PATTERN SELECTION IN THE EUTECTIC GROWTH – THERMODYNAMIC INTERPRETATION

The \((Zn)\) – single crystal strengthened by the \(E = (Zn) + Zn_{16}Ti\) eutectic precipitate is subjected to directional growth by the Bridgman’s system and current analysis. Experimentally, the strengthening layers (stripes) are generated periodically in the \((Zn)\) – single crystal as a result of the cyclical course of precipitation which accompanies the directional solidification. These layers evince diversified eutectic morphologies like irregular rods, regular lamellae, and regular rods. The L – shape rods of the \(Zn_{16}Ti\) – intermetallic compound appear within the first range of the growth rates when the irregular eutectic structure is formed. Next, the branched rods transform into regular rods and subsequently the regular rods into regular lamellae transitions can be recorded. The regular lamellae exist only within a certain range of growth rates. Finally, the regular rods re-appear at some elevated growth rates.

A new solution to the diffusion equation is provided to describe the micro-field of the solute concentration in the liquid adjacent to the front of the growing eutectic structure. The solution is based on the mass balance in the considered system. Moreover, the existence of the protrusion of the leading eutectic phase over the wetting one is required by the mass balance. The appearance of the \(d\) – protrusion in the growing eutectic is well confirmed by the experimental observations of the frozen solid/liquid interface. The mentioned solution satisfies the concept of the eutectic coupled growth according to which undercooling of the leading phase is less than undercooling of the wetting eutectic phase. Also, the Ti – solute micro-segregation / redistribution is analyzed within the matrix of the single crystal. The micro-segregation is described as a result of the solution to the adequate, newly developed differential equation. The definition for the solute redistribution is given by the subsequently / separately formulated relationship. This definition takes into account both extent - and intensity of the solute redistribution.

Finally, the entropy production is calculated for the regular lamellae-, and for the regular rods formation, respectively. The entropy production is a function of some parameters which define the eutectic phase diagram, coefficient of the diffusion in the liquid, and some capillary parameters connected with the mechanical equilibrium located at the triple point of the solid/liquid interface. Branches formation is related to the marginal stability. A new criterion is formulated and subjected to successful verification. It is: \textit{in the structural – thermodynamic competition the winner is this kind of the pattern for which minimum entropy production has a lower value}

\textbf{Keywords:} Criterion of lower minimum entropy production, Structural competition, Marginal Stability, Irregular growth, Microsegregation

\begin{align*}
d & \quad \text{protrusion of the leading phase above the wetting phase, [m]}, \\
D & \quad \text{coefficient of diffusion in the liquid, [m}^2/{s}], \\
k & \quad \text{partition ratio, [at.%/at.%]}, \\
N & \quad \text{solute concentration, [at.%]}, \\
N_E & \quad \text{eutectic concentration of titanium, [at.%]}, \\
N_0 & \quad \text{nominal solute concentration in a given alloy, [at.%]}, \\
r_\alpha & \quad \text{half the radius of the } \alpha \text{ – eutectic phase rod, [m]}, \\
r_\beta & \quad \text{sum of the half the radius of the } \alpha \text{ – eutectic phase rod and the width of the } \beta \text{ eutectic phase (matrix), [m]}, \\
S_\alpha & \quad \text{half the width of the } \alpha \text{ – eutectic phase lamella, [m]}, \\
S_\beta & \quad \text{half the width of the } \beta \text{ – eutectic phase lamella, [m]}, \\
t & \quad \text{time, [s]}, \\
T & \quad \text{temperature, [K]}, \\
v & \quad \text{crystal growth rate, [m/s]}, \\
\varepsilon & \quad \text{amplitude of the s/l interface perturbation, [m]}, \\
\lambda_{SL} & \quad \text{critical wavelength of perturbation generated at the s/l interface, [m]},
\end{align*}

1. Introduction

The growth of the \((Zn)\) single crystal strengthened by the \(E = (Zn) + Zn_{16}Ti\) precipitate was performed by the Bridgman’s system. Experimentally, the strengthening layers (stripes) are
generated periodically in the (Zn) – single crystal as a result of the cyclical course of precipitation which accompanies the directional solidification. These layers evince diversified eutectic morphologies like irregular rods, regular lamellae, and regular rods. Transformations of the mentioned structures (one into other) were observed at some threshold growth rates. It is obvious that the eutectic structures formation is subjected to the competition.

Thus, it is postulated that the thermodynamics of irreversible processes is able to explain / justify the structural transformations. For that reason, a new criterion is formulated to describe eutectic morphologies competition which results in the appearance of the wining structure.

The criterion is: in the structural – thermodynamic competition the winner is this kind of the pattern for which minimum entropy production is lower.

An application of such a criterion requires to calculate the entropy production per unit time for both eutectic regular structures: lamellar structure and rod-like structure. Subsequently, the entropy production is to be subjected to minimization in order to formulate the so-called Growth Law for considered structures.

The (Zn) – single crystal growth proceeds in a stationary state in the Bridgman’s system with constant both the v – growth rate and \( G = \partial T/\partial z \) – thermal gradient. Thus, the application of the theorem of minimum entropy production can be assumed in this situation.

After some rearrangements and in a general form, [1,2], entropy production per unit time and unit volume associated with the mass transfer only is given as follows:

\[
\sigma_D = -\frac{DR_p \psi}{N_l (1 - N_f)} \left[ \text{grad} \cdot N_i \right]^2 \quad T = T_{s/l} = \text{const.} \tag{1}
\]

\( R_p \) is the gas constant, \( \psi \) – thermodynamic factor, and \( T_{s/l} \) – temperature of the solid / liquid interface.

