Solidification / microsegregation model applied to description of diffusion soldering / brazing

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Education and Culture
Non-equilibrium solidification

**Scheil’s theory**

*Scheil’s theory for the non-equilibrium solidification / microsegregation*

- Solute concentration in the liquid
  \[ N_L(x;0) = N_0(1-x)^{k-1} \]

- Solute concentration at s/l interface
  \[ N_S(x,0) = kN_0(1-x)^{k-1} \]

- Solute redistribution in the solid
  \[ N_B(x,0) = kN_0(1-x)^{k-1} \]

Redistribution is a result of back-diffusion, but no diffusion in the solid
according to the Scheil’s model, thus \( \alpha = 0 \), and \( N_B(x,0) = N_S(x,0) \)

E. Scheil, Zeitschrift für Metallkunde, 34, (1942), 70-80
Scheil’s model for the non-equilibrium solidification / microsegregation can be developed for multi-peritectic or multi-peritectic/eutectic systems.

**FIG. 1**

**FIG. 2**

arbitrary phase diagram: multi-peritectic system, FIG. 1
multi-peritectic eutectic system, FIG. 2
Non-equilibrium solidification
Solute behaviour

Scheil’s model for the non-equilibrium solidification / microsegregation is now developed for multi-peritectic or multi-peritectic eutectic systems

- Solute concentration in the liquid
  \[ N_L(x;0) = N_{i-1} \left( \frac{1 - x}{1 - x_{i-1}} \right)^{k_{i-1}} \]

- Solute concentration at s/l interface
  \[ N_S(x;0) = k_i N_{i-1} \left( \frac{1 - x}{1 - x_{i-1}} \right)^{k_{i-1}} \]

- Solute redistribution in the solid
  \[ N_B(x;0) = k_i N_{i-1} \left( \frac{1 - x}{1 - x_{i-1}} \right)^{k_{i-1}} \]

\( x \) amount of the growing solid, dimensionless

\[ x \in [x_{i-1}, x_i] \quad i = 1, \ldots, q \]
Non-equilibrium solidification

Initial conditions

Scheil’s model for the non-equilibrium solidification / microsegregation is now developed for multi-peritectic or multi-peritectic eutectic systems.

\[
\frac{dN_L(x,0)}{dx} = N_L(x,0) \frac{1-k}{1-x}
\]

travelling initial condition

\(N_0(x_0), N_1(x_1) \ldots\)

is applied to above differential equation

FIG. 3

Non-equilibrium solidification
Amount of the solid

Scheil’s model for the non-equilibrium solidification / microsegregation is now developed for multi-peritectic or multi-peritectic eutectic systems:

\[
x_i = 1 - \left( N_0 \right)^{1-k_1} \left( N_i \right)^{1-k_i-1} \prod_{j=1}^{i-1} \left( N_j \right)^{1-k_{j+1}-1} \frac{1}{k_{j+1}}
\]

\(i = 2, \ldots, q\)

\[
k = \frac{N_S(x;0)}{N_L(x;0)}
\]

\(k_i\) partition ratio for \(q = 1\)

\(i = 1, \ldots, q\)

\(x_i\) amount of the primary solid at a given peritectic reaction

\(i = 1, \ldots, q\)
Equilibrium solidification

solute concentration in the liquid

\[ N_L(x;1) = N_0(1 + kx - x)^{-1} \]

solute concentration at s/l interface

\[ N_S(x;1) = kN_0(1 + kx - x)^{-1} \]

solute redistribution in the solid

\[ N_B(1;1) = N_0 \]

*a general description of solidification/microsegregation is required!*
General theory for solidification / microsegregation

Brody-Flemings theory

A general theory has already been proposed by Brody and Flemings, but according to the theory, back-diffusion parameter tends to infinity: \( \alpha \to \infty \); moreover, no description for the solute redistribution in the solid is given and mass balance is not satisfied.

However, back-diffusion parameter should tend to unity: \( \alpha \to 1 \).

\[
\alpha = \frac{D_S t_f}{L^2} \quad \rightarrow \quad \alpha = \frac{t_f}{t_d}
\]

with

\[
t_d = \frac{L^2}{D_S}
\]

Really, when \( t_f = t_d \) then \( \alpha = 1 \).

