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ON THE GROWTH KINETICS OF LAMELLAR TERNARY EUTECTICS OF THE αβγ-KIND

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ABSTRACT

Producing ternary lamellar eutectics (TLE) of the αβγ-kind (α, β, γ the constituent phases of TLE) has so far eluded the efforts of experimenters. A detailed analysis of the experimental results obtained so far revealed that this is not a failure of the experimenters or an imperfection of the eutectics growth methods used, but a result of some fundamental factors governing the TLE growth. To disclose these factors, a growth model of TLE has been developed which, along with the solute diffusion, accounts for the growth kinetics of the constituent phases. The application of some reasonable simplifications made it possible to reduce the problem at hand to a set of linear algebraic equations, which solution determined all the parameters of TLE growth. Based on the model, a "selection criterion" was formulated that allows assessing the prospects of successfully growing TLEs of the αβγ-kind. The worked-out equations together with the "selection criterion" were implemented to assess the chances of growing viable TLEs in some ternary systems.

Keywords: *ternary eutectics, solidification, growth models, mass transfer, metals.*

INTRODUCTION

In the past few decades, the growth of eutectics has been a subject of considerable theoretical and experimental research [1 - 27]. This interest is well understood because the eutectics combine uniquely the physical properties of their constituent phases and thus could be considered natural composites; one recalls that some of the widely used in the industry steels, bronzes, solders, etc. are composed entirely, or contain, eutectics in their structure [19]. Another advantage of eutectics (eutectoids) as a structural material is their low production cost because these are produced in a very competitive way - during the solidification or the heat treatment of the incipient alloy. Hence, it is not surprising that up to this moment eutectics- (eutectoids-) based materials enjoy a permanent interest among the researcher and new materials developers. Initially, the research was predominantly limited to binary eutectics thus leading to a considerable accumulation of knowledge on the subject [1 - 17]. That experimental and theoretical knowledge prompted some researchers to extend their inquiries into a new field, the production of ternary lamellar eutectics (TLE) of αβγ-kind [18, 19]. (Here α, β, γ denote the constituent phases of the TLE.) The motivation behind that interest is understandable; most of the commercial materials of interest are composed of several components ($K \geq 3$), thence, keeping in mind the Gibbs rule, the number of phases that could be precipitated and incorporated into the eutectic increases substantially. Respectively, the chances of producing materials with unique properties also increase.

The early experimental attempts to produce TLEs were carried out in the late sixties of the past century by Cooksey and Hellawell [18]. It was expected that solidifying melts with composition matching, or close to the nonvariant eutectic composition and temperature, will readily produce TLEs with a stacking sequence αβγ-αβγ. Surprisingly, this was not the case. None of the experiments carried out at that time was successful. Instead of the expected lamellas sequence, αβγ-αβγ , the eutectics showed a wide variety of pseudo-ternary eutectic structures, that is, a microstructure of arbitrarily arranged combinations of the phases α, β, and γ. Recently, two research groups renewed that research in a new attempt to produce TLEs of the αβγ-kind (their target was the E2-eutectic in the Bi-In-Sn system) [24 - 26]. A partial success was reported from one of these groups, which claimed to obtain small domains of In-In_2Bi-Sn in one of their attempts [26].

The failure in growing experimentally ternary lamellar eutectics, whose phase structure could be preselected at will, prompted some researchers in developing theories or models of the growth of αβγ-eutectics. The obvious way to do that was to extend the already existing theories of binary eutectics growth. However, these failed to explain why achieving growth of lamellar eutectics with predetermined stacking arrangement of the kind, αβγ-αβγ, is so difficult, if not impossible.

The fact that there is no confirmed report on growing TLEs, suggests that this is not merely a coincidence but that the problem has a fundamental nature. The present research aims to obtain a mathematical solution to the TLE growth problem, if possible, an analytical one [17], thus finding a reasonable explanation for; why producing TLE is associated with such difficulties. The goals of the research should be, thus, formulated as:

(i) Formulation of a feasible model of TLEs growth and obtaining a solution. The model formulated should allow, the determination of the compositions of the eutectic's constituent phases, the rate of the eutectic growth, the lamellar spacing, and the phases' fractions as a function of the applied undercooling;

(ii) Providing an answer to why producing TLEs is associated with such difficulties.

EXPERIMENTAL

The research below is carried out by numerical modeling of the process of growth of an αβγ-kind eutectic, hence, a numerical experiment. The problem at hand is thus treated as two independent tasks; (i) solution to the solute transfer problem; (ii) determining the TLE constituent phases' growth rate as a function of the applied undercooling and the composition of the matrix/constituent phases. The solution to the problem as a whole, thus, will be a combination of those obtained in (i) and (ii).

The solute transfer (diffusion) problem: The mass transfer at eutectic growth of TLEs of the type, αβγ–αβγ, allows an analytical solution when the following conditions are fulfilled:

(1) The eutectic's growth is time-independent (steady-state), hence, the compositions of the eutectic's constituent phases, $C_i^{m(ph)}$, the lamellae spacing λ, and the volume fractions of the involved phases, f^{ph} are also time-independent (here the indices denote; *m*-matrix, *ph*-phase, *i*-index of the dissolved component);

(2) The solidification front is planar, i.e., the factors that could lead to the curving of the interface surface, e.g. the surface tension between the matrix and the constituent phases, are neglected;

(3) The diffusion coefficients of the dissolved components and the temperature are constants. The diffusion in the solid phases is negligible;

(4) The compositions of the involved constituent phases and the temperature are close to those at equilibrium, C_i^{ph}, C_{ie}^{m}, and T_e (indicated with a subscript – *e*). Hence; $T = T_e - \Delta T$, $C_i^m = C_{ie}^m \pm \Delta C_i^m$ and $C_i^{ph} = C_{ie}^{ph} \pm \Delta C_i^{ph}$. Where: ΔT and $\Delta C_i^{m(ph)}$ are the deviations of the temperature and phases' compositions from their equilibrium values. It is assumed that $\Delta T / T_e << 1$ and $\Delta C_i^{m(ph)} << 1$.

(5) The mathematical problem is two-dimensional, i.e., $C_i^{m(ph)}\left(x,z\right)$ (see Fig. 1) and $C_i^m\left(x,\infty\right) \to C_{ie}^m$;

(6) Due to the periodicity of the eutectic structure (the phases are ordered as -αβγ-αβγ-) it is valid; $C_i^m\left(x,z\right) = C_i^m\left(x+\lambda,z\right)$, $\partial C_i^m\left(x,z\right)/\partial x = \partial C_i^m\left(x+\lambda,z\right)/\partial x$.

(7) The growth rate of the colony, respectively, the growth of the constituent phases, *v*, and the temperature *T* in the eutectic cell are constants.

The solute transfer in the melt and the solids is governed by the second Fick's equation [10, 28 - 30]:

$$\frac{\partial^2 C_i^m}{\partial x^2} + \frac{\partial^2 C_i^m}{\partial z^2} + \frac{v}{D_i}\frac{\partial C_i^m}{\partial z} = 0$$

$$(i \in \{1,2\} \text{ and } ph \in \{\alpha,\beta,\gamma\}) \qquad (1)$$

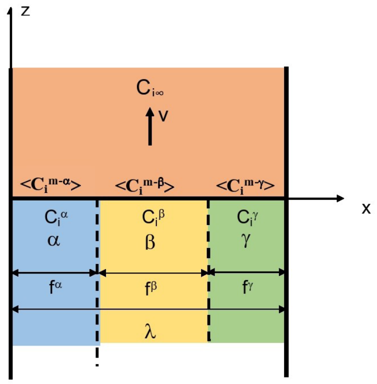


Fig. 1. Scheme of the eutectic cell showing the geometry of the problem and the used notations; the growth rate, *v*, the cell width, λ, the phases' fractions, f^{ph}, and the average solute concentrations - $\left\langle C_i^{m-ph}\right\rangle$, and C_i^{ph} ($i\in\{1..2\}$, $ph\in\{\alpha,\beta,\gamma\}$).