Eq. (1) is ready to be introduced into Eq. (2) in order to calculate entropy production per unit time, separately for lamellar -, and rod-like eutectic structure formation within the layers strengthening the (Zn) – single crystal. However, the average entropy production is to be calculated, [2]:

\[
P_D = \int \sigma_D dV \tag{2}
\]

The current description is connected with the mass transfer in the liquid adjacent to the s/l interface but contained in the diffusion zone: \( z_D \approx D/\nu \) (in the \( z \) – direction). Entropy production associated with the heat transfer is neglected, \( \sigma_T = 0 \).

The \( V – \) volume is the key parameter for the subsequent calculation / solution of the integral, Eq. (2). It leads to the separation of integration which now, will be made simultaneously for the lamellar -, and rod-like structure formation. The \( V – \) volume has already been defined for the lamellar -, and the rod-like structure formation, [2].

The \( V – \) volume is reproduced periodically in the regular eutectic morphology. However, this volume is not the same for every new solidification rate. Therefore, the average entropy production is to be calculated, [2]:

\[
a) \quad \bar{P}_D^l = \frac{1}{S_a + S_b} \int \sigma_D dV \tag{3a}
\]

\[
b) \quad \bar{P}_D^r = \frac{1}{\pi (r_a + r_b)^2} \int \sigma_D dV \tag{3b}
\]

Next, Eq. (4) is obtained by introducing Eq. (1) into Eq. (2):

\[
P_D = \frac{DR_p \psi}{N_l (1 - N_f)} \int \left[ \text{grad} \cdot N_i \right]^2 dV \tag{4}
\]

According to the thermodynamics of irreversible processes, the stationary state is defined by the criterion of minimum entropy production, [3]. Thus, the application of this criterion allows for defining the size of the regular eutectic structure.

The eutectic transformation proceeds under the stationary state in such a way that the regular lamellae / rods, growing at an imposed thermal gradient and a constant solidification rate, evince inter-phase spacing (\( \lambda, R \)) which corresponds to the minimum entropy production.

Therefore, the mathematical optimization of the regular morphology formation described by the entropy production leads to the formulation of the so-called Growth Law for lamellar or rod-like structure, respectively, [4].

Additionally, application of the concept of marginal stability, [5], to define the operating range for the irregular eutectic structure formation will be shown in the next chapter.

Moreover, descriptions of both irregular – into regular structure transformation (debranching), and regular rod-like -, into regular lamellar structure transformation will be delivered.

Finally, examination of the newly developed theory for the solute micro-field formation with the verification of the local mass balance which allows to display the leading phase protrusion will be performed.

The entropy production per unit time and unit volume, Eq. (1), has been determined for the isothermal s/l interface. The geometry of this isothermal interface should be bound with the shape of the transition layer, [6,7].

Finally, calculation of the entropy production per unit time, Eq. (4), was performed for the \( 0 \leq z \leq z_D \) – boundary layer, where, \( z_D \approx D/\nu \), [4].

Calculation of the entropy production per unit time, Eq. (4), is currently limited to the entropy production associated with the mass transfer only. It is self-explanatory because heat transfer runs very quickly in comparison with the mass transfer. Thus, contribution of the heat transfer to the entropy production is negligible, [8].

2. Irregular eutectic growth

Irregular eutectic growth has been observed in the strengthening layer of the (Zn) – single crystal for the \( 0 < v \leq v_1 \) – growth rates range, [2]. Certain models for irregular eutectic structure...
formation are based on the diffusion in the liquid and the s/l interface undercooling, [9], and [10].

The current model shows the possibility to adapt two thermodynamic conditions to the description of irregular structure growth. It is justified because two extremely different types of morphology can be selected. First, the eutectic structure with the maximum perturbation of the non-faceted phase interface could be distinguished. Second, the regular eutectic structure (in some areas well visible within generally irregular morphology) would also be exposed. The first structure is associated with state of marginal stability, while the second one refers to stationary state, Fig. 1.

In the analyzed irregular eutectic growth, some fluctuations of the solute concentration are connected with the phenomenon of branching and resultant perturbation of the real solute concentration field, \( \delta \tilde{\Omega}_{\text{NL}}(s,z) \) and \( \delta \tilde{\Omega}_{p}(r,z) \), respectively. The fluctuation / perturbation occurs in the direct neighborhood of the stationary state, Fig. 1. This fluctuation gives rise to the appearance of the so-called excess entropy production.

In these areas (branching regions) of the irregular eutectic morphology formation, the system rotates around the stationary state which is essentially associated with the regular structure which forms locally at the minimum entropy production.

In the current model, a marginal stability is assumed to control the maximum fluctuation of the solute concentration field and resultant maximum perturbation of the s/l interface shape. Both states (stationary state and marginal stability) are selected in the generally irregular structure, Fig. 1. At the marginal state, corresponding to the transition between stability and instability, the excess entropy production vanishes, [5], and the mentioned perturbations do not develop. The wavelength of the considered perturbation is assumed to be equal to the \( \lambda_{\text{SL}} \) – wavelength, Fig. 2.

