diagrams. The current model is a kind of the development of the precedent models delivered for eutectic alloys solidification and resulting solute redistribution, [1-24]. Some examples of the model application are mentioned.

## 1. Scheil's type model with peritectic reactions

The Scheil's model [1], (with  $\alpha = 0$ ), has been successfully developed for solidification of some alloys from the multi-peritectic phase diagrams, [25-29]. The following equation is formulated to describe the **solidification path**:

$$N^L(x;0) = N_{i-1} \left[ (1-x)/(1-x_{i-1}) \right]^{k_i-1} \quad (1)$$

$$x \in [x_{i-1}, x_i], \quad i = 1, \dots, q$$

$$x_i = 1 - (N_0)^{1/(1-k_i)} (N_i)^{1/(k_i-1)} \prod_{j=1}^{i-1} (N_j)^{1/(k_j-1) - 1/(k_{j+1}-1)} \quad (1a)$$

$$i = 2, \dots, q$$

The **s/l interface path** is given as:  $N^S(x;0) = k N^L(x;0) = k N_{i-1} \left[ (1-x)/(1-x_{i-1}) \right]^{k_i}$ . Since  $\alpha = 0$ , and no diffusion occurs, [6], the **redistribution path**  $N^B(x;0)$  means the same as the **s/l interface path**,  $N^B(x;0) \equiv N^S(x;0)$ . The mass balance is satisfied in this model, [25-29].

## 2. Micro-segregation with finite back-diffusion and peritectic transformations

Solidification accompanied by the peritectic transformation results in the intermetallic phase or compound formation.

$$x_i + liquid(N_i) \Rightarrow [x_i^{\max} - x_i^{\min}] \quad (2)$$

Formation of the intermetallic phase/compound can be described by an universal definition of the partition ratio which varies with the  $N_i^L(T) - liquidus$  line, Eq. (3).

$$k_i(N_i^L) = k_i^0 + k_i^L N_{i-1} / N_i^L(T) \quad i = 1, \dots, q \quad (3)$$

The  $N_{i-1}$  solute concentration is equal to the  $N_0$  – nominal solute concentration for the first solidification range (with  $i = 1$ ). When,  $k_i^L = 0$ , then the partition ratio becomes constant:  $k_i = k_i^0$ . Additionally,

$$l_i^0 = \begin{cases} L^0, & i = 1; \\ L^0 - \sum_{j=1}^{i-1} x_j^{\max}, & i = 2, \dots, n \end{cases} \quad (4)$$

$$x_i^0 = \begin{cases} X^0, & i = 1; \\ X^0 - \sum_{j=1}^{i-1} x_j^{\max}, & i = 2, \dots, n \end{cases}$$

$$\alpha_i^D = D_S t_i^f / R_i^2 \quad (5a)$$

$$\alpha_i^D = D_S t_i^p / (R_i^{\max} - R_i^{\min})^2 \quad (5b)$$

## 2a. Solidification with constant partitioning

Intermetallic phase formation is usually accompanied by a constant partitioning. Thus,  $k_i^L = 0$  in Eq. (3) and  $k_i(N_i^L) = k_i^0 = const.$  is to be assumed:

$$\frac{dN_i^L}{dx} = \frac{(1-k_i^0) N_i^L}{l_i^0 + \alpha_i^D k_i^0 x - x} \quad (6)$$

Eq. (6) can be solved with the use of the so-called travelling initial condition:  $N_i^L(0, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) = N_{i-1}$  which is applied at every peritectic transformation appearing sequentially as visible in a given phase diagram.

Consequently, the solution to the differential equation for micro-segregation, Eq. (6), defines the **solidification path**:

$$N_i^L(x, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) = N_{i-1} \left[ (l_i^0 + \alpha_i^D k_i^0 x - x) / l_i^0 \right]^{(k_i^0-1)/(1-\alpha_i^D k_i^0)} \quad (7)$$

The micro-segregation which results from the partitioning is given as follows:

$$N_i^S(x, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) = k_i^0 N_i^L(x, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) \quad (8)$$

Eq. (8) describes the *s/l interface path*, that is: solute concentration at the s/l interfaces which appeared during solidification in sequence. However, the *redistribution path* is to be described separately:

$$N_i^B(x, x_i^0, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) = \left[ \begin{matrix} 1 + \beta_i^{ex}(x, x_i^0, l_i^0, k_i^0) \\ \beta_i^{in}(x_i^0, \alpha_i^D, l_i^0, k_i^0) \end{matrix} \right] N_i^S(x, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) \quad (9)$$