\( t_f \) local solidification time, \( t_d \) time necessary for homogenization.

RESULT a general description of solidification/microsegregation is always required!
General theory for solidification / microsegregation

solute concentration in the liquid $\Rightarrow$

$$N_L(x; \alpha) = N_0 (1 + \alpha k x - x)^{\frac{k-1}{1-\alpha k}}$$

solute concentration at s/l interface $\Rightarrow$

$$N_S(x; \alpha) = k N_0 (1 + \alpha k x - x)^{\frac{k-1}{1-\alpha k}}$$

solute redistribution in the solid

$$N_B(x; x_0, \alpha) = N_S(x; \alpha) + \beta_{ex}(x; x_0) \beta_{in}(x_0, \alpha) N_L(x; \alpha)$$

$$x \in [0, x_K] \quad x_0 \in [0, x_K] \quad \beta(x; x_0, \alpha) = \beta_{ex}(x; x_0) \beta_{in}(x_0, \alpha)$$

$$0 \leq \alpha \leq 1$$

$x_0$ parameter representing freezing $\equiv$ amount of the solid when solidification is arrested

Generalization

proposed equations are reducible to: Scheil’s equations for \( \alpha = 0 \) and description of equilibrium solidification for \( \alpha = 1 \)

\[ N_S^\beta(x; x_K, \alpha) \equiv N_B(x; x_K, \alpha) \]

\[ \left( \alpha E_k \right) \frac{k-1}{1-\alpha E_k} = \frac{N_E}{N_0} \]

FIG. 4 schematic view of solute redistribution for four representative values of back-diffusion parameter
Diffusion soldering / brazing Phenomena

# dissolution
# solidification
# solid / solid transformations

# dissolution prepares initial solution within zone, \( dx \)
for solidification
# solidification forms sub-layers within the solder/braze
# solid/solid transformations usually occur after
completion of both phenomena: dissolution + solidification

• solute concentration of the initial solution is equal to: \( N_0 \)
• zone \( dx \) is formed by dissolution just at the surface of a substrate, perpetually
• next, solidification of a given zone \( dx \), is expected
• some reactions occur during solidification !!!
Solid / liquid interface

2D solidification
formation of cellular morphology

x  current amount of the growing solid (layer)  \( 0 < x < x_K \)
X^0  amount of solid (layer) for which solidification is stopped and morphology frozen
x_K  amount of solid (layer) just before precipitation of the so-called last droplet of the liquid (eutectic)
Distance

2D solidification formation of cellular morphology

\[ \lambda \] distance from the axis of symmetry of a given cell
\[ Y^0 \] distance at which solidification is arrested and morphology frozen
\[ Y_K \] solid / precipitate boundary
Application of 2D model to 1D model of multi-layer formation

2D solidification formation of cellular morphology

\( \lambda \) distance from the substrate surface
\( X^0 = 1 \) amount of multi-layer at which solidification is stopped and morphology frozen
\( t^F \) time of the completion of solidification

1D solidification leading to formation multi-layer
X\(^0\), L\(^0\)  Model 2D

**amount of the arrested solid within i - range of solidification, during diffusion soldering/brazing**

\[
x^0_i = \begin{cases} 
X^0, & i = 1; \\
X^0 - \sum_{j=1}^{i-1} x^\text{max}_j, & i = 2, \ldots, n;
\end{cases}
\]

**amount of the liquid at a beginning of i - range of solidification, during diffusion soldering/brazing**

\[
l^0_i = \begin{cases} 
L^0, & i = 1; \\
L^0 - \sum_{j=1}^{i-1} x^\text{max}_j, & i = 2, \ldots, n;
\end{cases}
\]

*a peritectic reaction occurs at the end of a given range, according to a model referred to phase diagram for stable equilibrium*
Fundamentals of the „zone $dx$” - model

dissolution leads to ensure $N_0$ solute concentration within each $dx$
dissolution path:
$N_F \Rightarrow N_0$
solidification occurs within each $dx$
solidification path:
$N_0 \Rightarrow N_F$

CONCLUSIONS:
no freezing is possible for fraction $dx$!
- therefore $X^0 = 1$, for each $dx$
- when solidification is arrested,
  $X^0 = 1$, for the sum of all $dx$ solidified before arresting

