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### **Pattern Selection in Crystal Growth**

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#### 1. Introduction

Ebeling & Ashby, 1966 were able to prove that the Cu – single crystal can be strengthened by spherical particles of the  $SiO_2$  – phase. Zarubova & Sestak, 1975 studied the analogous phenomenon in the Fe single crystals strengthened by the Si – addition. In the current study, the phenomenon of strengthening is observed in the hexagonal (Zn) – single crystal equipped with regular stripes which contain the Zn-16Ti intermetallic compound.

The studied (Zn) – single crystal was doped by the small amount of titanium and copper. The addition of copper modifies the specific surface free energy at the solid/liquid (s/l) interface. The specific surface free energies are to be determined in the current description for the triple point of the s/l interface to ensure the mechanical equilibrium. Copper does not form an intermetallic compound with the zinc but is localized in the zinc/titanium solid solution, (Zn). The titanium forms, additionally, the intermetallic compound with the zinc,  $Zn_{16}Ti$ . The (Zn)- $Zn_{16}Ti$  system is the pseudo-binary eutectic system. It exists an opportunity to control the growth of the (Zn) – hexagonal single crystal, and first of all to control the width of the (Zn)- $Zn_{16}Ti$  – stripes which appear cyclically in the single crystal.

Some experiments were performed by means of the *Bridgman* system with the moving thermal field. The system was equipped with the graphite crucible of the sophisticated geometry. It allowed to localize a crystal seed of the desired crystallographic orientation just at the crucible bottom.

The full thermodynamic description of the (Zn) – single crystal growth with periodic formation of the (Zn)- $Zn_{16}Ti$  – stripes requires to consider the model for solute redistribution (Wołczyński, 2000). Next, a steady-state solution to the diffusion equation which yields the solute micro-field in the liquid at the s/l interface is given, (Wołczyński, 2007). The above solution involves a proper localization of the thermodynamic equilibrium at the inter-phase boundary (together with the mechanical equilibrium). This solution also allows for calculating the entropy production in such a system and additionally for describing the transition from lamellar into rod-like structure, (Wołczyński, 2010).

#### 2. Solute redistribution within the (Zn) - Single crystal growing cyclically

Solute redistribution along the single crystal changes significantly due to localization of the *liquidus* and *solidus* lines in the phase diagram. In the case of the (Zn) – single crystal which contains strengthening stripes, Fig. 1a, the Ti – solute redistribution should be measured along the part of the (Zn) – single crystal formed between two neighbouring stripes, Fig. 1b.



Fig. 1. (Zn) – single crystal structure; a. stripes localized cyclically in a (Zn) - single crystal (scheme), b. the *F* - distance between stripes;  $(Zn) \equiv \alpha$ , c. rod-like morphology of a stripe.

#### 2.1 Use of the Zn-Ti phase diagram for the control of the (Zn) - Single crystal growth

According to the Zn-Ti phase diagram the solubility of the Ti in the Zn is equal to 0.000546 at.% at the ambient temperature, Fig. 2. Thus, the strengthening by a solubility is to be neglected. However, an experiment was made to study a strengthening by the eutectic precipitates, for three (I, II, III) solute contents.



Fig. 2. Zn-Ti phase diagram with the localization of the eutectic point,  $N_E = 0.18 [wt.\%Ti]$ , (Murray, 1990), and all studied nominal solute concentration of the single crystal: I, II, III.

Since the difference between melting point of the Zn and eutectic temperature is small it involves a possibility of the single crystal strengthening by the periodic precipitates of eutectic phase ((Zn) + Zn<sub>16</sub>Ti). The (Zn) – eutectic phase, Fig, 1b, Fig. 1c, is the same as in the bulk single crystal. Therefore, it is to be supposed that the Zn<sub>16</sub>Ti eutectic phase (intermetallic compound) is only responsible for the strengthening of the (Zn) – single crystal.

A peculiar construction of the Zn-Ti phase diagram, Fig. 2, involves a possibility in the control of the precipitates amount. However, a proper model for the solute segregation / redistribution is necessary to predict the amount of the eutectic or intermetallic phase precipitation within a given single crystal.

In the current study the *Bridgman* furnace was working as a closed system and the control of strengthening could be done, to some extent, by an adequate choose of a nominal concentration of titanium in the alloy used for single crystal growth, Fig. 2, and by applying a proper growth rate, v, on which the  $\alpha(v)$  back-diffusion parameter depends.

The selection of the nominal solute concentration decides on the stripe thickness as visible in Fig. 2. The nearest is the distance between nominal solute concentration on the *liquidus* line and the eutectic point the wider are the stripes.

Moreover, the applied growth rate decides on the stripes morphology. Three ranges of growth rates were distinguished in the discussed (Zn) – single crystal formation: a. at some low growth rates, the L – shape irregular rod-like structure appears in stripes, b. at some middle growth rates the regular lamellar structure is observed in stripes, c/ at the elevated growth rates the regular rod-like structure exists as an exclusive morphology of stripes.

It is evident that two transformations of morphology were recorded. At the first threshold growth rate the L-shape irregular rods were transformed into the regular lamellae. This transformation cannot occur immediately since the L-shape rod-like into lamellar structure transition is accompanied by the irregular into regular morphology transition. Thus, this transformation occurred continuously within a certain range of rates. However, the lamella into rod transition occurred just at the second threshold rate, immediately.

The control of the stripe thickness can be explained while applying the equilibrium solidification to the *Bridgman* system, Fig. 3.



Fig. 3. Solidification paths ( $I \rightarrow N_0 / k$ ) and ( $III \rightarrow N_0 / k$ ) for an equilibrium solidification of the (Zn) - single crystal with: a.  $N_0 = I = 0.01 [wt.\%Ti]$ , and b.  $N_0 = III = 0.1 [wt.\%Ti]$ .

The precipitation is impossible for the equilibrium solidification with the nominal solute concentration:  $N_0 = I = 0.01$ , since  $N_0 / k < N_E$ , Fig. 3a. The precipitation is always ensured for the nominal solute concentration:  $N_0 = III = 0.1 [wt.\%Ti]$ , since  $N_0 / k > N_E$ , Fig. 3b. Moreover, the solidification occurs along the solidification path cyclically, and precipitates are rejected at the end of each cycle to form the stripes.