Under (1-8), the following boundary conditions apply:

$$C_i^m(0,z)=C_i^m(\lambda,z);\ \partial C_i^m/\partial x\big|_{x=0}=\partial C_i^m/\partial x\big|_{x=\lambda}$$

$$\partial C_i^m/\partial z\big|_{z=0}=-v\left(C_i^m(x,0)-C_i^{ph}(x,0)\right)/D_i,$$

$$C_i^{ph}(x,0)=\begin{cases}C_i^\alpha(x,0),\ x\in\left\{0,\lambda f^\alpha\right\}\\ C_i^\beta(x,0),\ x\in\left\{\lambda f^\alpha,\lambda\left(f^\alpha+f^\beta\right)\right\}\\ C_i^\gamma(x,0),\ x\in\left\{\lambda\left(f^\alpha+f^\beta\right),\lambda\right\}\end{cases}$$

$$C_i^m(x,\infty)=C_{ie}^m$$

Here, D_i signifies the diffusion coefficient of the *i*th component in the matrix and λ is the width of the eutectic cells (cf. conditions 1 - 7).

The analytical solution of (1) is given in detail in Appendix 1 (cf. Eqs. (A1.8)):

$$f^\alpha\left\langle C_i^{m-\alpha}\right\rangle+f^\beta\left\langle C_i^{m-\beta}\right\rangle+\left(1-f^\alpha-f^\beta\right)\left\langle C_i^{m-\gamma}\right\rangle=C_{ie}^m \tag{2}$$

$$\left\langle C_i^{m-\alpha}\right\rangle=C_{ie}^m+Pe_i\sum_{n=1}^{\infty}b_{in}\sin\left(2n\pi f^\alpha\right)\Big/f^\alpha$$

$$\left\langle C_i^{m-\gamma}\right\rangle=C_{ie}^m-Pe_i\sum_{n=1}^{\infty}b_{in}\sin\left(2n\pi\left(f^\alpha+\right.\right.$$

$$\left.\left.+f^\beta\right)\right)\Big/\left(1-f^\alpha-f^\beta\right).$$

with:

$$b_{in}=-\left[\left(C_i^\alpha-C_i^\beta\right)\sin\left(2n\pi f^\alpha\right)+\left(C_i^\beta-\right.\right.$$

$$\left.\left.-C_i^\gamma\right)\sin\left(2n\pi\left(f^\alpha+f^\beta\right)\right)\right]\Big/\left(4\pi^3n^3\right)$$

Here, $\left\langle C_i^{m-ph}\right\rangle$ are the averaged solute concentrations in the matrix phase at the eutectic's interface obtained after implementation of the original idea of Jackson and Hunt (JH) [10], and, $Pe_i=\lambda v/D_i$ is the Peclet number (cf. Appendix 1 and Fig. 1 for details). The solution to the transport problem, however, provides only six of the equations required to match the number of equations and unknowns. The missing equations should be, therefore, fetched by the growth kinetics of the constituent phases - α,β,γ and the mass balances of the solute in the eutectic cell.

The growth rate of the TLE's constituent phases: The present research employs a growth kinetics theory [31, 32], which states that the growth of each of the constituent phases from the matrix is governed by a set of non-linear algebraic equations that read [31]:

$$\partial G^{ph}/\partial C_i^{ph}-\left(\partial G^m/\partial C_i^m\right)\left(1-v/v_0^{ph}\right)=0 \tag{3a}$$

$$G^m-G^{ph}+RT\ln\left(1-v/v_0^{ph}\right)+\sum_{i=1}^{2}\left(\partial G^m/\partial C_i^m\right)\left(C_i^{ph}-C_i^m\right)=0$$

$$i\in\{1..2\},\ ph\in\{\alpha,\beta,\gamma\}. \tag{3b}$$

Here: $G^{m(ph)}\left(C_i^{m(ph)},T\right)$ are the Gibbs free energies of the matrix (*m*) and each of the constituent phases (*ph*) (the matrix could be a liquid or a solid phase), *R* is the universal gas constant, $v_0^{ph}=v_0^{Tph}\exp\left(-Q^{m-ph}/RT\right)\exp\left(-G^{ph}/RT\right)=$ $=v_0^{Tph}\exp\left(-{}^*Q^{m-ph}/RT\right)$ is a parameter [31], Q^{m-ph} is the activation energy of the process, ${}^*Q^{m-ph}=Q^{m-ph}+G^{ph}$ is the relative to the G^{ph} activation energy, $v_0^{Tph}=\nu a$ is a preexponential factor, ν is the vibrational frequency ~10^{12} s^{-1}, and *a* is the jump-distance of the matrix solute atoms, commensurable with the lattice constant [11].

The mass conservation equations: The set of equations above should include the equations of mass conservation in the eutectic cell:

$$f^\alpha C_i^\alpha+f^\beta C_i^\beta+\left(1-f^\alpha-f^\beta\right)C_i^\gamma=C_{i\infty}^m\quad i\in\{1,2\}, \tag{4}$$

thus, making the TLEs growth problem closed - the number of unknowns is matched by the number of equations.

Summing up the results so far shows that the equations (2), (3), and (4) form a closed system of

17 nonlinear algebraic equations with (v, f^{α}, f^{β}, $\left\langle C_i^{m-ph}\right\rangle$, C_i^{ph}, Pe_i) as unknowns:

$$f^{\alpha}C_i^{\alpha}+f^{\beta}C_i^{\beta}+\left(1-f^{\alpha}-f^{\beta}\right)C_i^{\gamma}=C_{ie}^{m}$$

$$f^{\alpha}\left\langle C_i^{m-\alpha}\right\rangle+f^{\beta}\left\langle C_i^{m-\beta}\right\rangle+\left(1-f^{\alpha}-f^{\beta}\right)\left\langle C_i^{m-\gamma}\right\rangle=C_{ie}^{m}$$

$$\left\langle C_i^{m-\alpha}\right\rangle-C_{ie}^{m}=Pe_i\sum_{n=1}^{\infty}b_{in}\sin\left(2n\pi f^{\alpha}\right)\Big/f^{\alpha}$$

$$\left\langle C_i^{m-\gamma}\right\rangle-C_{ie}^{m}=-Pe_i\sum_{n=1}^{\infty}b_{in}\sin\left(2n\pi\left(f^{\alpha}+\right.\right.$$

$$\left.\left.+f^{\beta}\right)\right)\Big/\left(1-f^{\alpha}-f^{\beta}\right)\qquad i\in\{1,2\};\ ph\in\{\alpha,\beta,\gamma\}$$

$$\partial G^{ph}/\partial C_i^{ph}-\left(\partial G^{m}/\partial\left\langle C_i^{m-ph}\right\rangle\right)\left(1-v/v_0^{ph}\right)=0$$

$$G^{m}-G^{ph}+RT\ln\left(1-v/v_0^{ph}\right)+$$

$$+\sum_{i=1}^{2}\left(\partial G^{m}/\partial\left\langle C_i^{m-ph}\right\rangle\right)\left(C_i^{ph}-\left\langle C_i^{m-ph}\right\rangle\right)=0\qquad(5)$$

Thence, provided that the material's properties (these are the physicochemical and the thermophysical properties of the involved phases), D_i, and Q^{m-ph} ($^{*}Q^{m-ph}$), together with the parameters, C_{ie}^{m}, and ΔT, are known, the Eqs. (5) could be solved and the 17 unknowns determined explicitly. The width of the eutectic cell, λ, is evaluated as, $\lambda=Pe_iD_i/v$. In this way, Eqs. (5) achieve the first of the objectives set out in the Introduction.