- the diffusion soldering occurs at a constant temperature, $T_R$
- the liquid solution $N^F$ is not undercooled
- the liquid solution $N_0$ is strongly undercooled

CONCLUSION !
- peritectic reactions are undercooled
peritectic reactions !
Real temperature of joining, $T_R$
Equilibrium temperature, $T_L$

**FIG. 9**

parameters playing role in the model referred to phase diagram for stable equilibrium

$N_0$ – initial content of the solute in the undercooled liquid
$N_1$ – content of the solute at first peritectic reaction
$N_2$ – content of the solute at second peritectic reaction
$N_F$ – final content of the solute in the liquid
Driving force for solidification
Model Stable equilibrium

\[ \Delta T = T_L - T_R = T(N_L) - T_R \]

at the \( N_F \) - solute content in the liquid solidification process is completed
and:
\[ \Delta T = 0 \]

scheme valid for each zone \( dx \)
created during solidification

FIG. 10
Initial transient stable formation of the phases

**FIG. 11**

- $dx$ is just formed and initial transient solidification begins
  - Al-liquid filler metal starts to be melted: $\text{Al (s) } \rightarrow \text{Al}$
  - solidification (or birth) of first primary phase $\text{AlNi}$ is to be expected at $t_{11}^B = 0$
  - at time $t_{32}^B$ the $\text{Al}_3\text{Ni}_2$ birth takes place and stable $\text{AlNi}$ phase transforms continuously into the $\text{Al}_3\text{Ni}_2$ dominant phase

At time $t_{32}^{S/M}$ stable solidification transforms into metastable process
Competition

Al₃Ni₂ phase grows instead of AlNi phase

FIG. 12

at time $t_{32}^{S/M}$ competition between initial transient stable solidification and metastable solidification is completed and metastable process begins according to the criterion of maximum temperature of the s / l interface:

$T_{11}^* > T_{32}^*$ at $N_0 = \text{const.}$

number of degrees of freedom

$f = 0$

daughter to Gibbs Phase Rule

$f = c - p + 1 = 0$

since

c = 2 Ni, Al

p = 3 undercooled liquid within zone $d\chi$, AlNi, Al₃Ni₂
Filler metal transformation

scheme of the transformation

definition of $N^F$

$\text{TRANSFORMATION:}$

$\text{liquid}\ (N_1) + \text{Al} \rightarrow \text{liquid}\ (N^F)$

$f = c - p + 1 = 0$

since

$c = 2\ Ni,\ Al$

$p = 3\ dx,\ Al_3Ni_2,\ N^F$

liquid ($N_1$) remains after solidification of the dominant $Al_3Ni_2$ phase
Birth of coupled phase

FIG. 15

number of degrees of freedom
\[ f = 0 \]
according to Gibbs Phase Rule
\[ f = c - p + 1 = 0 \]
since
\[ c = 2 \text{ Ni, Al} \]
\[ p = 3 \text{ undercooled liquid within the zone } dx, (N_0), \]
\[ \text{Al}_3\text{Ni}_2 \text{ and Al}_3\text{Ni} \]

scheme of the coupled phase birth

first peritectic phase that is, dominant phase has already its height equal to \( h_{32} \)

at time \( t_{31}^B \) the birth of \( \text{Al}_3\text{Ni} \) phase is observed
Birth of coupled phase
Experimental confirmation

FIG. 16

birth of the coupled phase Al₃Ni on the surface of dominant phase Al₃Ni₂ as observed experimentally

solidification is faster or slower; it depends on the local orientation

by courtesy of Dr J. Janczak-Rusch, EMPA, Dübendorf, Switzerland
Birth of coupled phase
Experimental confirmation