The scheme shown in Fig. 1 was primarily designed for one of the first models for the irregular structure growth, [9]. Usually, the so-called operating range was associated with the geometry of the perturbed interface of the faceted phase, [10]. Yet, some experimental observations of the frozen s/l interface do not confirm the existence of this perturbation, [11]. For this reason, the existence of this perturbation has been removed from the current model / scheme, whereas regular and excess protrusions of the leading, faceted phase have been introduced, Fig. 1.

Fig. 1. Model for the irregular eutectic structure formation; distinguished: the \( \text{ms} \) – marginal stability, and the \( \text{ss} \) – stationary state; the \( d_{e} \) – excess protrusion (referred to the appearance of the \( \delta T_{e} \) – kinetic undercooling of the s/l interface of the faceted, leading phase; \( \alpha \) – faceted eutectic phase, \( \beta \) – non-faceted eutectic phase; dashed line – former state of the marginal stability state.

Fig. 2. Interface’s tendency to instability (rate of perturbation propagation) versus the \( \lambda_{p} \) – wavelength of the perturbation, shown schematically according to the stability / instability theory, [12], which is adapted for the description of branching, [13].

The \( \lambda_{\text{SL}} \) – wavelength introduced into the scheme, Fig. 1, is defined as follows:

\[
\lambda_{\text{SL}} = 2 \pi \left[ \frac{1}{\Gamma_{\beta} \left( m_{\beta} G_{C} - G \right)} \right]^{0.5}
\]

with \( \Gamma_{\beta} \) – the Gibbs-Thompson’s parameter for the \( \beta \) – non-faceted phase, \( G_{C} \) – solute concentration gradient at the s/l interface of the \( \beta \) – non-faceted phase, \( G \) – thermal gradient at the s/l interface of the \( \beta \) – non-faceted phase, [13].

The structural analysis of the strengthening layer situated in the (Zn) – single crystal allows to reveal both extreme situations: a) the moment when the regular eutectic structure is formed, b) the moment when the maximal wavelength of the perturbation appears, Fig. 3.
The eutectic transformation proceeds under the stationary – marginal state in such a way that the irregular lamellae / rods, growing at an imposed thermal gradient and a constant rate of the macroscopic s/l interface displacement, but within the operating range of the local growth rates, evince average inter-phase spacing (\(\lambda\), or \(R\)) which results from the \(\lambda\), or \(R\) interphase spacing associated with the minimum entropy production of a given stationary state and \(\lambda_{SL}\) – wavelength of perturbation connected with the rotation around this state.

It is important for the current model, that the state of marginal stability can be located on the paraboloid of entropy production drawn for both generalized thermodynamic forces, \(X_T\), \(X_C\) (that is, drawn in the “thermodynamic” coordinate system), [14]. Therefore, the above statement can be illustrated by means of this paraboloid shown in Fig. 4.

The \(v_{SL}^* \Leftrightarrow \nu^*\) range, distinguished in Fig. 4, is the Operating Range for the irregular structure formation (when the imposed both: \(G^*\), \(\nu^*\) are constant). The paraboloid of the entropy production is transformed from the “thermodynamic” coordinate system (\(X_T\), \(X_C\) – generalized thermodynamic forces) into the “technological” coordinate system (\(\nu\), \(R\)) in agreement with the performed integration over the \(V\) – volume, Eq. (2), and under simplification / assumption that the paraboloid does not change its shape.
2.1. Irregular / regular structure transformation

The transformation of the branched irregular structure into the regular structure occurs within the $v_1 < v \leq v'_1$ – range of growth rates. Thus, it seems reasonable to provide the simplified model / scheme of the irregular structure formation to study the mentioned transformation, Fig. 5.

Fig. 5. Simplified model for the irregular structure formation within the $v_{SL} \leftrightarrow v \alpha$ – operating range, where $v$ is a given growth rate imposed in the studied experiment and also growth rate of the regular structure in some areas located within generally irregular eutectic morphology, and $v_{SL}$ is a corresponding rate of displacement of the maximally perturbed $s/l$ interface of the (Zn) – non-faceted – phase being currently under marginal stability.

The simplified scheme of the irregular structure formation allows to formulate a definition for the average interphase spacing. The following definition can be used to describe the growth of the lamellar eutectic structure:

$$\hat{\lambda} = 0.5\lambda + S_B + 0.5\lambda_{SL}$$

(6)

The analogous description / reduction can be delivered for the rod-like structure transformation, Fig. 5.

Then, $2R = R + r_a + 0.5\lambda_{SL} \rightarrow r_B + r_a + r_n + r_p = 2(r_a + r_p) \Rightarrow 2(S_B + S_n) = \hat{\lambda}$ due to both irregular - , into regular rod-like structure transformation, and subsequently regular rod-like - , into regular lamellar structure transformation, Fig. 6.

2.2. Ti – solute redistribution along the matrix of the (Zn) – single crystal

The differential equation for the solute micro-segregation which appears during solidification accompanied by eutectic reaction is delivered as follows:

$$dN^L(x;\alpha) = \left(1 - k\right)N^L(x;\alpha)$$

$$dx = 1 + \alpha k x - x$$

(7)

Fig. 6. Co-existence of different forms of the Zn$_{16}$Ti – compound as observed within the $v_1 \leftrightarrow v'_1$ – range of growth rates: 1) – transformation of irregular branched rods into regular rods (vanishing of branches); 2) – regular rods as a result of the “1” – structural transformation; 3) – transformation of regular rod into regular lamella; 4) – fully shaped regular lamella after the completed transformations, [2]

Thus, the solute concentration in the liquid (solidification path) is:

$$N^L(x;\alpha) = N_0 \left(1 + \alpha k x - x\right)^{(k-1)/(1-\alpha k)}$$

$$N^L(0,\alpha) = N_0$$

(8)

$$\alpha = D_S t/F^2$$

(9)

The $D_S$ – diffusion coefficient into the solid, [m$^2$/s] and $t$ – time, [s], necessary for the solidification of the $F$ – matrix length, [m], [2], are applied to the definition of the $\alpha$ – back-diffusion parameter (Fourier Number), Eq. (9); $x$ is the current amount of the growing grain (dendrite, cell).