#### 2.2 Model for the solute microsegregation / redistribution after the back-diffusion

A theory for solute microsegregation accompanied by the back-diffusion which is defined by the -  $\alpha$  parameter, has already been delivered, (Brody & Flemings, 1966), with:

$$\alpha = D_S t_1 L^{-2} \tag{1}$$

 $D_S$  - diffusion coefficient into the solid,  $[m^2/s]$ ;  $t_l$  - local growth time, [s]; L - half the crystal spacing, [m]. This theory is not able to describe the solute redistribution since the mass balance is not satisfied, there. Thus, an improved model, (Wołczyński, 2000), based on

the  $\alpha$  - back-diffusion parameter, Eq. (1) has been delivered. The model describes the solute redistribution after back-diffusion and can be used to calculate an amount of precipitates. The equation which describes the solute redistribution after back-diffusion is as follows:

$$N^{B}(x;X^{0},\alpha) = \left[k + \beta^{ex}(x;X^{0})\beta^{in}(X^{0},\alpha)\right]N^{L}(x;\alpha)$$
(2)

*k* - partition ratio, [*mole fr.* / *mole fr.*]; *x* - crystal amount, [dimensionless];  $x = X^0$  - crystal amount at arrested growth;  $\beta^{ex}$  - coefficient of redistribution extent, [dimensionless];  $\beta^{in}$  - coefficient of redistribution intensity, [dimensionless];  $N^L$  - liquid content, [*mole fr.*]; Eq. (3).

$$N^{L}(x;\alpha) = N_{0} \left(1 + \alpha \, k \, x - x\right)^{(k-1)/(1-\alpha k)} \tag{3}$$

The above equation results from the differential formula:

$$\left[1 + \alpha k x - x\right] dN^{L}(x;\alpha) = (1-k) N^{L}(x;\alpha) dx$$
(4)

Both,  $\beta^{ex}$  - coefficient of the redistribution extent and  $\beta^{in}$  - coefficient of the redistribution intensity are defined due to the mass balance consideration (Wołczyński, 2000). Their product  $\beta(x;X^0,\alpha) = \beta^{ex}(x,X^0)\beta^{in}(X^0;\alpha)$  is equal to zero:  $\beta(x;X^0,0) = 0$  for the non-equilibrium solidification (when  $\alpha = 0$ ). The product is equal to (1-k)(1-x) for the equilibrium solidification (when  $\alpha = 1$  with  $X^0 = 1$ ) that is:  $\beta(x;1,1) = (1-k)(1-x)$ . The single crystal growth occurs slowly, thus its growth is performed under condition close to the equilibrium state. The physical limitation for the the  $\alpha$  - back-diffusion parameter has also been determined while assuming:  $t_D = L^2 / D_S$ . Then,  $\alpha = t_l / t_D$  and finally,  $0 \le \alpha \le 1$ . with  $t_D$  - diffusion time necessary for the full homogeneity of the crystal. Thus, the mass balance is satisfied at each step of the crystal growth. Therefore, Eq. (2) can perfectly fit some measurement points obtained by the EDS technique. On the other side, the solute microsegregation is observable at the moving s/l interface during the experiment. Thus, the redistribution is the only concentration which can be measured after the crystal growth.

Usually, the crystal growth is accompanied by some precipitates. The growth rate, imposed in the *Bridgman* system for a single crystal growth (with a seed) v > 0, does not follow the equilibrium solidification. Thus, the solidification path is longer than that shown in Fig. 2. Therefore, it was possible to obtain precipitates even for the nominal solute concentrations:  $N_0 = I = 0.01 [wt.\%Ti]$ ,  $N_0 = II = 0.02 [wt.\%Ti]$ , when the imposed growth rate, v, involves an elongation of the solidification path beyond the eutectic point ( $N_E = 0.18 [wt.\%Ti]$ ) till the  $N_K$  - point on the *liquidus* line.  $N_K$  is also the solute content in the liquid at the end of solidification, [*mole fr.*]( $N_0$ ,  $N_E$  are to be expressed in [*mole fr.*] while calculating  $N_K$ ). The ratio between an amount of the crystal,  $x_K$ , and an amount of precipitate,  $i_K$ , depends

$$x_{K} / i_{K} = (N_{E} - N_{0}) / (N_{K}(\alpha, N_{0}) - N_{E})$$
(5)

The end of solidification path is:  $N_K(\alpha, N_0) = N^L(x_K, \alpha)$ , and  $x_K$  is defined as follows:

on the mentioned elongation beyond the eutectic point by the solidification path:

$$x_{K}(\alpha, N_{0}) = \frac{1}{1 - \alpha k} \left[ 1 - \left( N_{E} / N_{0} \right)^{\frac{1 - \alpha k}{k - 1}} \right] \text{ when } 0 \le \alpha \le \alpha_{E} \left( N_{0} \right)$$
(6a)

$$x_{K}(\alpha, N_{0}) = 1 \qquad \text{when} \qquad \alpha_{E}(N_{0}) < \alpha \le 1$$
(6b)

with  $(\alpha_E k)^{\frac{k-1}{1-\alpha_E k}} = N_E / N_0$ , (Wołczyński, 2000).

According to the above considerations,  $i_K(\alpha, N_0) = 1 - x_K(\alpha, N_0)$ , [dimensionless]. The precipitate is divided into the so-called equilibrium precipitate:  $i_E(N_0) = i_K(1, N_0)$  and non-equilibrium precipitate:  $i_D(\alpha, N_0) = i_K(\alpha, N_0) - i_E(N_0)$ .

The precipitate visible in the crystal reproduces the s/l interface shape which existed "historically" at a given stage of the (Zn) - single crystal growth, Fig. 4.



Fig. 4. A stripe deflected by the perturbation wave created at the solid / liquid interface during the (Zn) - single crystal growth; the stripe (precipitate) contains the (Zn) – phase coherent with the bulk single crystal and rods of the  $Zn_{16}Ti$  – intermetallic compound; the stripe follows the pattern which seems to be the result of a solitary wave, ( $\varphi$ ).

#### 2.3 Measurement / simulation of the Ti - Solute redistribution along the single crystal

The solute redistribution model, discussed above, allows to make some simulations of the Ti – solute redistribution for the (Zn) – single crystal growth. The simulation is developed to fit the measurement points obtained by the EDS technique, Fig. 5. The Ti – solute redistribution was measured along the bulk (Zn) – single crystal just between two neighbouring stripes and for two different samples.