As discussed, there is only one report in the literature (with some reservations expressed by the authors that reported it) on growing a viable TLE. Analysis of the solution obtained allows identifying a specific relationship between the parameters of the TLE and the material properties of the involved phases, D_i, f^{ph}, $\left\langle C_i^{m-ph}\right\rangle$, v_0^{ph}, and C_i^{ph}. Indeed, dividing,

$f^{\alpha}\left(\left\langle C_1^{m-\alpha}\right\rangle-C_{1\infty}^{m}\right)\Big/\sum_{n=1}^{\infty}b_{1n}\sin\left(2n\pi f^{\alpha}\right)=Pe_1$ by

$f^{\alpha}\left(\left\langle C_2^{m-\alpha}\right\rangle-C_{2\infty}^{m}\right)\Big/\sum_{n=1}^{\infty}b_{2n}\sin\left(2n\pi f^{\alpha}\right)=Pe_2$ one

obtains the relation:

$$D_1/D_2=\left[\left(\left\langle C_2^{m-\alpha}\right\rangle-C_{2\infty}^{m}\right)\sum_{n=1}^{\infty}b_{1n}\sin\left(2n\pi f^{\alpha}\right)\right]\Big/\left[\left(\left\langle C_1^{m-\alpha}\right\rangle-\right.\right.$$

$$\left.\left.-C_{1\infty}^{m}\right)\sum_{n=1}^{\infty}b_{2n}\sin\left(2n\pi f^{\alpha}\right)\right]\qquad(6)$$

Bearing in mind that $\left\langle C_i^{m-ph}\right\rangle$ v_0^{ph}, and C_i^{ph} depend implicitly on the phases' physicochemical properties, it is readily understood that successful growth of TLEs could be achieved only if those properties are combined in a strictly defined way. Thence, growing TLE of αβγ-kind is subject to certain restrictions, as reflected by Eq. (6).

Therefore, the following "selection criterion" (SC) is valid: it is impossible to grow (e.g. by steady-state directional solidification) a TLE of the αβγ - kind, if the material's properties of the involved phases do not fulfill the unique combination between these properties, as implied by the relation (6), i.e., $D_1/D_2=\varphi\left(G^{m(ph)},\partial G^{m(ph)}/\partial C_i^{m(ph)},v_0^{ph},T\right)$. Here φ denotes an unknown function made explicit from the solution of the Eqs. (5). As it will be shown presently, condition (6), places very rigorous restrictions on the possibility of producing TLEs, which explains the difficulties encountered by the experimenters in growing those specific types of eutectics.

The considerations above can be extended to lamellar eutectics composed of four (-αβγδ-), five (-αβγδε-), or more phases. Obviously, due to the multitude of material and kinetic parameters that should be matched in a specific way, it could be readily surmised that the chances of growing such complex lamellar eutectics are negligible.

The formulation and the interpretation of the "selection criterion", Eq. (6), achieves the second of the goals set in the Introduction, showing the origin of the difficulties in growing TLEs.

Eqs. (5) are nonlinear and in their present form, they are difficult to solve even numerically [33]. Therefore, it would be highly desirable to simplify (5). For that purpose, one could readily rely on the assumptions made at the beginning of this Section (assumption (4)), which implicitly imply that, $v/v_0^{ph}<<1$, and, $C_i^{ph}\cong C_{ie}^{ph}$ By taking these circumstances into account the nine nonlinear Eqs. (3) are reduced to just three linear algebraic equations, with, ΔC_i^{m-ph} and v, as unknowns (cf. Appendix 2):

$$\sum_{i=1}^{2}\left(\partial G^{m}/\partial C_i^{m}\right)_e\Delta C_i^{m-ph}-RT\,v/v_0^{ph}=\left(S_e^{m}-S_e^{ph}\right)\Delta T\qquad(7)$$

Here, as above, $\Delta C_i^{m-ph}=\left\langle C_i^{m-ph}\right\rangle-C_{ie}^{m}$, and $S_e^{m(h)}$ are the entropies of the involved phases at equilibrium.

Making use of the assumption $C_i^{ph}\cong C_{ie}^{ph}$, the first pair of equations in (5), could be readily rewritten as (Recall that $i\in\{1,2\}$.):

$$f^{\alpha}C_{ie}^{\alpha}+f^{\beta}C_{ie}^{\beta}+\left(1-f^{\alpha}-f^{\beta}\right)C_{ie}^{\gamma}=C_{i\infty}^{m},\qquad(8)$$

which allows for evaluating, f^{α} and f^{β}. Optionally, these, together with, C_{ie}^{ph}, could be taken directly from the ternary phase diagram, if the latter is available in a graphical form.

Bearing in mind that, $f^{\alpha}C_{ie}^{m}+f^{\beta}C_{ie}^{m}+\left(1-f^{\alpha}-f^{\beta}\right)C_{ie}^{m}=C_{ie}^{m}$, after subtracting, C_{ie}^{m}, from the second pair of equations in (5), it is obtained:

$$f^{\alpha}\Delta C_{i}^{m-\alpha}+f^{\beta}\Delta C_{i}^{m-\beta}+\left(1-f^{\alpha}-f^{\beta}\right)\Delta C_{i}^{m-\gamma}=0 \tag{9}$$

Utilizing the values of the parameters, f^{α}, f^{β} and C_{ie}^{ph}, the JH series in (5) are readily evaluated.

From the third and the fourth pairs of the equations in (5) is readily noticed that:

$\Delta C_{i}^{m-\alpha}=-A_{i}\Delta C_{i}^{m-\gamma}/B_{i}$, and $\Delta C_{i}^{m-\alpha}=A_{i}Pe_{i}$.

Here and below the following notations are used for brevity:

$$A_{i}=\sum_{n=1}^{\infty}b_{ien}\sin\left(2n\pi f^{\alpha}\right)\Big/f^{\alpha};$$

$$B_{i}=-\sum_{n=1}^{\infty}b_{ien}\sin\left(2n\pi\left(f^{\alpha}+f^{\beta}\right)\right)\Big/\left(1-f^{\alpha}-f^{\beta}\right).$$

The simplifications carried out transform (5) from a system of 17 nonlinear equations into a system of nine linear equations with ΔC_{i}^{m-ph}, $v_{r}=v/v_{0}^{\alpha}$, and Pe_{i} as unknowns:

$$\begin{gathered}f^{\alpha}\Delta C_{i}^{m-\alpha}+f^{\beta}\Delta C_{i}^{m-\beta}+\left(1-f^{\alpha}-f^{\beta}\right)\Delta C_{i}^{m-\gamma}=0\\ i\in\{1,2\};ph\in\{\alpha,\beta,\gamma\}\\ \Delta C_{i}^{m-\alpha}=-A_{i}\Delta C_{i}^{m-\gamma}/B_{i}\\ \Delta C_{i}^{m-\alpha}=A_{i}Pe_{i}\\ \sum_{i=1}^{2}\left(\partial G^{m}/\partial C_{i}^{m}\right)_{e}\Delta C_{i}^{m-ph}-RTv_{r}\left(v_{0}^{\alpha}/v_{0}^{ph}\right)=\left(S_{e}^{m}-S_{e}^{ph}\right)\Delta T\end{gathered} \tag{10}$$

The set of Eqs. (10) is readily solved numerically [33] or analytically, via, e.g., [34]. The advantage of the analytical solution is that the relationship between, ΔC_{i}^{m-ph}, v_{r}, and Pe_{i}, and the material's parameters of the involved phases becomes apparent.