Additionally,

a/ coefficient of the extent of redistribution:

$$\beta_i^{ex}(x, x_i^0, l_i^0, k_i^0) = \frac{(1 - k_i^0)(x_i^0 - x)}{(l_i^0 + k_i^0 x_i^0 - x_i^0)} \quad (10)$$

b/ coefficient of the intensity of redistribution

$$\beta_i^{in}(x_i^0, \alpha_i^D, l_i^0, k_i^0) = \left\{ \begin{matrix} \alpha_i^D (2 \alpha_i^D k_i^0 - k_i^0 - 1) [(l_i^0 + k_i^0 x_i^0 - x_i^0)] \\ N_i^L(x_i^0, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) - l_i^0 \end{matrix} \right\} \times \left\{ \begin{matrix} (l_i^0 + k_i^0 x_i^0 - x_i^0) \\ \left[ (k_i^0 - 1) [(l_i^0)^2 N_i^L(x_i^0, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) - (l_i^0)^2] + \right. \\ \left. x_i^0 l_i^0 (2 (\alpha_i^D k_i^0 - 1) N_i^L(x_i^0, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) - \right. \\ \left. 2 \alpha_i^D k_i^0 + k_i^0 + 1) + (\alpha_i^D k_i^0 x_i^0 - x_i^0)^2 \right. \\ \left. N_i^L(x_i^0, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) \right] \end{matrix} \right\}^{-1} \quad (11)$$

are formulated by considering the mass balance in the envisaged system.

**2b. Solidification with varying partitioning**

Nothing opposes against the use Eq. (3) in full form in order to formulate the differential equation for micro-segregation dealing with the multi-peritectic phase diagrams and intermetallic phase/compound formation.

$$\frac{dN_i^L}{dx} = \frac{(1 - k_i^0) N_i^L - k_i^L N_{i-1}}{l_i^0 + \alpha_i^D k_i^0 x - x} \quad (12)$$

In this case, the following solution to Eq. (12), in an analytical form, is obtained:

$$N_i^L(x, \alpha_i^D, l_i^0, N_{i-1}, k_i) = \frac{N_{i-1}}{1 - k_i^0} \left\{ \begin{matrix} k_i^L + (1 - k_i^0 - k_i^L) \\ \left[ (l_i^0 + \alpha_i^D k_i^0 x - x) / l_i^0 \right]^{(k_i^0 - 1) / (1 - \alpha_i^D k_i^0)} \end{matrix} \right\} \quad (13)$$

The travelling initial condition:  $N_i^L(0, \alpha_i^D, l_i^0, N_{i-1}, k_i) = N_{i-1}$  was applied to Eq. (12) to formulate the definition of the *solidification path*, Eq. (13). Furtherly, the Eq. (13) is rearranged to define the *s/l interface path*:

$$N_i^S(x, \alpha_i^D, l_i^0, N_{i-1}, k_i) = k_i^0 N_i^L(x, \alpha_i^D, l_i^0, N_{i-1}, k_i) + k_i^L N_{i-1} \quad (14)$$

The *redistribution path* is described separately, as supposed previously:

$$N_i^B = \left[ \begin{matrix} 1 + \beta_i^{ex}(x, x_i^0, l_i^0, k_i) \\ \beta_i^{in}(x_i^0, \alpha_i^D, l_i^0, k_i) \end{matrix} \right] N_i^S(x, \alpha_i^D, l_i^0, N_{i-1}, k_i) \quad (15)$$