Then, the solute micro-segregation at the moving (and disappearing) $s/l$ interface (s/l interface path) is given as follows:

$$N^S(x;\alpha) = k N_0 \left(1 + \alpha k x - x\right)^{(k-1)/(1-\alpha k)}$$

(10)

Finally, the solute redistribution after back-diffusion (redistribution path) within the solid could be described as:

$$N^B(x;X^0,\alpha) =$$

$$\left[ k + \beta^{ex}(x;X^0) \beta^{in}(X^0,\alpha) \right] N^L(x;\alpha)$$

(11)

where, $k$ – partition ratio, [mole fr./mole fr.]; $x$ – current amount of the growing crystal, [dimensionless]; $X^0$ – amount of crystal when its growth is arrested and morphology is frozen, [dimensionless]; $\beta^{ex}$ – coefficient of the redistribution extent, [dimensionless]; $\beta^{in}$ – coefficient of the redistribution intensity, [dimensionless].

The confrontation of the Ti – solute redistribution (measurement points) with the theoretical solute redistribution is shown in Fig. 7, for the $F$ – matrix length.
As the solute redistribution is the only measurable parameter, the Ti – solute micro-segregation is presented theoretically only, on the basis of calculation of the \( N_S(x;0) \), \( N_S(x;\alpha) \) – function, Eq. (10), Fig. 7.

The mentioned model allows to calculate the solute redistribution and the amount of eutectic precipitate. Thus, the \( i_K \) – total amount of the precipitate, Fig. 8b, is:

\[
i_K(\alpha, N_0) = 1 - x_K(\alpha, N_0)
\]

(12)

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

when \( 0 \leq \alpha \leq \alpha_E( N_0) \) (12a)

\[
x_K(\alpha, N_0) = 1 \quad \text{when} \quad \alpha_E( N_0) < \alpha \leq 1
\]

(12b)

with the definition of the \( \alpha_E \) – threshold back-diffusion parameter:

\[
(\alpha_E \ k)^{-\alpha_E k} = \frac{N_E}{N_0}
\]

(13)

The \( i_K \) – total eutectic precipitate consists of the \( i_E \) – equilibrium precipitate, \( i_E(N_0) = i_K(1, N_0) \), and \( i_D \) – non-equilibrium precipitate, \( i_D(\alpha, N_0) = i_K(\alpha, N_0) - i_E(N_0) \).

The above model, Eq. (7)–Eq. (13) is reducible to the equilibrium solidification, (EQS in Fig. 8a), and to the Scheil’s theory, [15], (SCHEIL in Fig. 8a) and is able to describe the rapid solidification, (RS in Fig. 8a) while taking into account the partition ratio behavior shown schematically in Fig. 8a. Both models can be compared to each other from the viewpoint of the mass balance satisfaction, Fig. 8b.

Fig. 8a. Evolution of the partition ratio versus solidification rate according to the current model of the solute segregation/ redistribution; \( k_0 \) – equilibrium partition ratio, \([\text{mole fr./mole fr.}]\); \( v_{ES} \) – threshold solidification rate (crystal growth rate) just between Scheil’s theory application and the beginning of rapid solidification, [m/s]; \( v_{PS} \) – solidification rate (crystal growth rate) above which partition-less solidification occurs only, [m/s].

Fig. 8b. Solute redistributions a) according to the Scheil’s theory, \( N^B(x;0) = N^S(x;0) \), (blue line) and b) according to the current model, \( N^B(x;X^0,\alpha) = N^E(x;X_E,\alpha) + \beta = \beta^{ex}(x;X^0) + \beta^{in}(X^0,\alpha) \), (red line)

When the partition ratio reaches unity above the \( v_{PS} \) – rate then \( N^E(x;0) = N_0 \), which yields from Eq. (8), solute micro-segregation becomes equal to: \( N^E(x;0) = N_0 \) (segregation-less solidification, [25]), which yields from Eq. (10), and solute redistribution becomes equal to: \( N^B(x;X^0,\alpha) = N^S(x;0) = N^E(x;0) = N_0 \), as it yields from Eq. (11) with the coefficient of the redistribution.
extent $\beta_{\text{ex}}(x; X^0) = 0$ (according to its definition: $\beta_{\text{ex}}(x; X^0) = k(1 - k)(X^0 - x)/(1 + kX^0 - X^0)$, [16]).

The back-diffusion parameter, (Fourier Number), Eq. (9) evolution is presented in Fig. 9, in agreement with the current model of the solute segregation / redistribution. It is evident that the current model of solute redistribution can be developed for multi-component alloys according to the modification mode analyzed in [26].