The theoretical solute microsegregation is calculated twice: a.  $N^{S}(x,0) = kN^{L}(x,0)$  - without the presence of back-diffusion, (Scheil, 1942), b.  $N^{S}(x,\alpha) = kN^{L}(x,\alpha)$  - with the presence of back-diffusion phenomenon, (Wołczyński, 2000), Fig. 5. The theoretical amount of the bulk crystal,  $x_{K}(\alpha)$  and corresponding amount of the ((Zn) + Zn\_{16}Ti) – precipitate,  $i_{K}(\alpha)$  (red lines) are also shown. The theoretical solute redistribution is calculated for a selected value of the  $\alpha$  - back-diffusion parameter, ( $0 \le \alpha \le 1$ ), [dimensionless], and additionally for  $X^{0} = 1$ . The partition ratio is applied due to the Zn-Ti phase diagram for the stable equilibrium as equal to k = 0.11[wt.% / wt.%], (Murray, 1990).



Fig. 5. Ti – solute redistribution as calculated for two alloys of the nominal Ti – solute concentration equal to: 0.02 *wt*.% and 0.1 *wt*.%, respectively; (Boczkal et al., 2010).

#### 3. Solute micro-field in the liquid and the strengthening phase protrusion

The eutectic precipitates are formed under stationary state from the non-homogeneous liquid phase, (Jackson & Hunt, 1966). The solution to the diffusion equation gives a description of the solute concentration micro-field ahead of the s/l interface. The recent solution to the diffusion equation supposes the existence of the mechanical equilibrium at the triple point of the s/l interface and the thermodynamic equilibrium along the interphase boundary, (Wołczyński, 2007). The steady-state solution to the diffusion equation is given separately for each eutectic lamella:  $\alpha$  - phase lamella, and  $\beta$  - phase lamella. So, a. for the  $\alpha$  - eutectic phase formation (the (Zn) – phase in the Zn – Ti system),

$$\delta C(x,z) = \sum_{n=1}^{\infty} A_{2n-1} \cos\left(\frac{(2n-1)\pi x}{2S_{\alpha}}\right) \exp\left(-\frac{(2n-1)\pi}{2S_{\alpha}}z\right)$$
(7)

$$A_{2n-1} = -\frac{4}{(2n-1)\pi} \int_{0}^{S_{\alpha}} f_{\alpha}(x) \cos\left(\frac{(2n-1)\pi x}{2S_{\alpha}}\right) dx \quad n = 1, 2, \dots$$
(7a)

b. for the  $\beta$  - eutectic phase formation (the Zn<sub>16</sub>Ti – compound in the Zn – Ti system),

$$\delta C(x,z) = \sum_{n=1}^{\infty} B_{2n-1} \cos\left(\frac{(2n-1)\pi(x-S_{\alpha}+S_{\beta})}{2S_{\beta}}\right) \exp\left(-\frac{(2n-1)\pi}{2S_{\beta}}z\right)$$
(8)

$$B_{2n-1} = -\frac{4}{(2n-1)\pi} \int_{S_{\alpha}-S_{\beta}}^{S_{\alpha}} f_{\beta}(x) \cos\left(\frac{(2n-1)\pi(x-S_{\alpha}+S_{\beta})}{2S_{\beta}}\right) dx \quad n = 1, 2, \dots$$
(8a)

*C* - solute concentration within the micro-field formed in the liquid, [at.%];  $S_j$  - half the width of the eutectic phase lamellae, [m],  $(j = \alpha, \beta)$ , respectively;  $f_j$  - function used in formulation of the boundary condition for the  $\alpha$  and  $\beta$  - eutectic phases formation, [at.%],  $(j = \alpha, \beta)$ , respectively; x, z - geometrical coordinates, [m].

The total mass balance is satisfied within the solute concentration micro-field, Eq. (9), Fig. 6. D - diffusion coefficient in the liquid,  $[m^2 / s]$ ; v - crystal growth rate, [m / s], identical to the thermal field movement rate in the *Bridgman* system; moreover,

$$B_{2n-1} = A_{2n-1} \left( S_{\alpha} / S_{\beta} \right)^2, \quad n = 1, 2, \dots$$
 (9a)

The satisfaction of the total mass balance is shown in Fig. 6. The local mass balance is also satisfied, Fig. 7. But, in the case of the local mass balance the phase protrusion is to be considered, Eq. (10).

$$\int_{0}^{S_{\alpha}} \delta C(x,0) dx + \int_{S_{\alpha}}^{S_{\alpha}+S_{\beta}} \delta C(x,d) dx = 0$$
(10)

*d* - protrusion of the  $\beta$  - leading eutectic phase over the  $\alpha$  - wetting eutectic phase, [m].



Fig. 6. Total mass balance within the solute concentration field for an eutectic system growing under stationary condition;  $C_E$  - eutectic concentration of the solute, [at.%].



Fig. 7. Local mass balance within the solute concentration field for an eutectic system growing under stationary condition.

The protrusion of the eutectic leading phase, predicted theoretically, Fig. 7, and formerly observed experimentally, (Davies, 1964) has also been revealed within the stripes which contain the  $((Zn) + Zn_{16}Ti)$  eutectic, Fig. 8.



Fig. 8. ((Zn) + Zn<sub>16</sub>Ti) regular rod-like eutectic revealed in the stripes (the EDS observation); the x, z - coordinate system presents the localization of the Ti – solute concentration field; the d - leading phase protrusion is defined due to the (Zn) – single crystal growth arresting.

Since the (Zn) – single crystal growth was arrested and the s/l interface was frozen, it is also possible to reveal the s/l interface shape of the non-faceted (Zn) – eutectic phase, Fig. 9.



Fig. 9. Frozen solid / liquid interface of the  $((Zn) + Zn_{16}Ti)$  regular eutectic revealed within the strengthening stripes; a. the EDS observation, b. identification of the eutectic phases: the  $Zn_{16}Ti$  faceted phase, the (Zn) – non-faceted phase, the frozen liquid, the parabolic envelope (yellow dashed line) superposed onto the s/l interface of the (Zn) – phase.