Consequentially, the definition of the coefficient of the extent of redistribution is given by the following formula:

$$\beta_i^{ex}(x, x_i^0, l_i^0, k_i) = \frac{k_i^0 l_i^0 (1 - k_i^0 - k_i^L) (x_i^0 - x)}{(l_i^0 + k_i^0 x_i^0 - x_i^0) (k_i^0 l_i^0 + k_i^L l_i^0 - k_i^L x)} \quad (16)$$

whereas the analytical form of the coefficient of the intensity of redistribution is:

$$\beta_i^{in}(x_i^0, \alpha_i^D, l_i^0, k_i) = \left[ \begin{matrix} a_3 k_i^L (1 - k_i^0) (a_4 - l_i^0 N_{i-1} + x_i^0) \\ (l_i^0 + k_i^0 x_i^0 - x_i^0) (\alpha_i^D - 1) \end{matrix} \right] \times \left[ \begin{matrix} a_2 a_3 l_i^0 k_i^0 N_{i-1} (a_2 l_i^0 + k_i^L x_i^0 (\alpha_i^D - 1) + \\ a_5 (k_i^0 l_i^0 + k_i^L l_i^0 - k_i^L x_i^0) (\alpha_i^D - 1) + \\ a_1 a_2^2 N_{i-1} (a_6 f_2 - a_3 l_i^0 k_i^0) \\ (l_i^0 + \alpha_i^D k_i^0 x_i^0 - x_i^0) - a_2^2 a_6 f_1 l_i^0 N_{i-1} \end{matrix} \right]^{-1} \quad (17)$$

where the applied hyper-geometrical function:

$${}_2F_1(a, b, c, x) = 1 + \frac{a b x}{1! c} + \frac{a(a+1) b(b+1) x^2}{2! c(c+1)} + \dots = \sum_{k=0}^{\infty} \frac{(a)_k (b)_k x^k}{(c)_k k!} \quad (17a)$$

has the following properties:

$$f_1 = {}_2F_1 \left( \frac{\alpha_i^D k_i^0 - k_i^0}{\alpha_i^D k_i^0 - 1}, 1; \frac{2 \alpha_i^D k_i^0 - k_i^0 - 1}{\alpha_i^D k_i^0 - 1}; \frac{k_i^L}{k_i^0 (\alpha_i^D k_i^0 + \alpha_i^D k_i^L - 1)} \right) \quad (17b)$$

$$f_2 = {}_2F_1 \left( \frac{\alpha_i^D k_i^0 - k_i^0}{\alpha_i^D k_i^0 - 1}, 1; \frac{2 \alpha_i^D k_i^0 - k_i^0 - 1}{\alpha_i^D k_i^0 - 1}; \frac{k_i^L (l_i^0 + \alpha_i^D k_i^0 x_i^0 - x_i^0)}{k_i^0 l_i^0 (\alpha_i^D k_i^0 + \alpha_i^D k_i^L - 1)} \right) \quad (17c)$$

and

$$\begin{aligned} a_1 &= \left[ (l_i^0 + \alpha_i^D k_i^0 x_i^0 - x_i^0) / l_i^0 \right]^{(k_i^0 - 1) / (1 - \alpha_i^D k_i^0)} ; \\ a_2 &= k_i^0 + k_i^L - 1; \quad a_3 = k_i^0 \alpha_i^D + k_i^L \alpha_i^D - 1 ; \\ a_4 &= \frac{N_{i-1} (l_i^0 - x_i^0) (k_i^L - a_1 a_2)}{1 - k_i^0} ; \\ a_5 &= \ln \frac{k_i^0 l_i^0 + k_i^L l_i^0 - k_i^L x_i^0}{k_i^0 l_i^0 + k_i^L l_i^0} ; \\ a_6 &= (k_i^0 l_i^0 + k_i^L l_i^0 - k_i^L x_i^0) (\alpha_i^D k_i^0 - 1) . \end{aligned}$$

### 2c. Amount of the peritectic phase

The  $(x_i^{\max} - x_i^{\min})$  – amount of the peritectic phase which results from peritectic transformation, Eq. (2), can also be calculated due to the mass balance consideration. At first, the definition of the  $x_i^{\max}$  – parameter is determined:

$$\begin{aligned} & x_i^{\max} (x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) = \\ & x_i^{\text{mem}} (x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0); \end{aligned}$$

when  $r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) > (N_i - k_{i+1}^0 / N_i) \times$  (18)

$$\left[ \begin{array}{l} x_i^{\text{mem}} (x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) - \\ x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) \end{array} \right]$$

$$r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) =$$

$$k_{i+1}^0 / N_i x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) -$$

$$\int_0^{x_i} N_i^B(x, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) dx$$
(18a)