This steady state solution to the diffusion equation:

$$\frac{\partial^2 \delta N^L}{\partial x^2} + \frac{\partial^2 \delta N^L}{\partial z^2} + \frac{v \partial \delta N^L}{D \partial z} = 0,$$

is obtained for the liquid adjacent to the $\alpha$ – phase, and to the $\beta$ – phase, separately:

a) for the $\alpha$ – eutectic phase formation (the Zn$_{16}$Ti – phase in the Zn – Ti system),

$$\delta N^L(x, z) = \sum_{n=1}^{\infty} A_{2n-1} \cos \left(\frac{(2n-1)\pi x}{2S_{a}}\right) \exp \left(-\frac{(2n-1)\pi z}{2S_{a}}\right)$$

b) for the $\beta$ – eutectic phase formation (the (Zn) – phase in the Zn – Ti system),

$$\delta N^L(x, z) = \sum_{n=1}^{\infty} \frac{B_{2n-1}}{2S_{\beta}} \cos \left(\frac{(2n-1)\pi x - S_{\alpha} + S_{\beta}}{2S_{\beta}}\right)$$

where, $f_j$ – function used in the boundary conditions, [mole fr.], ($j = \alpha, \beta$), respectively; $x, z$ – geometrical coordinates, [m]; $\delta N^L(x, z)$ – difference between the $N^L(x, z)$ – varying solute concentration, and the $N_{E}$ – eutectic concentration of the solute.

The above solution ensures the satisfaction of the local mass balance, Eq. (15), under condition that the strengthening phase protrusion, $d$, is taken into account, Fig. 11.

$$\int_{S_{a} - S_{\beta}}^{S_{a}} f_{\beta}(x) \cos \left(\frac{(2n-1)\pi (x - S_{\alpha} + S_{\beta})}{2S_{\beta}}\right) dx \quad n = 1, 2, …$$

The local mass balance, Fig. 11, corresponds well with the phase diagram, Fig. 12, illustrating the eutectic coupled growth, $\Delta T_{a} \neq \Delta T_{p}$, assumed in the model, [18].

The protrusion of the eutectic leading phase (strengthening phase), predicted theoretically, Fig. 11, and observed experimentally [19,20,27] has also been exposed within the layers containing the ((Zn) + Zn$_{16}$Ti) eutectic, Fig. 13. The higher is growth rate, $v$, the smaller is protrusion, $d$:
Eq. (16) can be supported by the use of a proper Growth Law, \((S_\alpha + S_\beta) = f(\nu)\), [4]. Similar analysis could be developed for the rod-like structure formation, Fig. 13.

2.4. Structural – thermodynamic competition within the strengthening layer

As confirmed experimentally, four ranges of growth rate: \(0 \leftrightarrow \nu_1; \nu_1 \leftrightarrow \nu_2\); \(\nu_1 \leftrightarrow \nu_3\), are selected for the different patterns appearance on the basis of the performed observations, [20]. Thus, it is postulated to compare the entropy production calculated for both rod-like –, and lamellar structure formation, [4]. First of all, however, evolution of the mechanical equilibrium situated at the triple point of the \(s/l\) interface is to be determined. The evolution of the mechanical equilibrium is a function of the \(\nu\) – growth rate, [4], and accompanied anisotropy of the surface free energies. This evolution involves some changes of the \(\sigma_{(Zn)}^{(Zn)}\) – surface free energy of the (Zn) – non-faceted phase, and the \(\sigma_{(Zn)}^{Zn_{16}Ti}\) – boundary free energy versus growth rate, Fig. 14.

The values of the \(\sigma_{(Zn)}^{(Zn)}\), \(\sigma_{(Zn)}^{Zn_{16}Ti}\), Fig. 14, and additionally estimated, value of the \(\sigma_{(Zn)}^{Zn_{16}Ti}\) – parameter, have been introduced into calculation of the entropy production calculated previously, [4], for the formation of both regular structures, Fig. 15.
Fig. 14. Changes of the \( \sigma_{(Zn)} \) – specific surface free energy of the (Zn) – non-faceted phase, and the \( \sigma_{(Zn) \text{-} \text{Zn}_{16} \text{Ti}} \) – boundary free energy; both parameters determined by a heuristic method with a minimum for lamellar eutectic growth; the \( \sigma_{(Zn) \text{-} \text{Zn}_{16} \text{Ti}} \) – specific surface free energy is to be determined with the use of the parallelogram of vectors shown in [4].

Fig. 15a. Entropy production for the formation of regular, eutectic structures; plotted for the \( v = 1.8 \) – growth rate, [mm/h]; situation of the \( R \) – average rod-like spacing; minimum for the rod-like structure formation is situated lower; \( 0 < v \leq v_1 \).

Fig. 15b. Entropy production for the formation of regular, eutectic structures; plotted for the \( v = 5 \) – growth rate, [mm/h]; both minima are at the same level; transformation of regular rods into regular lamellae expected; \( v = v_1 \).

Fig. 15c. Entropy production for the formation of regular eutectic structures; plotted for the \( v = 6 \) – growth rate, [mm/h]; minimum for the lamellar structure formation is localized lower; \( v_1 < v \leq v_2 \).

Fig. 15d. Entropy production for the formation of regular eutectic structures; plotted for the \( v = 10 \) – growth rate, [mm/h]; both minima are at the same level; transformation of regular lamellae into regular rods expected; \( v = v_2 \).

Fig. 15e. Entropy production for the formation of regular eutectic structures; plotted for the \( v = 16 \) – growth rate, [mm/h]; minimum for the rod-like structure formation is localized lower; \( v_2 < v \).
Eventually, it is reasonable to gather all the $P_D^{\text{min}}$ – minima for both studied structures to present their evolution in function of the $v$ – growth rate, Fig. 16.