Since the revealed solid/liquid interface has a parabolic shape, Fig. 9, and no interface destabilization is observed, it is evident that the obtained structure is the regular structure.

#### 4. Thermodynamic selection of the pattern in the growing eutectic structure

(Zn) – single crystal growth occurs under stationary state in the *Bridgman* system with an imposed constant growth rate. Neither, the thermal field does not vary during solidification. Eventually, the Zn<sub>16</sub>Ti eutectic phase (compound) has the same size, Fig. 10, and an interphase spacing should not vary during crystal growth.

It should be emphasized that the only condition which defines the stationary state is the criterion of minimum entropy production, (Prigogine, 1968).



Fig. 10. A strengthening stripe ((Zn) + Zn<sub>16</sub>Ti) within the (Zn)  $\stackrel{-}{=}$  single crystal frozen during its growth in the *Bridgman* system; the Zn<sub>16</sub>Ti - rods are all of the same size, mainly.

Many eutectic systems exhibit either a lamellar or rod-like structure depending on solidification conditions, (Elliott, 1977). It is well visible in the case of directional growth of the Al-Si eutectic alloy, (Toloui & Hellawell, 1976) and (Atasoy, 1984). Moreover, a transition from the lamellar structure into the rod-like structure is observable at a the threshold growth rate typical for a given eutectic alloy, (Cupryś et al., 2000).

Especially, growth rate plays a crucial role in the lamella into rod transformation. Some impurities also involve the transition, (Steen & Hellawell, 1975). The impurities change the specific surface free energies and finally modify a mechanical equilibrium at the triple point

of the solid/liquid interface. However, according to the current model assumptions, the mechanical equilibrium varies (rotates) at the s/l interface of the (Zn) – single crystal not only with the copper addition but with solidification conditions (growth rate) as well. An imposed growth rate results in the crystal orientation. Some changes of the orientation from an initial state into a final one give also an effect on the lamella.rod transition.

In the case of the (Zn) – single crystal growth two threshold rates were revealed for the changes in the stripes morphology, as mentioned above. First threshold growth rate,  $v_1$ , is connected with the transition from the L – shape irregular (with branches) rod-like structure into the regular lamellar structure. Second threshold growth rate,  $v_2$ , is associated with the transition from the regular structure into the regular rod-like structure.

#### 4.1 Promotion of the rod-like structure or lamellar structure formation

The formerly developed theory (Jackson & Hunt, 1966) has tried to predict the threshold rate at which a structural transition should occur. The theory (Jackson & Hunt, 1966) is based on the description of the s/l interface undercooling with the undercooling defining both lamellar growth and rod-like growth, Eq. (11).

$$\left(\Delta T_{L}^{*}\right)^{2} = 4 v m^{2} a^{L} Q^{L}; \quad \left(\Delta T_{R}^{*}\right)^{2} = 4 v m^{2} a^{R} Q^{R}$$
(11)

 $\Delta T_L^*$  - s/l interface undercooling for the lamellar structure formation, [K];  $\Delta T_R^*$  - s/l interface undercooling for the rod-like structure formation, [K]; v - growth rate, [m/s];  $1/m = 1/m_{\alpha} + 1/m_{\beta}$ , with:  $m_{\alpha}$  - slope of the  $\alpha$  - *liquidus* line, [K/at.%];  $m_{\beta}$  - slope of the  $\beta$  - *liquidus* line, [K/at.%],  $a^L;a^R;Q^L;Q^R$  - parameters associated with the eutectic system capillarity and with a given phase diagram, (Jackson & Hunt, 1966).

This description yields a certain inequality, (Jackson & Hunt, 1966), according to which the rods or lamellae are formed, Fig. 11.



Fig. 11. Prediction of rod-like or lamellar structure formation, (Jackson & Hunt, 1966).

For the isotropic s/l interfacial free energies the r. h. s. of the considered inequality is equal to one, Fig. 11. The discussed inequality, shown in Fig. 11, yields a result, according to which, when the following inequality:  $1/(1+\xi) < 0.32$ , is satisfied (for the assumed isotropy) then a rod-like structure is stable form, (Jackson & Hunt, 1966). However, this parameter is equal to 0.114,  $(1/(1+\xi)=0.114)$ , for the Al-Si system. Thus, the rod-like structure should be the stable form. Meanwhile, according to experimental observations a lamellar structure is formed instead of a rod-like structure. Moreover, the lamellar structure transforms into the rod-like structure at a threshold growth rate. It is evident that the inequality, illustrated in Fig. 11, is completely misleading. The discerning analysis shows that the above inequality is able to predict whether an eutectic alloy will manifest lamellar

or rod-like structure, only. Thus, the discussed inequality characterizes a given phase diagram. The inequality cannot be applied to describe the lamella into rod transition.

#### 4.2 Thermodynamics of the eutectic s/l interface formation in the pattern selection

Thermodynamics of the eutectic s/l interface formation has already been discussed to some extent, (Wołczyński, 2010). The consideration was focused on the Al-Si eutectic alloy which manifests the irregular structure (with branches) due to directional solidification. It is known that the regular structure areas exist among the generally irregular structure, Fig. 12. It results from the experimental observations of lamellar and rod-like structures formation that the threshold growth rate at which the transformation lamella into rod begins, is equal to 400 [ $\mu m/s$ ]. The transition is completed at the growth rate equal to about 700 [ $\mu m/s$ ]. Both structures coexist within the operating range for the lamella into rod transition, (400  $\mu m/s \div 700 \mu m/s$ ), as visible in Fig. 13b, but the lamellar structure is obtainable below the threshold solidification rate, exclusively, as it is shown in Fig. 13a.



 $\lambda_i$  - inter-lamellar spacing for the regular structure, [m];  $\lambda_s^i + 2S_\beta$  - inter-lamellar spacing for the maximal destabilization of the s/l interface of the  $\alpha$  - non-faceted phase,  $\alpha \equiv (Al)$ , [m] Fig. 12. Generally irregular eutectic structure formation; scheme, (Fisher & Kurz, 1980).



Fig. 13. A cross-sectional morphology of a directionally solidifying Al-Si irregular eutectic; a. for  $v = 370 \,\mu m / s$ , and thermal gradient equal to G = 100 K / cm, (lamellae exclusively); b. for  $v = 500 \,\mu m / s$ , and thermal gradient equal to G = 40 K / cm, (lamellae + rods).