$$x_i^{\text{mem}} (x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) =$$

$$\left\{ \begin{array}{l} x_i^0; x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) + \\ \left[ \begin{array}{l} x_i(\alpha_i^P, l_i^0, k_{i+1}^0 / N_i, N_i, k_{i+1}^0) - \\ x_i(\alpha_i^P, l_i^0, k_{i+1}^0 / N_i, N_i, k_i^0) \end{array} \right] \times \\ \left[ \begin{array}{l} x_i(\alpha_i^P, l_i^0, k_{i+1}^0 / N_i, N_i, k_i^0) - \\ x_i(0, l_i^0, k_{i+1}^0 / N_i, N_i, k_i^0) \end{array} \right] \times \\ \left[ \begin{array}{l} x_i(1, l_i^0, k_{i+1}^0 / N_i, N_i, k_i^0) - \\ x_i(0, l_i^0, k_{i+1}^0 / N_i, N_i, k_i^0) \end{array} \right]^{-1} \end{array} \right\}$$
(18b)

$$x_i^{\max} (x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) =$$

$$x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) +$$

$$r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) / (N_i - k_{i+1}^0 / N_i);$$

when  $r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) \leq (N_i - k_{i+1}^0 / N_i) \times$  (19)

$$\left[ \begin{array}{l} x_i^{\text{mem}} (x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) - \\ x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) \end{array} \right]$$

Next, the definition of the  $x_i^{\min}$  – parameter required by Eq. (2), is delivered:

$$\int_0^{x_i^{\min}} \left[ \begin{array}{l} N_i^B(x + x_i - x_i^{\min}, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) - \\ N_i^B(x, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) \end{array} \right] dx +$$

$$\int_{x_i^{\min}}^{x_i} \left[ \begin{array}{l} k_{i+1}^0 / N_i - N_i^B(x, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) \end{array} \right] dx =$$
(20)

$$\left[ \begin{array}{l} x_i^{\max} \left( \begin{array}{l} x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, \\ N_i, k_i^0, k_{i+1}^0 \end{array} \right) - \\ x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) \end{array} \right]$$

Finally, the  $x_i$  – amount of primary phase which enters into peritectic transformation, Eq. (2), is developed with the use of Eq. (7) formulated for constant partitioning:

$$x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) =$$

$$l_i^0 \left[ 1 - \alpha_i^D k_i^0 \right]^{-1} \left[ 1 - (N_i / N_{i-1})^{(1 - \alpha_i^D k_i^0) / (k_i^0 - 1)} \right]$$
(21a)

However, the  $x_i$  – amount of primary phase is to be determined due to adequate rearrangement of Eq. (13) formulated for varying partitioning.

$$x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i) =$$

$$l_i^0 \left[ 1 - \alpha_i^D k_i \right]^{-1} \left[ 1 - (N_i / N_{i-1})^{(1 - \alpha_i^D k_i) / (k_i - 1)} \right]$$
(21b)

Eq. (2)–Eq. (21) have found practical application in the description of different technologies, like: diffusion soldering, [30–34], diffusion brazing, [36,37], ceramic spraying on metallic substrate, [30], and D-gun spraying of Fe–Al particles onto steel substrate, [35,38].

The current mathematical approach can be fully introduced into the numerical simulation of the continuous casting technology, [39,40], or into a simple description of the crystal growth for which an improvement of material properties by means of unidirectional solidification is required, [41].

### 3. Concluding remarks

The new definition for the partitioning has been formulated, Eq. (3). This formula has an universal character and can be successfully applied in the description of the intermetallic phase/compound formation. Its full form should rather be used in the case when the *liquidus* and *solidus* lines have particular localization or complicated shape. Even, the use of the full form of the partition ratio definition, Eq. (3) results in the analytical solution, Eq. (13), to the differential equation for micro-segregation, Eq. (12). All the terms of this definition, Eq. (3) have the same unit.

Both solutions, Eq. (7), Eq. (13), to the differential equations, Eq. (6), Eq. (12), respectively, have an universal character. Therefore, these solutions are reducible to the analogous solution obtained for eutectic alloys, [24], while applying  $k_i^L = 0$ , and  $l_i^0 = L^0$  with  $q = 1$ .

The definition of the solute redistribution can be introduced into the formula which determines the degree of solute macro-segregation:  $i_{\text{macr.}} = [N_{\text{max}}^B - N_{\text{min}}^B] / N_0$ , [42]. It allows for illustrating the so-called macro-segregation maps, [43].

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