FIG. 17

birth of the coupled phase $\zeta$ on the surface of dominant phase $\delta$
as observed experimentally

by courtesy of Prof. E. Guzik and Dr D. Kopyciński,
University of Science and Technology,
Kraków, Poland
Perpetual formation of zone, $dx$ by the liquid, $N^F$

zone $dx$ is formed just at the surface of substrate

the liquid $N^F$ reacted with substrate Ni so long as zone, $dx$, becomes liquid the reaction leads to creation of the solute concentration equal to the $N_0$ the value of the $N_0$ depends on the real temperature, $T_R$, imposed by technology

cellular morphology of sub-layers

$\text{liquid (}N^F\text{) } + \text{ substrate (}Ni\text{) } \rightarrow \text{ undercooled liquid (}N_0\text{)}$

the liquid ($N^F$) diffuses along the channels between cells

FIG. 18
Undercooled peritectic reactions
Metastable conditions

undercooled liquid \( (N_0) \) diffuses along internal channels towards the solid/liquid interface of cells. Dominant phase solidifies due to first undercooled peritectic reaction. Coupled phase solidifies due to second undercooled peritectic reaction. Solidification is completed at time, \( t_S \).

At time, \( t_M \), first solid / solid transformation takes place.

**FIG. 19**

undercooled peritectic reaction under metastable conditions can also be described by reaction resulting from phase diagram for stable equilibrium: **primary phase + liquid \( \rightarrow \) peritectic phase**
Undercooled peritectic reactions
Metastable conditions

undercooled liquid \((N_0)\) diffuses along internal channels towards the solid/liquid interface of cells

peritectic reactions
Fe/Zn/Fe joint

undercooled peritectic reaction under metastable conditions can also be described by reaction resulting from phase diagram for stable equilibrium: primary phase + liquid \(\rightarrow\) peritectic phase

FIG. 20
Completion of solidification

CONCLUSION: time $t_S$ depends on thickness of foil applied for joining

FIG. 21

- no more zone $dx$
- $ss$ zone remains
- $s$ zone remains
- both sub-layers are fully formed
- $N_0$ concentration is conserved due to mass balance
- channels still exist internal & external
- no more $N^F$ - liquid

Each sub-layer consists of cells
Operating range for solidification

FIG. 22

Operating range for solidification

model referred to phase diagram for stable equilibrium

formation of $\text{Al}_3\text{Ni}_2$–$\text{Al}_3\text{Ni}$ multi-layer on Ni - substrate

formation of multi-layer follows mechanism of undercooled peritectic reactions at $T_R$ technological temperature

according to phase diagram for stable equilibrium:

$\text{primary (AlNi)} + \text{liquid (N}_1\text{)} \rightarrow \text{Al}_3\text{Ni}_2$

$\text{primary (Al}_3\text{Ni}_2\text{)} + \text{liquid (N}_2\text{)} \rightarrow \text{Al}_3\text{Ni}$
Solidification path

**Ni-Al phase diagram**

**Fe-Zn phase diagram**

Reduced $N_0 \rightarrow N_1 \rightarrow N_2$ and full $N_0 \rightarrow N_1 \rightarrow N_2 \rightarrow N^F$ solidification path;

Reduced $k_1 N_0 \rightarrow k_1 N_1 \rightarrow k_2 N_1 \rightarrow k_2 N_2$

And full $k_1 N_0 \rightarrow k_1 N_1 \rightarrow k_2 N_1 \rightarrow k_2 N_2 \rightarrow k_3 N_2 \rightarrow k_3 N^F$

Historical, $N^S$, s/l interface path

Ni/Al/Ni

A peritectic reaction occurs at the end of a given solidification range
Redistribution coefficient, $\beta$

**FIG. 25**

- $N^L_{s}$: solute concentration in the liquid
- $N^S$: solute concentration at the s/l interface
- $N^B$: solute redistribution after back diffusion

![Diagram](image_url)
Back-diffusion parameter, $\alpha$

back-diffusion parameter
arbitrary phase diagram

\[ \alpha^D = 0 \quad \text{axis corresponding to the Scheil’s theory} \]
\[ \alpha^D > 0 \quad \text{axis corresponding to the general model for solidification / microsegregation} \]