The thermodynamics of the s/l interface involves the calculation of the Gibbs' free energy for the considered eutectic system. The Gibbs' free energy formulas which are concerning the s/l interface formation are as follows, for the regular lamellar and regular rod-like structure:

$$\Delta G_{L}^{*} = v \lambda Q_{CW}^{L} - a_{CW}^{L} \lambda^{-1} \quad \Delta G_{R}^{*} = v R Q_{CW}^{R} - a_{CW}^{R} R^{-1}$$
(12)

Eq. (12) was developed from Eq. (11) by means of the transformation of the undercooling into the *Gibbs'* free energy.

 $\Delta G_L^*$ ;  $\Delta G_R^*$  - *Gibbs'* free energy for regular lamellar or rod-like growth, respectively,  $|J/m^3|$ ;  $\lambda \equiv \lambda_i$  - inter-lamellar spacing, [m]; R - inter-rod spacing, [m].

$$Q_{CW}^{L} = \left[ m \left( L_{\alpha} \xi + L_{\beta} \right) / T_{E} \right] \left[ P^{*} \left( 1 + \xi \right) N_{0} / \left( \xi D \right) \right]$$
(13a)

$$Q_{CW}^{R} = \left[ m \left( L_{\alpha} \xi + L_{\beta} \right) / T_{E} \right] \left[ 4E N_{0} / (\xi D) \right]$$
(13b)

$$a_{CW}^{L} = \left\{ m \left( 1 + \xi \right) \left[ \sigma_{\alpha}^{L} \sin \theta_{\alpha}^{L} / m_{\alpha} + \left( \sigma_{\beta}^{L} \sin \theta_{\beta}^{L} \right) / \left( \xi m_{\beta} \right) \right] + \sigma_{\alpha\beta}^{L} \right\}$$
(14a)

$$a_{CW}^{R} = 2\left\{m\sqrt{1+\xi}\left[\sigma_{\alpha}^{R}\sin\theta_{\alpha}^{R} / m_{\alpha} + \left(\sigma_{\beta}^{R}\sin\theta_{\beta}^{R}\right) / \left(\xi m_{\beta}\right)\right] + \sigma_{\alpha\beta}^{R} / \sqrt{1+\xi}\right\}$$
(14b)

$$\xi = S_{\beta} / S_{\alpha} \quad \text{with} \quad \lambda = 2(S_{\alpha} + S_{\beta}) \tag{15a}$$

$$r_{\alpha} = 1 / \sqrt{1 + \xi} \quad \text{with} \quad R = r_{\alpha} + r_{\beta} \tag{15b}$$

 $L_{\alpha};L_{\beta}$  - heat of fusion per unit volume of a given eutectic phase,  $[J/m^3]; T_E$  - eutectic melting point, [K];  $P^*$ , E - parameters referred to lamellae width, (Jackson & Hunt, 1966);  $N_0$  - difference of the solubility of the B – eutectic element in the A – element and solubility of the A – element in the B – element, according to a given eutectic phase diagram, [at.%]; *D* – diffusion coefficient in the liquid,  $[m^2/s]$ ;  $\sigma_j^L$  – specific surface free energy for the lamellar structure,  $j = \alpha, \beta$ ,  $[J/m^2]$ ;  $\sigma_j^R$  – specific surface free energy for the rod-like structure,  $j = \alpha, \beta, [J/m^2]$ ;  $\sigma_{\alpha\beta}^R$  –  $\alpha/\beta$  phase boundary free energy for lamellar structure,  $[J/m^2]$ ;  $\sigma_{\alpha\beta}^R$  –  $\alpha/\beta$  phase boundary free energy for lamellar structure,  $[J/m^2]$ ;  $\sigma_{\alpha\beta}^{R} - \alpha / \beta$  phase boundary free energy for the rod-like structure,  $[J / m^{2}]$ . Geometry for both types of eutectic morphology is shown in Fig. 14.



Fig. 14. Geometrical parameters defining both morphologies; a. inter-lamellar spacing,  $\lambda$  in the regular structure; b. rod/(rod + matrix) radiuses in the regular structure, Eq. (15).

Some rearrangements of Eq. (12) allows to formulate the following inequality:

$$\left\{ m \left[ a_{\alpha}^{L} / m_{\alpha} + a_{\beta}^{L} / \xi m_{\beta} \right] + \sigma_{\alpha\beta}^{L} / (1 + \xi) \right\} / \left\{ m \left[ a_{\alpha}^{R} / m_{\alpha} + a_{\beta}^{R} / \xi m_{\beta} \right] + \sigma_{\alpha\beta}^{R} / (1 + \xi) \right\}$$

$$> 4 \left( E / P^{*} \right) \left( 1 / (1 + \xi) \right)^{1.5}$$

$$(16)$$

The obtained inequality was developed in the same manner as the inequality illustrated in Fig. 11. The developed inequality cannot predict the lamella into rod transformation in the eutectic system. Analogously to the mentioned theory, (Jackson & Hunt, 1966), this inequality can be applied, Eq. (16), to some extent, in order to predict, only, whether a given eutectic system (phase diagram) promotes the lamellae or rods formation.

Therefore, the *Gibbs'* free energy, Eq. (12), was calculated with applying the evolution (with the growth rate) of a mechanical equilibrium at the triple point of the s/l interface, Fig. 15.



Fig. 15. Evolution (with varying growth rate) of the s/l interface curvature for the regular eutectic growth and adequate mechanical equilibrium situated at the triple point, (scheme).