![Zn-Zn$_{16}$Ti phase diagram](image)

Fig. 16. Values of the minimum entropy production for all the ranges of the experimentally imposed rates for the (Zn) – single crystal growth

3. Concluding remarks

The current theory proves that morphological transformations observed within the layers strengthening the (Zn) – single crystal have the thermodynamic background. Since the experiment was performed under stationary state, the only criterion which could be used in such a model is the theorem of minimum entropy production. Therefore, entropy production was calculated for both morphologies formation and subsequently, subjected to the minimization. Then, the application of the postulated criterion: in the structural – thermodynamic competition the winner is this kind of the pattern for which minimum entropy production is lower, has been successfully verified. This verification was obtained by:

a) analysis of the Zn-Zn$_{16}$Ti phase diagram and some accompanying experiments performed within four ranges of the growth rates,
b) calculation of the entropy production for both examined eutectic structures,
c) development of the Growth Law for both eutectic structures appearance,
d) application of the concept of marginal stability to define the Operating Range for the irregular eutectic structure formation,
e) descriptions of both irregular – into regular structure transformation (debranching), and regular rod-like – into regular lamellar structure transformation,
f) examination of the newly developed theory for the solute micro-field formation with the verification of the local mass balance which allows to display the leading phase protrusion.

The entropy production per unit time and unit volume, Eq. (1), has been determined for the isothermal s/l interface. The geometry of this isothermal interface should be bound with the shape of the transition layer, [21].

Calculation of the entropy production per unit time, Eq. (2), is currently limited to the entropy production associated with the mass transfer only. It is self-explanatory because heat transfer runs very quickly in comparison with the mass transfer. Thus, contribution of the heat transfer to the entropy production is negligible, [8].

Moreover, calculation of the entropy production per unit time, Eq. (2), is performed for the $0 \leq z \leq z_D$ – boundary layer, where, $z_D \approx D/v$.

A deviation from the thermodynamic equilibrium, usually measured as the $\Delta T$ – undercooling, is identical for the both eutectic phases, $\Delta T = \Delta T_a = \Delta T_b$, in the first approximation. However, calculation of the entropy production allows to apply different real values of undercooling, $\Delta T_a \neq \Delta T_b$ [4].

Originally, according to the thermodynamics of irreversible processes, the $P_D$ – entropy production is the function of the $X_T$ – primary thermodynamic force, and the $X_C$ – coupled thermodynamic force, [22]. However, integration, Eq. (4), transforms the calculation of the entropy production from this „thermodynamic” coordinate system into the $(v, S_a + S_b)$; $(v, r_a + r_b)$ – „technological” coordinate system, [4]. The entropy production plotted in the “thermodynamic” coordinate system has the shape of the paraboloid. Initially, (for simplification) it was assumed that the mentioned paraboloid conserves its geometrical shape in spite of the applied mathematical transformation, $P(X_T, X_C) \rightarrow P(v, S_a + S_b)$; $P(X_T, X_C) \rightarrow P(v, r_a + r_b)$, Fig. 17. However, there is a good prerequisite for plotting a real shape (function) of the entropy production.

A significant advantage of the performed transformation is that the entropy production was integrated over two variables: $z$, and $x$, only. This result is in the coupling with the solution to diffusion equation, [6], which is expressed in function of the same variables: $z$, and $x$, [4].

Particularly, at the $v_K$ – critical growth rate, perturbation disappears, the regular structure is formed exclusively, and completion of the $B \Rightarrow A$ transition is satisfied.

The $\text{AMEP}$ – trajectory contains all the local minima at which the stationary processes can proceed, and $\text{BMS}$ – trajectory is bounded with the marginal stability for which the excess entropy production reaches zero, $v_{\text{GL}}(v) < v$, as $\lambda_{\text{GL}}(v) > 2r_p(v)$.

Additionally, $2r_p > r_a + r_b$; $R(v)$ – function, denoted as GL, shows the speculative position of the Growth Law, (developed in [4]), plotted, however within the primary coordinate system, $X_T, X_C$. The $\text{MS}$ is speculative position of the corresponding marginal stability.

Not only is the whole spectrum of the inter-phase spacing produced during the (Zn) – single crystal growth (during the system oscillation between the $\text{AMEP}$ – trajectory, and the $\text{BMS}$ – trajectory) but also is the debranching proceeded continuously in the $v_1 \leftrightarrow v'_1$ – range of growth rates as well. Thus, according to the current experiment, the $B \Rightarrow A$ transition begins at the imposed $v_1$ – rate and is completed at the imposed $v'_1$ – rate, when the $A$ – attractor is the only state of stability. In reality,
this is the stationary state as the entropy production reaches the local minimum of the paraboloid under investigation for the $v_1$ – growth rate. The mentioned structural / thermodynamic oscillation and debranching are shown schematically in Fig. 18.

At the $v_1$ – growth rate the $R_1$ – spacing appears (A – attractor), and at the same time, the marginal stability (B – bifurcation located at the maximum of the $B_{\text{MS}}$ – marginal stability trajectory) is created at the s/i interface of the non-faceted phase moving with the $v_{\text{SLI}}$ – rate.

Between the $v_1$ - and $v_1$ – growth rate, the solidification is translating continuously (dashed blue-red line in Fig. 18) from the $P_{\text{DL}}^R$ – paraboloid onto the $P_{\text{DL}}^L$ – paraboloid of the entropy production.

