Criterion of the minimum entropy production in unidirectional solidification

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Thermodynamics of the irreversible processes allows to describe the growth of regular lamellar or rod-like eutectics while applying the minimum entropy production criterion, [1].

The application of such a criterion leads to the formulation of the growth law for a given lamellar or rod-like structure formation, [2]. The formulated growth law says: *"at an imposed thermal gradient, represented by its component, $\partial T / \partial x$, and at a given growth rate, v, an eutectic reaction occurs under stationary state, in such a way that the selected inter-lamellar spacing, λ, or inter-rod spacing, R, within the regular structure is associated with the local minimum entropy production for the process under investigation*".

The adequate growth law is given as follows:

a/ for the lamellar eutectic structure formation,

$$3W_3\left(\lambda^2 v\right)^2 + 2W_1\lambda^3 v + \left(W_6 + W_7\right)\lambda^2 v = W_4 + W_5 \qquad (1)$$

W_n are coefficients which contain some material parameters and $\partial T / \partial x$, $n = 1,...,7$,

b/ for the rod-like eutectic structure formation,

$$3V_3\left(R^2 v\right)^2 + 2V_1 R^3 v + \left(V_6 + V_7\right)R^2 v = V_4 + V_5 \qquad (2)$$

V_n are coefficients which contain some material parameters and $\partial T / \partial x$, $n = 1,...,7$.

After some rearrangements, the above growth laws are reduced to the known description of eutectic growth, (3), obtained by the Jackson – Hunt's theory, [3], due to minimization of the undercooling of the solid/liquid interface and according to the condition $\partial \Delta T / \partial \lambda|_v = 0$.

$$\lambda^2 v = const._{JH}^{R} \qquad R^2 v = const._{JH}^{R} \qquad (3)$$

According to the reduction, the growth laws (1) and (2) are written as follows:

$$\lambda^2 v = -W_7 / \left(3W_3\right) \quad \text{and additionally} \quad -W_7 / \left(3W_3\right) = const._{JH}^{L} \qquad (4a)$$

$$R^2 v = -V_7 / \left(3V_3\right) \quad \text{and additionally} \quad -V_7 / \left(3V_3\right) = const._{JH}^{R} \qquad (4b)$$

It can be concluded from the equation (4) that not only the Jackson – Hunt's equations (3) are the particular case of the current growth laws (1), (2), but the condition of minimum undercooling is the particular case of the criterion of minimum entropy production as well.

However, in the case the growth of irregular eutectics subjected to the unidirectional solidification the use the criterion of minimum entropy production is to be accompanied by the simultaneous application of the concept of marginal stability referred to the solid / liquid interface of the non-faceted eutectic phase, [4]. The formulated growth law, says: "*at an imposed thermal gradient represented by its components $\partial T / \partial x, \partial T / \partial z$, and at a given growth rate, v, an eutectic reaction occurs under stationary / marginal state in such a way, that the selected inter-lamellar spacing possess an average width, $\bar{\lambda}$, described by the relationship, $\bar{\lambda}\left(\lambda, \lambda_m\right)$, where, the λ - parameter is associated with minimum entropy production for a given stationary state, and, λ_m - parameter is connected with marginal wavelength created by the perturbation appeared at the solid / liquid interface of the non-faceted phase, and marginal stability is referred to a given rotation around stationary state*".

The proposed growth law for the irregular lamellar structure formation is given as follows:

$\bar{\lambda} = 0.5\lambda + S_{\beta}^{i} + 0.5\lambda_m$ (5)

where, λ is defined by the growth law (1), S_{β}^{i} is shown in Fig. 1, and λ_m is a wavelength of perturbation $\lambda_m = 2\pi\left(\Gamma / \left(|m| G_C - G\right)\right)^{0.5}$, Fig. 1, Γ is the Gibbs-Thomson's coefficient, m is the liquidus line slope, $G_C = -(v/D)(1-k)N_E$, $G = \partial T / \partial z$, D is the diffusion coefficient, k is the partition ratio, and N_E is the mole fraction of the solute in an eutectic alloy.

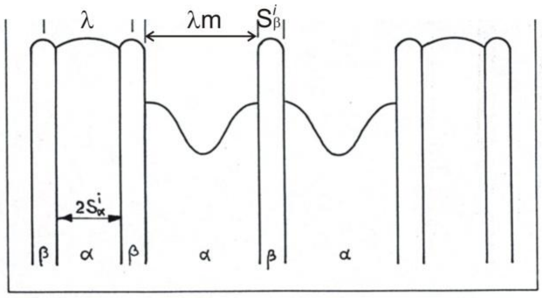

Fig. 1. Scheme of the irregular eutectic growth; λ is the inter-lamellar spacing for the areas where the regular structure is the exclusive form; λ_m is the wavelength of a perturbation created at the solid / liquid interface of the non-faceted phase; S_{β}^{i} is a width of the non-coupled lamella.

The formation of the irregular eutectic structure can be explained as an oscillation between an attractor (point A in Fig. 2.), situated at the local minimum of the paraboloid which represents entropy production for the eutectic growth and a marginal stability situated at the bifurcation point (point B in Fig. 2.) of the same paraboloid. The attractor is connected with the regular structure formation (λ - parameter) and the bifurcation point is associated with maximum instability of the solid / liquid interface when the perturbation achieves the marginal stability (wavelength of the perturbation is equal to the λ_m - parameter in the B – point). The lamellae branching occurs just at the bifurcation point.