Replacing $\Delta C_{i}^{m-\alpha}$ with their equals in (6) allows for defining the implicit function, φ, introduced above, respectively, reformulating SC in an explicit form:

In (11), for sake of brevity, were introduced the following notations:

$L_{i}=A_{i}/B_{i}$; $M_{i}=\dfrac{1}{RT}\left(\dfrac{\partial G^{m}}{\partial C_{i}^{m}}\right)_{e}$; $N^{ph}=\dfrac{\left(S_{e}^{m}-S_{e}^{ph}\right)}{RT}\Delta T$

and $K_{i}=\left[f^{\alpha}L_{i}-\left(1-f^{\alpha}-f^{\beta}\right)\right]/f^{\beta}$.

Along with (11), additional conditions apply; for obvious reasons, the cooperative growth rate v_{r}, $v_{0}^{\alpha}/v_{0}^{\beta}$, $v_{0}^{\alpha}/v_{0}^{\gamma}$, and the Peclet numbers, Pe_{i}, should be positive.

The analytical form of the "selection criterion" is now revealed showing the complex interrelation between the material's properties of the involved phases and the diffusion coefficients of the solutes. It should be borne in mind, however, that in contrast with (6), (11) is valid as long as the assumptions made in this section are valid.

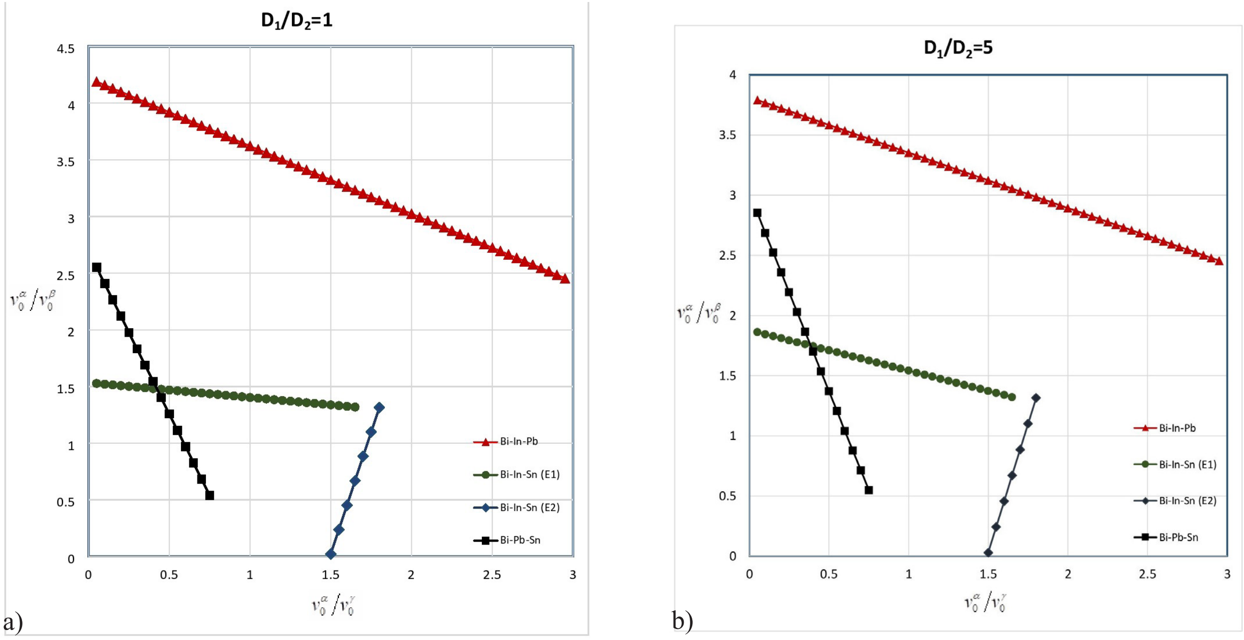
RESULTS AND DISCUSSION

The worked-out set of Eqs. (10), and the "selection criterion" (11), were employed in studying the growth of TLEs in the ternary systems; Bi-In-Pb, Bi-In-Sn, and Bi-Pb-Sn [35 - 42]. The data used in the calculations are listed in Table 1 (regarding the thermodynamic data of the phases, the reader is referred to the cited sources). Solving the governing Eqs. (10) and applying the "selection criterion", allowed determining (for fixed undercooling) the dependencies between the material's parameters that would allow producing of viable TLEs in the studied ternary systems; cf. the plots in Fig. 2a - c (D_{1}/D_{2}, vs. $v_{0}^{\alpha}/v_{0}^{\beta}$ and $v_{0}^{\alpha}/v_{0}^{\gamma}$) and Fig. 3 ($v_{0}^{\alpha}/v_{0}^{\beta}$ vs. $v_{0}^{\alpha}/v_{0}^{\gamma}$ and D_{1}/D_{2}).

To imagine how restrictive is the imposed SC, it suffices to note that the plots in Fig. 2(a) – 2(c), are obtained after 4.10^{4} trials. One especially notes the Bi-In-Sn (E2) of which only seven trials fulfilled the SC. Recall that this is the eutectic alloy where TLE has reportedly been identified [26].

Eqs. (10) and (11) allow solving the inverse problem too, that is, using the experimental results of TLE growth to obtain the values of certain material's parameters. For instance, the unknown kinetic parameter - ${}^{*}Q^{m-ph}$ (Q^{m-ph}). It should be noted that the results below would be meaningful only if Bottin-Rousseau et al. [26], had indeed identified TLE in their experiments. Assuming their claims are correct, and employing the

$$\frac{D_{1}}{D_{2}}=-\frac{B_{1}}{B_{2}}\frac{M_{1}}{M_{2}}\frac{\left[N^{\alpha}\left(K_{1}/v_{0}^{\gamma}-1/v_{0}^{\beta}\right)+N^{\beta}\left(L_{1}/v_{0}^{\gamma}+1/v_{0}^{\alpha}\right)-N^{\gamma}\left(L_{1}/v_{0}^{\beta}+K_{1}/v_{0}^{\alpha}\right)\right]}{\left[N^{\alpha}\left(K_{2}/v_{0}^{\gamma}-1/v_{0}^{\beta}\right)+N^{\beta}\left(L_{2}/v_{0}^{\gamma}+1/v_{0}^{\alpha}\right)-N^{\gamma}\left(L_{2}/v_{0}^{\beta}+K_{2}/v_{0}^{\alpha}\right)\right]} \tag{11}$$



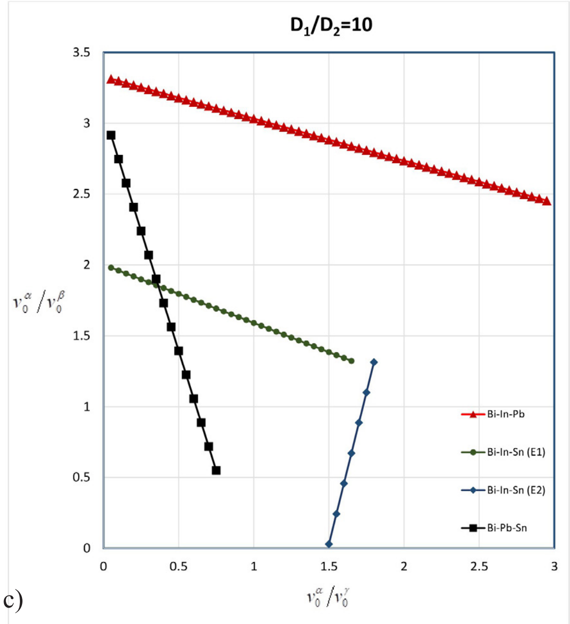


Fig. 2. Graphs illustrating the effect of the “selection condition” at different ratios of, v_0^α/v_0^β, v_0^α/v_0^γ, and D_1/D_2 (Fig. 2a; D_1/D_2 = 1, Fig. 2b; D_1/D_2 = 5, and Fig. 2c; D_1/D_2 = 10). Viable TLEs are produced only of those phases, which v_0^α/v_0^β, v_0^α/v_0^γ, and D_1/D_2 obey the dependencies shown in the graphs. Notice the differences in the regions of compatibility between the phase systems studied. All calculations were carried out at ΔT = -5 K. Under the general notations, α, β and γ are meant the phases specific to each of the studied systems (e.g., for the Bi-Pb-Sn system, β on the graph should be replaced with ε, etc., see Table 1).