 $\alpha \equiv Si$ , and  $\beta \equiv (Al)$  - eutectic phases;  $\sigma_{\alpha} \equiv \sigma_{\alpha}^{L}$  or  $\sigma_{\alpha} \equiv \sigma_{\alpha}^{R}$ ;  $\sigma_{\beta} \equiv \sigma_{\beta}^{L}$  or  $\sigma_{\beta} \equiv \sigma_{\beta}^{R}$ ;  $\sigma_{\alpha-\beta} \equiv \sigma_{\alpha\beta}^{L}$  or  $\sigma_{\alpha-\beta} \equiv \sigma_{\alpha\beta}^{R}$ ;  $\theta_{\alpha} \equiv \theta_{\alpha}^{L}$  or  $\theta_{\alpha} \equiv \theta_{\alpha}^{R}$ ;  $\theta_{\beta} \equiv \theta_{\beta}^{L}$  or  $\theta_{\beta} \equiv \theta_{\beta}^{R}$ , Fig. 15. The mechanical equilibrium for the both structure types is:

$$\sigma_{\alpha}^{L}\sin\theta_{\alpha}^{L} \mp \sigma_{\beta}^{L}\sin\theta_{\beta}^{L} - \sigma_{\alpha\beta}^{L} = 0; \quad \sigma_{\alpha}^{R}\sin\theta_{\alpha}^{R} \mp \sigma_{\beta}^{R}\sin\theta_{\beta}^{R} - \sigma_{\alpha\beta}^{R} = 0$$
(17)

The *Gibbs'* free energy, Eq. (12) calculated for the threshold growth rate is shown in Fig. 16. The threshold growth rate in calculation equals  $v = 400 \,\mu m / s$ ;  $\Delta G^* \equiv \Delta G_L^*$  or  $\Delta G^* \equiv \Delta G_R^*$ , respectively; dot L – denotes localization of the average inter-lamellar spacing,  $\overline{\lambda}$  and dot R – denotes localization of the average inter-rod spacing,  $\overline{R}$ ;  $\theta_{\alpha}^{L}; \theta_{\beta}^{L}; \theta_{\alpha}^{R}; \theta_{\beta}^{R}$  – angles, Fig. 15.

All the minima of the *Gibbs'* free energy for considered growth rates are gathered in Fig. 17. According to the result of the *Gibbs'* free energy calculation this structure is stable form which has its minimum situated lower, Fig. 17. Thus, the calculation allows to determine the threshold growth rate, when minima are at the same level, Fig. 16. The operating range for transition cannot be described, alas. The present simulation, Fig. 17, was possible since the evolution of the s/l interface curvature, Fig. 18, was implemented into the calculation. The evolution involves some changes of crystallographic orientation of the s/l interface and

The evolution involves some changes of crystallographic orientation of the s/l interface and specific surface free energies together with inter-phase boundary free energy, Fig. 15.



Fig. 16. *Gibbs'* free energy simulated for the both structures formation at the threshold rate.



Fig. 17. *Gibbs'* free energy minima calculated for lamellar and rod-like structures formation; the critical growth rate,  $v_{kryt.}$ , for lamella into rod transition results from the trajectories intersection;  $v_{kryt.}$  is equal to the experimental threshold growth rate:  $v_{thr.}$ .



Fig. 18. A model of the s/l interface curvature evolution with the growth rates;  $v_{kryt} \equiv v_{thr}$ .

#### 4.3 Thermodynamics of the whole solidification of regular eutectic structure

Thermodynamics of the whole solidification process supposes a calculation of the entropy production for the regular structure growth, (Lesoult & Turpin, 1969). The regular structure areas can be easily distinguished among generally irregular structure, (Fisher & Kurz, 1980). The regular structure selection under stationary state with the assumption of an isothermal s/l interface is to be described by the criterion of minimum entropy production, (Kjelstrup & Bedeaux, 2008). The entropy production per unit time,  $P_S^D$ , S = R, L, is as follows:

$$P_S^D = \int_V \sigma \, dV \tag{18}$$

*V* is the so-called "thermodynamic macroscopic point" (volume) inside of which all essential fluxes are observed, (Glansdorff & Prigogine, 1971). *V* - volume is shown in Fig. 19.

$$\sigma = R^* \varepsilon C^{-1} (1 - C)^{-1} D \nabla^2 C \tag{19}$$

 $R^*$  - gas constant, [J/(mole K)];  $\varepsilon$  - thermodynamic factor, [dimensionless]; C - solute content, [at.%];  $\sigma$  - entropy production per unit time and unit volume,  $[mole fr.^2/(m^3s)]$ .



Fig. 19. *V* - volume, applied in calculation of the entropy production per unit time, Eq. (18); a. for the rod-like structure, z = g(r) - function which describes the s/l interface curvature;  $z_D$  - thickness of the diffusion zone, [m]; b. for the lamellar structure, z = g(x) - function which describes the s/l interface curvature;  $z_D$  - thickness of the diffusion zone, [m].

The solution to Eq. (18) gives the following result: a. entropy production (associated with the diffusion) for a rod-like structure formation:

$$P_{R}^{D} = V_{1} v \left(r_{\alpha} + r_{\beta}\right)^{-1} + V_{2} v \left(r_{\alpha} + r_{\beta}\right)^{-2} + V_{3} v^{2} + V_{4} v^{2} \left(r_{\alpha} + r_{\beta}\right) + V_{5} v^{3} \left(r_{\alpha} + r_{\beta}\right)^{2}$$
(20a)

b. entropy production (associated with diffusion) for a lamellar structure formation:

$$P_{L}^{D} = W_{1} v \left(S_{\alpha} + S_{\beta}\right)^{-1} + W_{2} v \left(S_{\alpha} + S_{\beta}\right)^{-2} + W_{3} v^{2} + W_{4} v^{2} \left(S_{\alpha} + S_{\beta}\right) + W_{5} v^{3} \left(S_{\alpha} + S_{\beta}\right)^{2}$$
(20b)

 $V_n$ ;  $W_n$  n = 1,...,5 - constants contain material parameters, (Wołczyński & Billia, 1996). The calculations of the entropy production applied to the Zn-Ti system are connected with some experimental observations. According to the observations, for:

- $0 < v < v_1$  irregular L-shape rods (equipped with branches) appear, Fig. 20,
- $v_1 < v < v'_1$  L-shape rods with disappearing branches and regular lamellae coexist, Fig. 21
- $v'_1 < v < v_2$  regular lamellae are formed exclusively within the range of growth rates, Fig. 22,
- $v > v_2$  regular rods are stable form within the range of growth rates, Fig. 23.

The characteristic crystal growth rates have the following experimentally determined value:  $v_1 \approx 5 \text{ mm} / h$ ;  $v_1 \approx 5.8 \text{ mm} / h$ ;  $v_2 \approx 10 \text{ mm} / h$ .



Fig. 20. ((Zn) + Zn<sub>16</sub>Ti) - eutectic morphology in stripes obtained for the growth rate  $v < v_1$ ; a. L-shape irregular rods; b. branching phenomenon with the frozen planar s/l interface.