Within the $v_1 \leftrightarrow v_2$ – range of growth rates the lamellar structure is formed, exclusively (blue line on the $A_{\text{MEP}}^L$ – trajectory).

At the $v_2$ – growth rate the lamellar structure formation is sharply interrupted, and the rod-like regular structure begins to appear immediately (red line on the $A_{\text{MEP}}^R$ – trajectory, Fig. 18).

The $G_{\text{LL}}$ – and $G_{\text{LR}}$ – function show the speculative positions of both $Growth Laws$, (developed in [4]), respectively (plotted, unfortunately, within the “thermodynamic” coordinate system).

The $MS$ – function presents the position of the state of the marginal stability for the irregular eutectic structure formation. It is assumed (for simplification) that the paraboloid of the entropy production drawn schematically in the $X_T, X_C$ – “thermodynamic” system does not change its shape after transformation into the $v, \lambda$, or $v, R$ – “technological” co-ordinate system.

---

Fig. 17. Paraboloid of the $P_{\text{DL}}^R$ – entropy production illustrating the irregular rod-like eutectic growth within the $X_T, X_C$ – coordinate system (the $v, R$ – coordinate system is also incorporated); A – attractor connected with the regular eutectic structure formation at the imposed $v_1$ – growth rate ($R_1$ – spacing characterizes the regular structure), and B – bifurcation which appears in the state of marginal stability, at the $v_{\text{SLI}}$ – growth rate; analogously, solidification proceeds at the $v_2$ – growth rate with $R_2 (v_2)$ – spacing, and adequate maximal wavelength of perturbation.

Fig. 18. Thermodynamic illustration for the formation of rod-like irregular structure, rod-like -, and lamellar regular structure in the strengthening layer of the (Zn) – single crystal; both the $P_{\text{DL}}^R$, and $P_{\text{DL}}^L$ – entropy production plotted as the paraboloids adequate for the $X_T, X_C$ – primary coordinate system (“thermodynamic” system); $X_T$ – generalized thermodynamic force associated with the heat transfer; $X_C$ – generalized thermodynamic force associated with the mass transfer.
The \( \frac{\partial (P_D)}{\partial a} \) \( \big|_{SV} \) = 0; \( \frac{\partial (P_D)}{\partial T} \) \( \big|_{SV} \) = 0 – criteria (in the “technological” coordinate system) were applied to obtain some expressions for the Growth Law. However, the criteria can be used in minimization under condition that: \( \min P_D (X_T, X_C) \Rightarrow \min P_D (V, S_a + S_p) \), and \( \min P_D (X_T, X_C) \Rightarrow \min P_D (r_a + r_p) \), precisely. Thus, the following equation is to be satisfied in the current theory:

\[
\begin{align*}
\frac{\partial P_D^L}{\partial X_T} \frac{\partial X_T}{\partial (S_a + S_p)} + \frac{\partial P_D^L}{\partial X_C} \frac{\partial X_C}{\partial (S_a + S_p)} & = 0, \\
\frac{\partial P_D^R}{\partial X_T} \frac{\partial X_T}{\partial (r_a + r_p)} + \frac{\partial P_D^R}{\partial X_C} \frac{\partial X_C}{\partial (r_a + r_p)} & = 0
\end{align*}
\]

(17)

The fulfillment of the above conditions, Eq. (17) has already been confirmed, [23]. On the other hand, the thermodynamics of irreversible processes provides the general criterion which is substantiated mathematically (the Liouville’s theorem) for the stationary process itself: \( \partial P/\partial X |_{SV} = 0 \).

The analyzed Growth Law, (developed in [4]), is general in form and is justified by the use of the criterion of minimum entropy production. The other versions of the Growth Law are also obtained, however, by the use of the intuitive condition of minimum undercooling, \( \Delta T = \text{min}., \) [6]. The last mentioned theory shows the Growth Laws as follows:

\[
X_T^2 = \text{const}_L, \text{ and } R^2 = \text{const}_R.
\]

(18)

It can be proved that the version of the Growth Laws, Eq. (18), are, from the mathematical point of view, the particular case of the current Growth Laws, (developed in [4]). It means, that the current Growth Law is reducible to Eq. (18). Moreover, the mentioned reduction justifies the use of the intuitive condition of minimum undercooling, however, under certain restrictions only.

The application of the anisotropy of surface energies, [4], is an advantage of the current theory over those which had not taken it into a full account. Although both specific surface free energies vary across a lamellar width or rod-like radius in the interface, their values are characteristic / constant for the triple point for a given growth rate, and fulfill the parallelogram of vectors. These subtle capillary parameters, Fig. 14, play an essential role in the calculation of the entropy production and in the behavior of the entropy production examined in function of growth rate, Fig. 16. It is justified because the capillary parameters form the s/l interface curvature. The s/l interface curvature is taken into account in the calculation of the entropy production, [4], according to the requirements imposed by the mechanical equilibrium situated at the triple point of the s/l interface.

The minimization of the average entropy production, calculated in [4], according to Eq. (3), provides a possibility for the formation of a quite new version of the Growth Law.

Selection / application of the two conditions which are responsible for the creation of the whole spectrum of the interphase spacing, Fig. 4, allows to define the \( v_2^* (v^*) \) \( \Rightarrow v^* \) – Operating Range for the irregular structure formation.