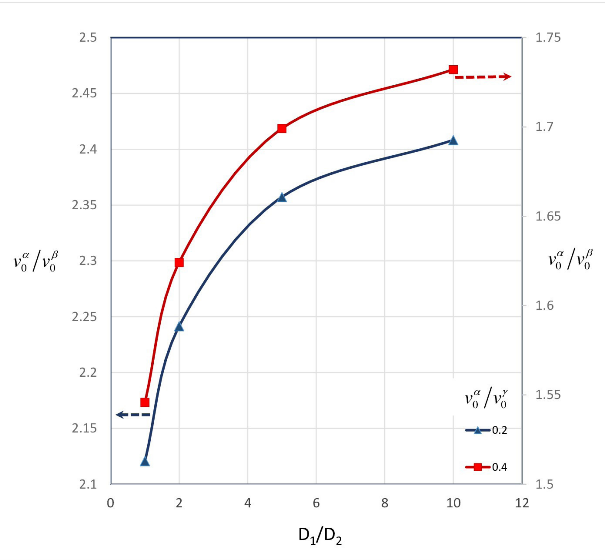


Fig. 3. Plots of v_0^α/v_0^β vs D_1/D_2 (the phase system Bi-Pb-Sn) showing D_1/D_2 vs v_0^α/v_0^β (v_0^α/v_0^γ = 0.2 and v_0^α/v_0^γ = 0.4, ΔT = -5 K).

results of Rex et al. for the growth rates of the phases (Bi), In$_2$Bi, and (Sn) [24, 25], allows for the $^*Q^{m-ph}$ evaluation. Bearing in mind the definition of v_0^α; $v_0^\alpha = v_0^{T\alpha}\exp\left(-{}^*Q^{m-\alpha}/RT\right)$, it is readily shown that:

$$^*Q^{m-\alpha} = -RT\ln\left[v/\left(v_0^{T\alpha}v_r\right)\right] \tag{12}$$

At $\Delta T = -0.3\,K$, $D_{Bi}/D_{Sn} \cong 2.75$, the measured growth rate of the eutectic colony was v=0.3 μm s^{-1} (cf. Rex et al. [24]). Feeding, that data into equations (10) and

Table 1. Selected data of the studied eutectics used in the calculations; the eutectic reactions, the eutectic's temperature T_e, compositions of the matrix and the constituent phases at T_e, and the sources of the thermodynamical data (The nomenclature of the phases is that used in the referenced papers.).

Eutectic Reaction	Eutectic temperature and composition of the constituent phases									References
System Bi-In-Sn										
	T_e [K]	C_{Bi}^{L}	C_{Sn}^{L}	$C_{Bi}^{(Sn)}$	$C_{Sn}^{(Sn)}$	C_{Bi}^{BiIn}	C_{Sn}^{BiIn}	$C_{Bi}^{(Bi)}$	$C_{Sn}^{(Bi)}$	
L→(Sn)+BiIn+(Bi)	350.0	0.394	0.245	0.267	0.509	0.5	0.	1.0	0.	[36,38-42]
	T_e [K]	C_{Bi}^{L}	C_{Sn}^{L}	C_{Bi}^{β}	C_{Sn}^{β}	C_{Bi}^{γ}	C_{Sn}^{γ}	$C_{Bi}^{BiIn_2}$	$C_{Sn}^{BiIn_2}$	
L→β+γ+$BiIn_2$	332.0	0.213	0.179	0.103	0.225	0.187	0.389	0.333	0.	[36,38-42]
System Bi-In-Pb										
	T_e [K]	C_{Bi}^{L}	C_{Pb}^{L}	$C_{Bi}^{(Bi)}$	$C_{Pb}^{(Bi)}$	C_{Bi}^{hcp-A3}	C_{Pb}^{hcp-A3}	C_{Bi}^{BiIn}	C_{Pb}^{BiIn}	
L→ (Bi)+hcp-A3+BiIn	346.02	0.491	0.240	1.0	0	0.33	0.570	0.5	0.	[35,41]
	T_e [K]	C_{Bi}^{L}	C_{Pb}^{L}	$C_{Bi}^{(Pb)}$	$C_{Pb}^{(Pb)}$	$C_{Bi}^{BiIn_2}$	$C_{Pb}^{BiIn_2}$	$C_{Bi}^{Bi_3In_5}$	$C_{Pb}^{Bi_3In_5}$	
L→ (Pb)+$BiIn_2$+Bi_3ln_5	341.82	0.32	0.103	0.	1.0	0.333	0.	0.375	0.	[35,41]
System Bi-Pb-Sn										
	T_e [K]	C_{Bi}^{L}	C_{Sn}^{L}	C_{Bi}^{β}	C_{Sn}^{β}	C_{Bi}^{ε}	C_{Sn}^{ε}	$C_{Bi}^{(Bi)}$	$C_{Sn}^{(Bi)}$	
L→β+ε+(Bi)	373.0	0.452	0.271	0.201	0.796	0.380	0.131	1.0	0.	[37]

(11) it is obtained: v_r=1.15 10^{-3} ($v_r = v/v_0^{\beta}$), v_0^{β}/v_0^{γ} = 0.0268 and $v_0^{\beta}/v_0^{In_2Bi} = 1.49$. The average lattice constant of the involved phases is ~3 Å, hence, the $v_0^{T(\beta)}$ would-be $v_0^{T(\beta)} \approx 300$ ms^{-1}. Utilizing Eq. (12) for the kinetic parameter ${}^{*}Q^{L-\beta}$ is readily obtained, ~38.5 kJ $mole^{-1}$. The corresponding values of the other two phases are then; ${}^{*}Q^{L-\gamma}$ ~28.5 kJ $mole^{-1}$ and ${}^{*}Q^{L-In_2Bi}$ ~39.6 kJ $mole^{-1}$, respectively, $Q^{L-\beta} = 58.7$ kJ $mole^{-1}$, $Q^{L-\gamma} = 48.4$ kJ $mole^{-1}$, and $Q^{L-In_2Bi} = 60.6$ kJ $mole^{-1}$. Using the calculated Pe_{Bi} = 0.0258 (this is our $i = 1$) and taking into account that at T_e, $D_{Bi} \cong 2.464$ 10^{-10} m^2s^{-1} [43 - 45] the width of the would-be eutectic cell is readily predicted; λ ≈ 21.19 µm.

The research here will be incomplete without a discussion on some topics, closely related to the results obtained and to the growth of ternary eutectics in general.

(i) On the mechanism of growth of the TLE's constituent phases: The differences in the values of the activation energies, Q^{m-ph}, suggest that the build-in of the solute atoms into the growing (α, β, γ)- phases of the eutectic is not a single-step process. If the opposite was true all these should have had matching or commensurable values. From those results, it could be inferred that the atoms of the solute, after reaching the matrix-phases interface, are first adsorbed on it and subsequently diffuse in the interface plane until building into the growing phases. The results, therefore, agree with the well-accepted mechanism of crystal growth at low undercooling [3, 11]. The values of, Q^{m-ph}-s, are thus the weighted average of the activation energies of the two processes above.