Fig. 21. Coexistence of L-shape rods (disappearing branches) and regular lamellae,  $v < v'_1$ .



Fig. 22. Lamellar ((Zn) + Zn<sub>16</sub>Ti) - eutectic morphology for the growth rate  $v_1 < v < v_2$ .

Arrows juxtaposed onto the morphology, Fig. 22, show the parabolic shape of the s/l interface of the (Zn) – non-faceted phase and emphasize the regularity of eutectic structure.



Fig. 23. Regular rods of the Zn<sub>16</sub>Ti – intermetallic compound obtained for  $v > v_2$ .

The calculation of the entropy production,  $P_D$ , applied to the Zn-Ti system is made with the implementation of the model for rotation of mechanical equilibrium around the triple point of the s/l interface, Fig. 24. The rotation is performed with the increasing growth rate and causes some changes of the s/l interface curvature of the non-faceted (Zn) – phase, Fig. 24.



Fig. 24. Rotation of the mechanical equilibrium around the triple point of the s/l interface.

The mechanical equilibrium is established by the parallelogram of the anisotropic specific surface free energies together with the  $\alpha / \beta$  - inter-phase boundary free energy, Fig. 24. As a result of the varying growth rate, the s/l interface curvature changes due to rotating crystallographic orientation.  $\sigma_{(Zn)} \equiv \sigma_{(Zn)}^L$  and  $\sigma_{Zn16-Ti} \equiv \sigma_{Zn16-Ti}^L$  - specific surface free energies for (Zn) - phase and  $Zn_{16}Ti$  - compound, respectively,  $[J / m^2]$ ;  $\sigma_{(Zn)-Zn16Ti}$  - interphase boundary free energy,  $[J / m^2]$ ;  $\theta_j$  - angles,  $[^0]$ ,  $j = (Zn), Zn_{16}Ti \equiv \alpha, \beta$ . The rotation of the mechanical equilibrium yields some changes of capillarity parameters.

The rotation of the mechanical equilibrium yields some changes of capillarity parameters. This is shown in function of the increasing growth rate, Fig. 25.



Fig. 25. Changes of the specific surface free energy,  $\sigma_{(Zn)}^L$ , and inter-phase boundary free energy,  $\sigma_{(Zn)-Zn_{16}Ti}$ ; as applied to calculation of the entropy production.

The appearance of the observed structure is accompanied by a proper entropy production, as postulated. The considered solidification occurs under stationary state, therefore, the entropy production,  $P_D$ , manifests its minimum. The calculations are made to show the competition between two eutectic regular structures: rod-like and lamellar structure, Fig. 26.



Fig. 26a. Competition between eutectic structures formation: regular rods among irregular L-shape rods and regular lamellae; shown for the growth rate, v = 1.8mm / h;  $0 < v < v_1$ .



Fig. 26b. Competition between eutectic structures formation: regular rods among irregular L-shape rods and regular lamellae; shown for the first threshold growth rate,  $v_1 \approx 5 mm / h$ .



Fig. 26c. Competition between eutectic structures formation: regular lamellae and regular rods; shown for the growth rate, v = 6 mm / h;  $v'_1 < v < v_2$ .



Fig. 26d. Competition between eutectic structures formation: regular lamellae and regular rods; shown for the second threshold growth rate,  $v_2 \approx 10 mm / h$ .



Fig. 26e. Competition between eutectic structures formation: regular lamellae and regular rods; shown for the growth rate; v = 16 mm / h,  $v > v_2$ .

It is visible that the entropy production calculated for the observed structure formation within a proper range of growth rates, locates its minimum lower than the entropy production determined for a competitive structure, Fig. 26.

Next, the calculated entropy productions were minimized in order to compare their minimal values for all studied growth rate ranges: a.  $0 < v < v_1$ , where the L-shape rods equipped with branches, (irregular eutectic structure) appear, Fig. 20, b.  $v_1 < v < v_1'$ , where the L-shape rods with disappearing branches and regular lamellae coexist, Fig. 21, c/  $v_1' < v < v_2$ , where the regular lamellae are exclusive form, Fig. 22, and d/  $v > v_2$ , where the regular rods are created, Fig. 23. The results of calculation are shown in Fig. 27.



Fig. 27. Comparison of minimal values of the entropy production calculated for both regular rod-like structure formation (formed twice) and regular lamellar structure formation.

The estimation of the average inter-rod spacing for the first rates range:  $0 < v < v_1$  requires to apply a definition of the mean value of the investigated spacing.

$$\overline{R} = 0.5R + R^i_\beta + 0.5\lambda^i_s \tag{21}$$

 $R = r_{\alpha} + r_{\beta}$  - defined within the areas of the regular structure, Fig. 14b, which are formed among the generally irregular structure, [m];  $R_{\beta}^{i}$  - radius of the non-coupled rod which manifests an excess protrusion over the s/l interface, [m], (Wołczyński, 1996).

$$\lambda_s^i = 2\pi \left( \Gamma_{(Zn)} / \left( G - m_{(Zn)} G_C \right) \right)$$
(22)

where  $\lambda_s^i$  - a wavelength of perturbation which appears at the s/l interface of the (Zn) – non-faceted phase, (as defined in Fig. 12.) [*m*], with  $\Gamma_{(Zn)}$  - *Gibbs-Thomson* capillarity parameter; *G* - thermal gradient at the s/l interface, [*K* / *m*]; *m*<sub>(Zn)</sub> - slope of the *liquidus* line of the (Zn) – phase, [*K* / *at*.%]; *G*<sub>C</sub> - solute concentration gradient at the s/l interface of the (Zn) – phase, [*at*.% / *m*]. In the range:  $v_1 < v < v'_1$ , the following transformation occurs:

$$\lambda_s^i \to R; \ R_\beta^i \to 0 \ \text{and finally} \ \overline{R} \to R$$
 (23)

It means that irregular rod-like structure transforms into the regular rod-like structure. This transition leads to the local disappearing of branches. Eventually, the regular rods transform into the regular lamellae within the range,  $v_1 < v < v'_1$ , Fig. 21.