FIG. 26

$N^S(X^0, \alpha^D) = N^B(X^0, X^0, \alpha^D)$
$N^S(X^0, 0) = N^B(X^0, X^0, 0)$

$T$

Concentration, $N / \text{mole fr.}$

Solid amount, $x$

$X^0$

$N^L$
Equations

\[ k_i(N_i^L) = k_i^0 + k_i^L \frac{N_{i-1}}{N_i^L} \]
universal definition of partition ratio

\[ x_i + \text{liquid}(N_i) \Rightarrow [x_i^{\text{max}} - x_i^{\text{min}}] \]
amount of peritectic phase due to reaction resulting from phase diagram

\[ x_i (\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i) = l_i^0 \left[ 1 - \alpha_i^D k_i \right]^{-1} \left[ 1 - \left( \frac{N_i}{N_{i-1}} \right) \frac{1 - \alpha_i^D k_i}{k_i - 1} \right] \]
amount of primary phase

\[
\frac{dN_i^L}{dx} = \frac{(1 - k_i^0 N_i^L - k_i^L N_{i-1})}{l_i^0 + \alpha_i^D k_i x - x}
\]
differential equation governing solidification / microsegregation

\[ N_i^L(0, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) = N_{i-1} \]
initial condition
Equations

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

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

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

\[ \beta_{i}^{\text{ex}}(x, x_{i}^{0}, l_{i}^{0}, k_{i}) = \frac{k_{i}^{0} l_{i}^{0} (1 - k_{i}^{0} - k_{i}^{L}) (x_{i}^{0} - x)}{(l_{i}^{0} + k_{i}^{0} x_{i}^{0} - x_{i}^{0})(k_{i}^{0} l_{i}^{0} + k_{i}^{L} l_{i}^{0} - k_{i}^{L} x)} \]

\[ \beta_{i}^{\text{in}}(x_{i}^{0}, \alpha_{i}^{D}, l_{i}^{0}, k_{i}) = [a_{3} k_{i}^{L} (1 - k_{i}^{0})(a_{4} - l_{i}^{0} N_{i-1} + x_{i}^{0})(l_{i}^{0} + k_{i}^{0} x_{i}^{0} - x_{i}^{0}) (\alpha_{i}^{D} - 1)] \times \]

\[ [a_{2} a_{3} l_{i}^{0} k_{i}^{0} N_{i-1}(a_{2} l_{i}^{0} + k_{i}^{L} x_{i}^{0} (\alpha_{i}^{D} - 1) + a_{5} (k_{i}^{0} l_{i}^{0} + k_{i}^{L} l_{i}^{0} - k_{i}^{L} x_{i}^{0}) (\alpha_{i}^{D} - 1)) + \]

\[ a_{1} a_{2}^{2} N_{i-1}(a_{6} f_{2} - a_{3} l_{i}^{0} k_{i}^{0})(l_{i}^{0} + \alpha_{i}^{D} k_{i}^{0} x_{i}^{0} - x_{i}^{0}) - a_{2}^{2} a_{6} f_{1} l_{i}^{0} N_{i-1}]^{-1} \]

\[ \beta^{\text{ex}} \text{ coefficient of the extent of redistribution} \]

\[ \beta^{\text{in}} \text{ coefficient of the intensity of redistribution} \]
Equations

\[ 2F_1(a, b, c, x) = 1 + \frac{abx}{1!c} + \frac{a(a+1)b(b+1)x^2}{2!c(c+1)} + \cdots = \sum_{k=0}^{\infty} \frac{(a)_k (b)_k x^k}{(c)_k k!} \]

\[
f_1 = 2F_1 \left( \frac{\alpha_i^D k_i^0 - k_i^0}{\alpha_i^D k_i^0 - 1}, 1; \frac{2\alpha_i^D k_i^0 - k_i^0 - 1}{\alpha_i^D k_i^0 - 1}; \frac{k_i^L}{k_i^0 (\alpha_i^D k_i^0 + \alpha_i^D k_i^L - 1)} \right) \]

\[
f_2 = 2F_1 \left( \frac{\alpha_i^D k_i^0 - k_i^0}{\alpha_i^D k_i^0 - 1}, 1; \frac{2\alpha_i^D k_i^0 - k_i^0 - 1}{\alpha_i^D k_i^0 - 1}; \frac{k_i^L (l_i^0 + \alpha_i^D k_i^0 x_i^0 - x_i^0)}{k_i^0 l_i^0 (\alpha_i^D k_i^0 + \alpha_i^D k_i^L - 1)} \right) \]
Equations

\[ a_1 = \left[ \frac{(l_i^0 + \alpha_i^D k_i^0 x_i^0 - x_i^0)}{l_i^0} \right] \frac{k_i^0 - 1}{1 - \alpha_i^D k_i^0} \]