(ii) Invariant relationships between λ, v, and ΔT: The analytical solution of (10) yields for λ and *v*:

$$v = -\frac{\left[N^{\alpha}\left(K_2 - K_1\right) + N^{\beta}\left(L_2 - L_1\right) + N^{\gamma}\left(L_1K_2 - L_2K_1\right)\right]}{\left[K_2\left(L_1/v_0^{\gamma} + 1/v_0^{\alpha}\right) + \left(L_2 - L_1\right)/v_0^{\beta} - K_1\left(L_2/v_0^{\gamma} + 1/v_0^{\alpha}\right)\right]} = I_v \Delta T \tag{13a}$$

$$\lambda v = \frac{D_1}{M_1 B_1} \frac{\left[N^{\alpha}\left(K_2/v_0^{\gamma} - 1/v_0^{\beta}\right) + N^{\beta}\left(L_2/v_0^{\gamma} + 1/v_0^{\alpha}\right) - N^{\gamma}\left(L_2/v_0^{\beta} + K_2/v_0^{\alpha}\right)\right]}{\left[\left(K_2 - K_1\right)/v_0^{\alpha} + \left(L_2 - L_1\right)/v_0^{\beta} + \left(L_1K_2 - L_2K_1\right)/v_0^{\gamma}\right]} = D_1 I_{\lambda} \Delta T \tag{13b}$$

In Eqs. (13), it is accounted for that near the equilibrium eutectic point $N^{ph} = I_0^{m-ph}\Delta T$, with I_0^{m-ph} , I_v and I_λ as material's constants. By dividing, or multiplying, the expressions in (13) the following invariant relations between λ and *v*, and the applied undercooling, ΔT are obtained:

$\lambda v/\Delta T = D_1 I_\lambda$ (14a), $v/\Delta T = I_v$ (14b), and
$\lambda/D_i = \left(I_\lambda/I_v\right)_i$ (14c). (14)

Remind, that these results are valid within the assumptions and simplifications made to obtain (10), i.e., relatively low undercooling and flat interface between the matrix and the eutectic's constituent phases (Recall that the contribution of the surface tension is neglected). The identity (14a) accounts for the solutal undercooling, ΔT_s, and is identical to that obtained by many authors who studied binary eutectics [1 - 10]. In this research, however, the interrelation between I_λ, and the material's parameters of the involved phases, is made explicit. Rearranging the members in (14a) and introducing a new parameter, $\omega_i \approx D_i/\lambda$ (ms^{-1}) - the rate of solute transport of the *i*th component in the TLE cell, one obtains, $v/\left(D_i/\lambda\right) = v/\omega_i = I_\lambda \Delta T$, which is interpreted as; a stable growth of a TLE would be achieved only then when the rates of TLE growth and solute transport within the eutectic cell, are commensurable. Notice the dependence of this interrelation on undercooling. In a sense, this is the principle on which the "selection criterion" is based. The identity (14b) indicates that the growth rate is proportional to the applied undercooling, which follows from the growth rate model employed [31], see Appendix 2. The identity (14c) could be interpreted as; the larger the diffusion coefficients the wider the eutectic cell. The practical significance of this identity lies in the ability, albeit limited, to control, via the diffusion coefficients, the TLEs (interlamellar spacing).

(iii) The λv^2 relationship at TLE: It could be shown that this relationship applies also to TLE. Indeed, Eq.14a predicts that the solutal undercooling at TLEs is, $\Delta T_s = \lambda v/\left(DI_\lambda\right)$, i.e., it is identical to that in binary eutectics. By reiterating the procedure described elsewhere [10], namely, adding a capillary undercooling term, $\Delta T_c = \Gamma/\lambda$, to ΔT_s and minimizing the as-obtained total undercooling $\Delta T = \Delta T_c + \Delta T_s$, it is readily obtained, $\lambda v^2 = \Gamma D I_\lambda$. Here G denotes the averaged Gibbs-Thomson coefficient, see e.g. [5], at the melt-solid interface. (Recall that Γ is proportional to the surface tension at the matrix - (α, β, γ)-interface.) Thence, by accounting for the surface tension a relationship, identical to that for binary eutectics, $\lambda v^2 = const.$, is obtained. In the past, the $\lambda v^2 = const.$ relationship was utilized to evaluate the growth rate of the eutectic colony [1 - 10, 47]. In the present approach, the growth rate results in directly from the solution of Eqs. (5), or Eqs. (10) (Eq. 13a) and is not of crucial importance as it is in the cited above papers. Nevertheless, it is remarkable that these two different approaches led to a similar result despite the different ways of treatment of the problem. The influence of capillary undercooling, ΔT_c, on the growth rate has been estimated before and found to be negligible [1 - 10]. Hence, the decision to neglect its influence on TLE growth in the present research. An estimate for the specific case studied here (Bi-In-Sn) yields, $\Delta T_c \cong 3.510^{-3}$ K (G$_{Bi\text{-}In}$ = 8.4±0.4 10^{-8} Km [49], λ ≈ 21.19 μm, which is ~ 1 % of the undercooling that is usually applied in the practice, e.g., as in [25] - $\Delta T = 0.3$ K.

(iv) On the dependence of the phases' compositions on the applied undercooling: When dealing with binary lamellar eutectics, a very convenient and widely used way of evaluating $\Delta C_i^{m(ph)}\left(\Delta T\right)$ is applied; One draws a tangent to the solvus (liquidus) line of the equilibrium phase diagram and the desired $\Delta C_i^{m(ph)}$ is evaluated by the slope, k, of the tangent; $\Delta C_i^{m(ph)} = k\Delta T$. This method, without proof of its correctness, is sometimes extended in the evaluation of the compositions of the undercooled phases in ternary eutectics. The reckonings below show that the method applies only to binary systems. Consider first a binary system in equilibrium. By varying the Gibbs equations, expressed via the chemical potentials of the components in the phases, μ_i^m and μ_i^{ph} [3, 48 - 50] and dividing the obtained results by the temperature variation, d*T*, yields a system of two equations:

$$\left(\frac{\partial \mu_1^m}{\partial C_1^m}\right)_e \frac{\delta C_1^m}{\delta T} - \left(\frac{\partial \mu_1^{ph}}{\partial C_1^{ph}}\right)_e \frac{\delta C_1^{ph}}{\delta T} = \left(\frac{\partial \mu_1^{ph}}{\partial T}\right)_e - \left(\frac{\partial \mu_1^m}{\partial T}\right)_e$$

$$\left(\frac{\partial \mu_2^m}{\partial C_1^m}\right)_e \frac{\delta C_1^m}{\delta T} - \left(\frac{\partial \mu_2^{ph}}{\partial C_1^{ph}}\right)_e \frac{\delta C_1^{ph}}{\delta T} = \left(\frac{\partial \mu_2^{ph}}{\partial T}\right)_e - \left(\frac{\partial \mu_2^m}{\partial T}\right)_e$$

with the slopes -$\delta C_1^m/\delta T$ and $\delta C_1^{ph}/\delta T$, as unknowns. Since the number of unknowns matches that of the equations the problem has a unique solution. This is not the case when two phases (*m* and *ph*) are in equilibrium in a three-component system. Applying the same approach, as above, one readily notices that the equations are less than the number of unknowns, $\delta C_i^m / \delta T$ and $\delta C_i^{ph} / \delta T$ ($i \in \{1,2\}$):