#### 5. Concluding remarks

A pattern selection among the eutectic morphologies is performed through the competition. In the case of the eutectic morphologies which were created within the stripes strengthening the (Zn) single crystal the L-shape irregular rods, regular lamellae or regular rods were revealed. According to the current model, this eutectic structure appeared which was the winner just in the thermodynamic competition. Therefore, it was necessary to determine the minimum entropy production for the appearance of the all studied structures. The formed structure had its minimum entropy production situated lower than the other participant of the competition. So, it has been proved that the regular L-shape rods (existing among the generally irregular L-shape rods) have their minimum entropy production situated lower than the minimum entropy production determined for the regular lamellae growth (when  $0 < v < v_1$ ). However, the regular lamellae are the winner within the growth rates range  $v_1 < v < v_2$ . Eventually, the regular rods exist exclusively when the growth rate fulfils the following inequality  $v > v_2$  since the minimum entropy production calculated for their formation is localized lower than the minimum entropy production determined for the regular lamellae growth, Fig. 27. Both minima being in competition are at the same level for the threshold growth rates,  $v_1$ , and  $v_2$ , Fig. 26b, Fig. 26d, respectively, (also Fig. 27).

It has been revealed that the leading eutectic phase (the  $Zn_{16}Ti$  intermetallic compound) was growing with the *d* - protrusion, Fig. 8, Fig. 9 and Fig. 10. The protrusion can be determined based on the solute concentration micro-field in the liquid ahead of the s/l interface, Eq. (7), and Eq. (8), but the local mass balance is to be considered, Eq. (10).

In fact, the theoretical definition for the protrusion results from the analysis of the local mass balance (Wołczyński, 2007) and is formulated for the slow solidification as follows:

$$\sum_{n=1}^{\infty} A_{2n-1} \frac{\left(-1\right)^{n-1}}{(2n-1)} \left[ 1 - \frac{S_{\alpha}}{S_{\beta}} \exp\left(-\frac{(2n-1)\pi}{2S_{\beta}}d\right) \right] = 0$$
(24)

 $A_{2n-1}$  - constant in the *Fourier* series. According to the observation of the leading phase protrusion, *d* , Fig. 8, Fig. 9 and Fig. 10, it is suggested to introduce the revealed protrusion into the structural scheme shown in Fig. 12.

Also, the operating range for the irregular eutectic growth (as defined in Fig. 12) can be justified by some structural observations. These observations are connected with the L-shape rod-like structure revealed for the growth rates range,  $0 < v < v_1$ . A typical spacing is to be distinguished within the operating range for the irregular eutectic growth:

a. the  $\lambda_i$  - spacing which is associated with the regular lamellar structure formation among generally irregular structure, (or the *R* - spacing which is associated with the regular rod-like structure formation, Fig. 28a); this spacing is referred to the criterion of the minimum entropy production,

b. the  $\lambda_s^i$  - spacing which corresponds to the maximal destabilization of the s/l interface of the (Zn) - non-faceted phase, Fig. 28b; this spacing (treated as perturbation wave,  $\lambda_s^i$ ), is referred to the state of marginal stability which is created at that very moment at the s/l interface.



Fig. 28. Selection of the spacing in the irregular eutectic growth; a.  $\lambda_i$  - spacing selected by the minimum entropy production, and b.  $\lambda_s^i$  - spacing selected by the marginal stability.

It is evident that the oscillation of the interlamellar or interrod spacing occurrs in the  $(Zn) - Zn_{16}Ti$  eutetcic system. The analyzed structural oscillation is shown schematically in Fig. 29.



Fig. 29. A paraboloid of the entropy production drawn in function of two thermodynamic forces ( $X_C, X_r$ ), with the added so-called "technological" coordinate system, ( $v, \lambda$ ).

 $X_c$  - generalized thermodynamic force associated with the mass transport, [at.%/m];  $X_r$  - generalized thermodynamic force associated with the heat transfer; [K/m]; v - crystal growth rate, [m/s];  $\lambda$  - inter-lamellar spacing within the regular eutectic structure, [m] The paraboloid of the entropy production is drawn schematically in the "thermodynamic" coordinate system, that is, in function of two thermodynamic forces. Next, it is assumed (for the simplicity) that the paraboloid does not change its shape when entropy production, P, is calculated for the crystal growth in function of v,  $\lambda$ , Eq. (20b) or v, R, Eq. (20a). Two trajectories are superposed onto the paraboloid, Fig. 29: a. A - trajectory of local minima of the paraboloid for the regular structure formation, Fig. 28a, /B - trajectory of the marginal stability referred to the maximal destabilization of the s/l interface, Fig. 28b. Both trajectories intersect each other (at K - point) for the critical thermal gradient,  $G_K$ , at which an oscillation disappears and irregular structure is completely transformed into

regular eutectic structure. However, for a given condition of solidification (crystal growth rate,  $v_1$ , and thermal gradient,  $G_1$ ), the destabilized s/l interface moves slower, with the  $v'_1$  - rate,  $(v'_1 < v_1)$ , and the perturbation wave,  $\lambda_s^i$ , is equal to  $\lambda_{s1}^s$ . On the other side, the regular structure appears at the  $v_1$  - rate and involves the  $\lambda_i = \lambda_{s1}^i$  - spacing formation, Fig. 29. Thus, the discussed oscillation occurs between both trajectories as shown for  $v_1$ ,  $G_1$ , Fig. 29.

The oscillation of the eutectic spacing, Fig. 28, is observed in the case of the irregular eutectic structure formation formed within the stripes strengthening the (Zn) - single crystal for the growth rates range equal to  $0 < v < v_1$ , as mentioned.

The discussed oscillation can be illustrated on the parabola of entropy production. Such a parabola is to be created by an intersection of the paraboloid, Fig. 29, by the plane given for the imposed thermal gradient, G = const., (Prigogine, 1980), as shown in Fig. 30.



Fig. 30. A parabola of the entropy production for the eutectic rod-like structure formation.

It results from the current model, Fig. 30, that:

- a. the regular part of the generally irregular eutectic structure is formed at the minimum entropy production localized at the A parabola minimum which performs the role of attractor for the eutectic system,
- b. the maximal destabilization at the s/l interface of the non-faceted eutectic phase is observed for the B marginal stability of the eutectic system which corresponds to the branching phenomenon (as visible in Fig. 12) and to maximal deviation from the attractor.

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