\[ a_2 = k_i^0 + k_i^L - 1 \]

\[ a_3 = k_i^0 \alpha_i^D + k_i^L \alpha_i^D - 1 \]

\[ a_4 = \frac{N_{i-1} (l_i^0 - x_i^0) (k_i^L - a_1 a_2)}{1 - k_i^0} \]

\[ a_5 = \ln \frac{k_i^0 l_i^0 + k_i^L l_i^0 - k_i^L x_i^0}{k_i^0 l_i^0 + k_i^L l_i^0} \]

\[ a_6 = (k_i^0 l_i^0 + k_i^L l_i^0 - k_i^L x_i^0) (\alpha_i^D k_i^0 - 1) \]
Equations

for $k_i^L = 0$

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

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

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

with

$r_i (\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) = k_{i+1}^0 N_i x_i (\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) - \int_0^{x_i} N_i^B (x, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i^0) dx$

and
Equations

\[
x_i^{\text{mem}} \left( x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0 \right) = \min \left\{ x_i^0; x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) + \left[ x_i(\alpha_i^P, l_i^0, k_i^0, N_i, N_i, k_i^0) - x_i(\alpha_i^P, l_i^0, k_{i+1}^0, N_i, N_i, k_i^0) \right] \times \left[ x_i(1, l_i^0, k_{i+1}^0, N_i, N_i, k_i^0) - x_i(0, l_i^0, k_{i+1}^0, N_i, N_i, k_i^0) \right]^{-1} \right\}
\]

it yields

\[
x_i^{\text{max}} \left( x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0 \right) = x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) + r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) / (N_i - k_{i+1}^0 N_i);
\]

when \( r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) \leq (N_i - k_{i+1}^0 N_i) \times \left[ x_i^{\text{mem}} \left( x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0 \right) - x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) \right] \)
Equations

\[ x_i^{\min} \]

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

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

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

however

\[ \lambda_1^K / \lambda_2^K = \lambda_3^K / \lambda_3^K \equiv \left( x_1^{\max} - x_1^{\min} \right) / \left( x_2^{\max} - x_2^{\min} + x_3 \right) \]

above equation is connected with the scheme shown in FIG. 8a
Simulation

FIG. 27

reproduction of planar (constant) profile of solute concentration (redistribution) and ratio of sub-layers thickness according to the operating range FIG. 22 and full solidification path (phase diagram for stable equilibrium)

points come from EDS measurement solidification arrested after 121 s

\[
\frac{\lambda_{K}^1}{\lambda_{K}^2} = \frac{\lambda_{K}^3}{\lambda_{K}^3} \approx \left( \frac{x_{1\max} - x_{1\min}}{x_{2\max} - x_{2\min}} \right) + x_{3} 
\]
First solid / solid transformation

FIG. 28

first solid/solid transformation:

\[ 2 \text{Al}_3\text{Ni} \rightarrow \text{Al}_3\text{Ni}_2 + \text{liquid (3Al)} \]

liquid (Al) precipitates and diffuses towards the axis of symmetry of joint

\[ \text{N}_0 \text{ is conserved during first solid/solid transformation} \]

when transformation is arrested then liquid (Al) shrinks and pores appear

RESULT time \( t_M \) seems to be typical for a given system

first solid / solid transformation named as a „mantis“ effect

\[ 2\text{Al}_3\text{Ni} \rightarrow \text{Al}_3\text{Ni}_2 + 3\text{Al} \]
First solid / solid transformation
Experimental confirmation

 liquid (Al) precipitated at the axis of symmetry of joint

FIG. 29 first solid / solid transformation within Ni/Al/Ni joint

by courtesy of Dr J. Janczak-Rusch, EMPA, Dübendorf, Switzerland

number of degrees of freedom

\[ f = 0 \]

according to Gibbs Phase Rule

\[ f = c - p + 1 = 0 \]

since

\[ c = 2 \text{ Ni, Al} \]
\[ p = 3 \text{ precipitated liquid (Al), Al}_3\text{Ni}_2, \text{ Al}_3\text{Ni} \]
First solid / solid transformation
Experimental confirmation