$$\begin{aligned}
&\left(\frac{\partial \mu_1^m}{\partial C_1^m}\right)_e \frac{\delta C_1^m}{\delta T} + \left(\frac{\partial \mu_1^m}{\partial C_2^m}\right)_e \frac{\delta C_2^m}{\delta T} - \left(\frac{\partial \mu_1^{ph}}{\partial C_1^{ph}}\right)_e \frac{\delta C_1^{ph}}{\delta T} - \left(\frac{\partial \mu_1^{ph}}{\partial C_2^{ph}}\right)_e \frac{\delta C_2^{ph}}{\delta T} = \left(\frac{\partial \mu_1^{ph}}{\partial T}\right)_e - \left(\frac{\partial \mu_1^m}{\partial T}\right)_e \\
&\left(\frac{\partial \mu_2^m}{\partial C_1^m}\right)_e \frac{\delta C_1^m}{\delta T} + \left(\frac{\partial \mu_2^m}{\partial C_2^m}\right)_e \frac{\delta C_2^m}{\delta T} - \left(\frac{\partial \mu_2^{ph}}{\partial C_1^{ph}}\right)_e \frac{\delta C_1^{ph}}{\delta T} - \left(\frac{\partial \mu_2^{ph}}{\partial C_2^{ph}}\right)_e \frac{\delta C_2^{ph}}{\delta T} = \left(\frac{\partial \mu_2^{ph}}{\partial T}\right)_e - \left(\frac{\partial \mu_2^m}{\partial T}\right)_e \\
&\left(\frac{\partial \mu_3^m}{\partial C_1^m}\right)_e \frac{\delta C_1^m}{\delta T} + \left(\frac{\partial \mu_3^m}{\partial C_2^m}\right)_e \frac{\delta C_2^m}{\delta T} - \left(\frac{\partial \mu_3^{ph}}{\partial C_1^{ph}}\right)_e \frac{\delta C_1^{ph}}{\delta T} - \left(\frac{\partial \mu_3^{ph}}{\partial C_2^{ph}}\right)_e \frac{\delta C_2^{ph}}{\delta T} = \left(\frac{\partial \mu_3^{ph}}{\partial T}\right)_e - \left(\frac{\partial \mu_3^m}{\partial T}\right)_e
\end{aligned}$$

which makes the system above undetermined; one of the $\delta C_i^{m(ph)} / \delta T$ stays unknown. Those considerations are consistent with the Gibbs rule [48 - 50] and prove the statement above; employing the graphical method in evaluating, $\Delta C_i^{m(ph)}(\Delta T)$, is inapplicable when the number of components exceeds 2, i.e., K ≥ 3. That result allows a geometrical interpretation; in a tangent plane to a point of an arbitrary surface, defined in the 3D space (e.g., a tangent plane to the solvus surface in the composition triangle), could be drawn an infinite number of tangent lines passing through this point.

CONCLUSIONS

The production of ternary lamellar eutectics has so far eluded the efforts of experimenters. To clarify the factors behind this inexplicable circumstance, a set of equations governing the growth of TLEs was worked out. The set of equations obtained initially (Eqs. (5)) proved difficult to solve, even numerically, thus making it to some extent impracticable. Making some realistic assumptions reduced those to a set of nine linear equations, respectively, which allowed for obtaining an analytical solution to the TLE's growth problem. It was noticed that not every solution of the as-obtained set of equations is acceptable. Thus, a criterion (termed here "selection criterion") was formulated which determines whether a specific 3-component system could produce viable TLE or not. The criterion states that; it is impossible to grow a TLE if some specific conditions between the transport and kinetic parameters are not fulfilled (Figs. 2 and 3). The results obtained show that: (i) a viable TLE could be produced when the kinetic parameters, v_0^{ph}, and the diffusion coefficients of the dissolved components are related in a certain way (Eq. 11), (ii) the violation of the "selection criterion" leads to unrealistic, from a physical point of view, values for ν, λ and Pe_i, e.g., negative values of some of these variables. Given that v_0^{ph}-s depend on the material properties of the involved phases (physicochemical as well as thermophysical), the difficulties encountered by experimenters in the growth of viable TLEs are readily explained; the violation of the 'selection criterion' makes growing specific TLEs impossible.

Applying the worked-out equations to published in the literature experimental data of the Bi-In-Sn ternary system, it was possible to estimate some important kinetic parameters that control the growth rate from the melt of specific phases in this system. Some topics closely related to the growth of eutectics are also discussed and relevant conclusions are drawn.

Appendix 1

Obtaining an analytical solution of (1): Introducing a new set of dimensionless variables; $X_i^m = C_i^m - C_{i\infty}^m$ $X_i^{ph} = C_i^{ph} - C_{i\infty}^m$, $\xi = x/\lambda$, $\eta = z/\lambda$, and $Pe_i = \lambda v / D_i$ (the Peclet number), transforms (1) and the boundary conditions to:

$$\frac{\partial^2 X_i^m}{\partial \xi^2} + \frac{\partial^2 X_i^m}{\partial \zeta^2} + Pe_i \frac{\partial X_i^m}{\partial \zeta} = 0 \tag{A1.1}$$

$$X_i^m(\xi, \infty) = 0 \tag{A1.1a}$$

$$X_i^m(0, \zeta) = X_i^m(1, \zeta) \tag{A1.1b}$$

$$\partial X_i^m / \partial \xi \big|_{\xi=0} = \partial X_i^m / \partial \xi \big|_{\xi=1} \tag{A1.1c}$$

$$\partial X_i^m / \partial \zeta \big|_{\zeta=0} = -Pe_i \left(X_i^m(\xi,0) - X_i^{ph}(\xi,0) \right) \tag{A1.1d}$$

and

$$X_i^{ph} = \begin{cases} X_i^{\alpha}, & \xi \in \left\{0,\ f^{\alpha}\right\} \\ X_i^{\beta}, & \xi \in \left\{f^{\alpha},\ f^{\alpha} + f^{\beta}\right\} \\ X_i^{\gamma}, & \xi \in \left\{f^{\alpha} + f^{\beta},\ 1\right\} \end{cases} \tag{A1.1e}$$

Eqs. A1.1 and the boundary conditions allow an analytical solution. The division of variables [10, 29, 30] in (A1.1) and accounting for (A1.1a) yields:

$$X_i^m\left(\xi,\zeta\right) = \left(Ae^{\mathrm{i}p\xi} + Be^{-\mathrm{i}p\xi}\right)\exp\left(-\left(Pe_i + \sqrt{Pe_i^2 + 4p^2}\right)\zeta\Big/2\right) \tag{A1.2}$$

The unknown parameters *p*, *A*, and *B* are evaluated by substituting in Eqs (A1.2) the boundary conditions (A1.1b - c) which yielded:

$$\begin{aligned} &A\left(1 - e^{\mathrm{i}p}\right) + B\left(1 - e^{\mathrm{i}p}\right) = 0 \\ &A\left(1 - e^{\mathrm{i}p}\right) - B\left(1 - e^{-\mathrm{i}p}\right) = 0 \end{aligned} \tag{A1.3}$$

A nontrivial solution of (A1.3) requires the determinant, $\Delta\left(p\right) = \begin{vmatrix} 1 - e^{\mathrm{i}p} & 1 - e^{-\mathrm{i}p} \\ 1 - e^{\mathrm{i}p} & -\left(1 - e^{-\mathrm{i}p}\right) \end{vmatrix}$, to be equal to zero [28].