The analyzed formation of the eutectic morphology proceeds according to the oscillation between stationary state and marginal stability, Fig. 17. The stationary state can be identified morphologically by the sinusoidal -, or parabolic shape of the s/l interface of the non-faceted phase. The sinusoidal shape is sometimes admitted, especially in the development of the formal description of the s/l interface curvature.

However, the parabolic shape seems to be typical of the regular eutectic structure, Fig. 3a, Fig 3c. The state of the marginal stability is identified by the wavy character of the maximally perturbed s/l interface of the non-faceted phase, Fig. 3b, Fig. 3c.

Calculation of the Ti – solute redistribution within the (Zn) – single crystal matrix, Fig. 7 visualizes that the material properties of the (Zn) – single crystal, as a whole, depend on the back-diffusion intensity during crystal growth, with the application of the definition: \( 0 \leq a \leq 1 \), Eq. (9).

The model for the solute redistribution, [24], illustrates that the width of the layer strengthening the single crystal also depends on the back-diffusion phenomenon, as explained in Eq. (12). It means that the back-diffusion controls the single crystal growth to a certain extent.

The leading phase protrusion, Fig. 3, and Fig. 13a, also seems to be essential for the resulting properties of the single crystal equipped with the strengthening layers. The observed protrusion appears in agreement with the theoretical prediction justified by the local mass balance, Fig. 11.

Contrary to the current model for the solute micro-field in the liquid adjacent to the s/l interface, [18], the mass balance is not satisfied in the former solution to the diffusion equation, [6]. The previous theory, [6], promotes the so-called ideally coupled eutectic growth, according to which, \( \Delta T_e = \Delta T_p \), whereas the present solution, [18], assumes the coupled eutectic growth only and the resultant inequality, \( \Delta T_e \neq \Delta T_p \), Fig. 12. This inequality, \( \Delta T_e \neq \Delta T_p \), is in harmony with the creation of the leading phase protrusion, Fig. 11.

The currently proposed description of the solute micro-field, [18], is the general theory, and therefore can be perfectly reduced (mathematically) to the previously provided model for the solute micro-field in the liquid, [6]. However, the reduction is possible under assumption that the width of the eutectic phases is equal to each other, \( S_a = S_p \). It means that the previous solution to the diffusion equation, [6], is associated with the virtual, symmetrical phase diagrams, only. Unfortunately, it is a significant restriction in the application of such a theory.

Thermodynamics of the irreversible processes requires the \( V – \) volume to be perfectly defined, [4], while integrating the entropy production per unit time and unit volume, Eq. (4). Moreover, the \( V – \) volume must contain the state of thermodynamic equilibrium, while the remaining part of this volume is under the deviation from this equilibrium. In the current model, the required deviation is defined in Fig. 12.

The present solution to the diffusion equation, Eq. (14), shows that the thermodynamic equilibrium is situated just at the
boundary between the liquid adjacent to the $\alpha$ – eutectic phase interface and that adjacent to the $\beta$ – eutectic phase interface, that means, this state is situated at the elongation of the $\alpha/\beta$ – interphase boundary, Fig. 11. Thus, the $V$ – volume contains the thermodynamic equilibrium as required. On the other hand, the s/l interface is under deviation from the thermodynamic equilibrium as expressed by Eq. (14).

A bifurcation from the plane s/l interface occurs when the $v$ – growth rate is higher than the certain threshold rate, while the imposed thermal gradient is constant, [28]. The $v_3$ – rate, in the presented experiments, seems to be such a threshold rate for the appearance of the nonplanar pattern evolution. Then, the strengthening layer might become similar to the solitary wave (in the microscale), Fig. 19a.

This layer seems to present the initial pattern which evolves rapidly into cells. This phenomenon is known as the manifestation of the inherent instability that appears at the s/l interface, [29].

The mentioned non-planar pattern should be annihilated when the Absolute Stability of the s/l interface is ensured by an elevated growth rate imposed upon the Bridgman’s system, and if the solute concentration is not subjected to any change, [30].

The above conclusion is confirmed by the current description of the solute micro-segregation and redistribution behavior for the growth rates greater than the $v_{PS}$ – rate, Fig. 8, Fig. 9. An application of this description is successfully performed in the case of the D-gun spraying of the small particles onto the steel substrate (or water substrate) as developed in [25].

The solute concentration is neither subjected to any change when the partition ratio becomes equal to unity in the case of eutectic growth, [31].

The eutectic rod-like structure observed during stationary solidification, Fig 19a, appears periodically. Almost similarly, the Cu – Cu$_2$O – eutectic structure forms during copper droplets coagulation in the liquid slag. The eutectic is located at the every constituent droplets periphery, Fig. 13b, and Fig. 19b. The Cu – core of droplets plays a role similar to the (Zn) – matrix of the investigated single crystal. However, contrary to the (Zn) – matrix which presents the Ti – solute redistribution, Fig. 7, the droplets cores contains pure copper (100 at. %). This is in agreement with the adequate phase diagrams.

The eutectic layers reinforce the (Zn) single crystal, as mentioned. The Cu – Cu$_2$O – eutectic, Fig. 13b, Fig. 19b, increases the wettability and decreases the specific surface free energy of

![Fig. 19. Rod-like eutectic; a) strengthening layer observed within the (Zn) – single crystal for the $v > v_3$ – growth rate, b) Cu – Cu$_2$O – regular eutectic, (e – areas), accompanying the Cu – droplets coagulation](image-url)
the copper droplet. As a result, the desired / required coagulation is easier. However, the coagulation is slightly more difficult when the lamellar eutectic precipitate appears.

REFERENCES