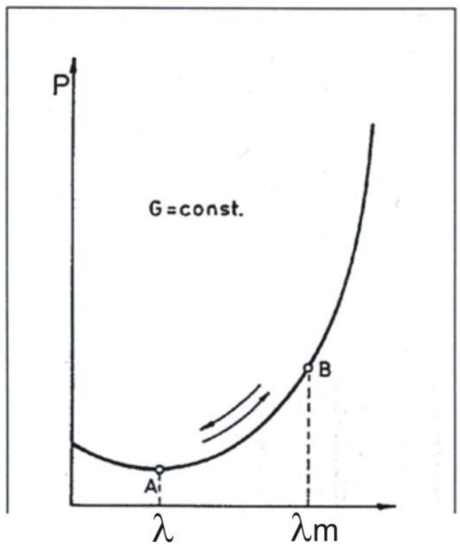

Fig. 2. Scheme of the structural spacing oscillation between an attractor given by the minimum entropy production and the marginal stability determined by the maximum instability of the solid / liquid interface of the non-faceted phase; all the attractors are situated on a trajectory of the local minima of the paraboloid which illustrates the entropy production; all the bifurcation points are situated on the trajectory of marginal stability which can be located on the same parabolid; an oscillation occurs between the mentioned trajectories and vanishes when the

Also, the transformation lamella ➔ rod observed in some eutectic systems can be successfully described by means of the laws delivered by the thermodynamics of irreversible processes. Based on the criterion of minimum entropy production a new procedure of pattern selection has recently been formulated [5]. According to this idea: "*this structure (lamellar or rod-like) is selected which exhibits the lower minimum entropy production*".

The lamella ➔ rod transformation is observed in such the eutectic systems like: Al-Si, Fe-C, $Fe-Fe_3C$ or $Zn-Zn_{16}Ti$. Three types of the transformation are observed: regular lamella into regular rod, irregular lamella into regular rod or irregular lamella into irregular rod.

Thus, irregular into regular structure is also expected. In this case the vanishing of the branches is to be observed. Consequently, the vanishing of oscillation between a point of bifurcation and an attractor, Fig. 2., should occur.

The critical growth rate, $v_{kryt.}$, (threshold for the lamella ➔ rod transformation) results from the intersection of the minimum entropy production calculated for the lamellar structure formation and the minimum entropy production determined for the rod-like structure formation as explained for the Al-Si eutectic alloy, Fig. 3.

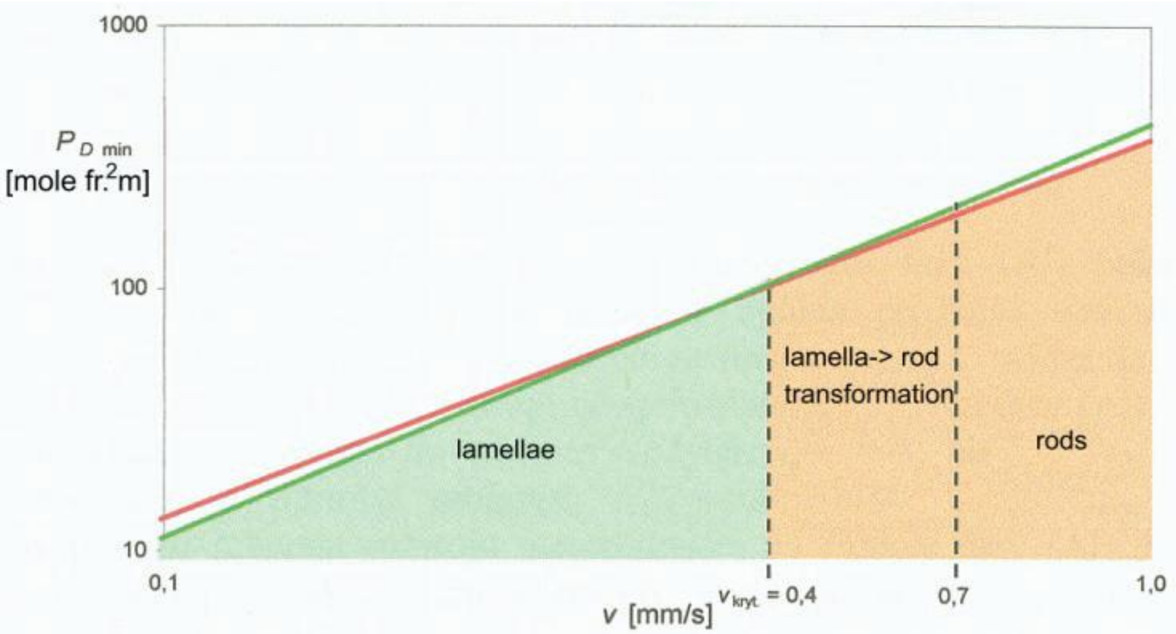

Fig. 3. Areas of the lamellar and rod-like structure formation; additionally the range of growth rates (within which the branching vanishes) is determined; entropy production minima are calculated for the regular lamellae and rods formation at different growth rates, typical for the unidirectional solidification of the Al-Si eutectic alloy.

According to the calculations presented in Fig. 3. the lamellae (with branches) are stable form below the threshold growth rate, $v_{kryt.}$, since the minima of entropy production for lamellar structure formation are located lower than the minima of entropy production for the rod-like structure formation. The regular rod-like structure appears above the threshold growth rate but rods are exclusively stable form over the range of transformation.

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