FIG. 30
first solid / solid transformation within Fe/Zn/Fe joint

by courtesy of Prof. E. Guzik and Dr. D. Kopyciński,
University of Science and Technology,
Kraków, Poland

FeZn$_{13}$ $\rightarrow$ FeZn$_{10}$ + liquid (3Zn)
$\zeta$ $\rightarrow$ $\delta$ + liquid (3Zn)

number of degrees of freedom

$f = c - p + 1 = 0$

since

c = 2  Fe, Zn
p = 3  precipitated (Zn), $\delta$, $\zeta$

liquid (Zn) precipitated at the axis of symmetry of joint

as observed
Simulation

FIG. 31

reproduction of the Al-solute redistribution across Al$_3$Ni$_2$–Al$_3$Ni multi-layer being in the contact with a Ni – substrate reduced solidification path; model referred to phase diagram for stable equilibrium

RESULT plane profile of simulated redistribution, $k_{i+1}N_i$, is obtainable, only
reproduction of the Zn-solute redistribution across $\delta-\zeta$ multi-layer being in the contact with a $(\Gamma_1 + \text{Fe})$ – substrate full solidification path; model referred to phase diagram for stable equilibrium

RESULT plane profile of simulated redistribution, $k_{i+1}N_i$, is obtainable, only
Sequence

sequence of phase appearance during solidification according to

1/ the $dx$ model (simulation):
   first $\text{Al}_3\text{Ni}_2$ next $\text{Al}_3\text{Ni}$

2/ phase diagram for stable equilibrium (peritectic reactions):
   first $\text{Al}_3\text{Ni}_2$ next $\text{Al}_3\text{Ni}$

3/ the birth: FIG. 16
   first $\text{Al}_3\text{Ni}_2$ next $\text{Al}_3\text{Ni}$

4/ criterion of maximum temperature of the s / l interface (metastable conditions):
   first $\text{Al}_3\text{Ni}_2$ next $\text{Al}_3\text{Ni}$

full solidification path; phase diagram for stable equilibrium formation of peritectic phases:

$\text{primary } x_i + \text{liquid } (N_j) \rightarrow k_{i+1}N_j$
Sequence
Theorem of maximum driving force

FIG. 34

the dominant phase $\text{Al}_3\text{Ni}_2$ appears first during solidification

by courtesy of Dr J. Golczewski, Senior Scientist
Max-Planck Institut für Metallforschung, Stuttgart, Germany
Sequence
Theorem of maximum driving force

the coupled phase Al$_3$Ni is consumed by the dominant phase Al$_3$Ni$_2$ during first s/s transformation, FIG. 35a

the dominant phase $\delta$ appears first during solidification FIG. 35b

FIG. 35

a/ first s/s transformation
b/ solidification

by courtesy of Prof. Hyuck-Mo Lee
Advanced Institute of Science and Technology, Yusung-Gu, Taejon, Korea
Arrested solidification
Frozen morphology

solidification arrested during the formation of the Ni-Al-Ni – joint

the thickening of the $\text{Al}_3\text{Ni}$ intermetallic compound continues (due to an applied arresting) along solidification path: $\text{NF} \rightarrow \text{NE}$, (FIG. 23)
this is accompanied by the appearance of an inter-layer of frozen $(\text{Al})^M$ in the middle an eutectic: $[\text{Al}_3\text{Ni}+(\text{Al})^S]$ is visible
the $(\text{Al})^M$ and $(\text{Al})^S$ phases are the metastable and stable eutectic phases, respectively

by courtesy of Dr J. Janczak-Rusch, EMPA, Dübendorf, Switzerland

thickening rate depends on crystallographic orientation of a given cell

by courtesy of Dr J. Janczak-Rusch, EMPA, Dübendorf, Switzerland
Concluding remarks

- The current model equations could be successfully applied to simulation with the use of phase diagram for metastable equilibrium. Simulated profiles would be more flexible to fit perfectly experimental points.
- Each slope of measured profile would be reproducible.

- The present description is able to give information about a value of diffusion coefficient, $D_s$.
- But analysis of the definition of back-diffusion parameter is needed.

- The proposed model could be developed for multi-component systems but determination of solidification path becomes more complicated as shown by H-W mode of calculation.

Solidification / microsegregation model applied to description of diffusion soldering / brazing