Resolving $\Delta\left(p\right) = 0$ yields, $\left(e^{\mathrm{i}p} + e^{-\mathrm{i}p}\right)/2 = \cos\left(p\right) = 1$ whence, $p_n = 2\pi n\,;\, n \in \left\{0..\infty\right\}$,and $A/B = -\left(1 - e^{-\mathrm{i}p}\right)/\left(1 - e^{\mathrm{i}p}\right)$ Substitution of *p*, in the preceding relation leads to an indefinite form, $\left(0/0\right)$ which after resolving yields, $A/B = 1$, or $A = B$. Thence, taking into account that every p_n yields a valid solution of (A1.1) it is obtained:

$$X_i^m\left(\xi,\zeta\right) = \sum_{n=0}^{\infty} A_{in}\left(e^{2\pi \mathrm{i}n\xi} + e^{-2\pi \mathrm{i}n\xi}\right)e^{-\frac{Pe_i + \sqrt{Pe_i^2 + 16\pi^2 n^2}}{2}\zeta} = \\ = \sum_{n=0}^{\infty} a_{in}\cos\left(2\pi n\xi\right)e^{-\frac{Pe_i + \sqrt{Pe_i^2 + 16\pi^2 n^2}}{2}\zeta} \tag{A1.4}$$

Expanding the boundary condition (A1.1e) in the Fourier series [28] and following the standard procedure of solving second-order partial differential equations allows the evaluation of a_{in}:

$$a_{in} = \frac{2\left[\left(X_i^{\alpha} - X_i^{\beta}\right)\sin\left(2n\pi f^{\alpha}\right) + \left(X_i^{\beta} - X_i^{\gamma}\right)\sin\left(2n\pi\left(f^{\alpha} + f^{\beta}\right)\right)\right]}{n\pi\left(1 - \sqrt{1 + 16\pi^2 n^2\, {}^{*}Pe_i^2}\right)}. \\ n \in \left\{1..\infty\right\} \tag{A1.5}$$

Here ${}^{*}Pe_i$ signifies the inverse Peclet number, ${}^{*}Pe_i = 1/Pe_i$. Taking into account that at eutectics' growth $D_i \approx 10^{-9}$ m^{2}s^{-1},$v \approx 10^{-5}$ ms^{-1}, and $\lambda \approx 10^{-6}$ m, for ${}^{*}Pe_i$ is valid, ${}^{*}Pe_i \approx 10^2$, thence, $16\pi^2 n^{2\,*}Pe_i^{\,2} >> 1$.

The denominator of (A1.5), $-1 - \sqrt{1 + 16\pi^2 n^2\, {}^{*}Pe_i^2} \approx -4\pi n\, {}^{*}Pe_i$. Thence:

$$a_{in} = -Pe_i\left[\left(X_i^{\alpha} - X_i^{\beta}\right)\sin\left(2n\pi f^{\alpha}\right) + \left(X_i^{\beta} - \right.\right. \\ \left.\left. - X_i^{\gamma}\right)\sin\left(2n\pi\left(f^{\alpha} + f^{\beta}\right)\right)\right]\Big/2\pi^2 n^2 \tag{A1.6}$$

As shown in Appendix 2, the growth rate of the constituent phases, $v^{ph}\left[X_i^m\left(\xi,0\right), X_i^{ph}\right]$, depends on $X_i^m\left(\xi,0\right)$. Thence, on the interface matrix-(α-β-γ) phases, v^{ph} will vary with, ξ , thus rendering the evaluation of the growth rate, *v*, impossible. Jackson and Hunt [10] proposed an ingenious way of overcoming that problem by averaging the solute concentrations at the matrix-(α,β,γ) interface. Employing their approach and replacing, $\left\langle X_i^{m-ph}\right\rangle$ and X_i^{ph} with their equals for the averaged concentrations on the matrix-(α,β,γ) interfaces $\left\langle C_i^{m-ph}\right\rangle$, is obtained:

$$\left\langle C_i^{m-\alpha}\right\rangle = C_{i\infty}^m + \frac{Pe_i}{f^{\alpha}}\sum_{n=1}^{\infty} b_{in}\sin\left(2n\pi f^{\alpha}\right);\ \left\langle C_i^{m-\gamma}\right\rangle = \\ = C_{i\infty}^m - \frac{Pe_i}{1 - f^{\alpha} - f^{\beta}}\sum_{n=1}^{\infty} b_{in}\sin\left(2n\pi\left(f^{\alpha} + f^{\beta}\right)\right); \\ \left\langle C_i^{m-\beta}\right\rangle = C_{i\infty}^m + \frac{Pe_i}{f^{\beta}}\sum_{n=1}^{\infty} b_{in}\left[\sin\left(2n\pi\left(f^{\alpha} + f^{\beta}\right)\right) - \sin\left(2n\pi f^{\alpha}\right)\right]. \tag{A1.7}$$

where:

$$b_{in} = -\left[\left(C_i^{\alpha} - C_i^{\beta}\right)\sin\left(2n\pi f^{\alpha}\right) + \left(C_i^{\beta} - C_i^{\gamma}\right)\sin\left(2n\pi\left(f^{\alpha} + \right.\right.\right. \\ \left.\left.\left. + f^{\beta}\right)\right)\right]\Big/\left(4\pi^3 n^3\right)$$

Multiplying the equations in (A1.7) by f^{α}, $1 - f^{\alpha} - f^{\beta}$ and f^{β}, respectively, and summing the results, allows for replacing the last of the equations in (A1.7) with the mass balance at the solid-melt interface. Thence, instead of (A1.7) is obtained:

$$f^{\alpha}\left\langle C_i^{m-\alpha}\right\rangle + f^{\beta}\left\langle C_i^{m-\beta}\right\rangle + \left(1 - f^{\alpha} - f^{\beta}\right)\left\langle C_i^{m-\gamma}\right\rangle = C_{ie}^m \\ \left\langle C_i^{m-\alpha}\right\rangle - C_{ie}^m = Pe_i\sum_{n=1}^{\infty} b_{in}\sin\left(2n\pi f^{\alpha}\right)\Big/f^{\alpha} \\ \left\langle C_i^{m-\gamma}\right\rangle - C_{ie}^m = -Pe_i\sum_{n=1}^{\infty} b_{in}\sin\left(2n\pi\left(f^{\alpha} + f^{\beta}\right)\right)\Big/\left(1 - f^{\alpha} - f^{\beta}\right) \tag{A1.8}$$

Appendix 2

Simplifying the set of Eqs. (4): Taking advantage of the fact that the values of $\left\langle C_i^{m-ph}\right\rangle$, C_i^{ph} and *T* are close to those at equilibrium, C_{ie}^{m}, C_{ie}^{ph} and T_e, and that $v/v_0^{ph} << 1$, $\left|C_i^{ph} - C_{ie}^{ph}\right| << 1$ and $\left|C_i^{m} - C_{ie}^{m}\right| << 1$, allows rewriting the Eqs (4a) as:

$$\partial G^{ph} / \partial C_{ie}^{ph} - \partial G^{m} / \partial C_{ie}^{m} = 0 \qquad \text{(A2.1)}$$

Thence, due to the assumption above, these are satisfied identically and drop out from (4).

The inequalities above further allow: (i) expanding the members in (4b) in series, around v/v_0^{ph}, C_{ie}^{m}, C_{ie}^{ph}, and T_e. Keeping only the linear terms of those expansions yields:

$$\ln\left(1 - v/v_0^{ph}\right) \cong -v/v_0^{ph} \ ;$$

$$G^{ph} = G_e^{ph} + \left(\partial G^{ph}/\partial T\right)_e \left(T - T_e\right) = G_e^{ph} - S_e^{ph}\Delta T \ ; \qquad \text{(A2.2a)}$$

$$G^{m} = G_e^{m} + \sum_{i=1}^{2}\left(\frac{\partial G^{m}}{\partial C_i^{m}}\right)_e \left(\left\langle C_i^{m-ph}\right\rangle - C_{ie}^{m}\right) + \left(\frac{\partial G^{m}}{\partial T}\right)_e \left(T - T_e\right) =$$

$$= G_e^{m} + \sum_{i=1}^{2}\left(\frac{\partial G^{m}}{\partial C_i^{m}}\right)_e \Delta C_i^{m-ph} - S_e^{m}\Delta T \ ; \qquad \text{(A2.2b)}$$

(ii) replacing, $\sum_{i=1}^{2}\left(\partial G^{m}/\partial C_i^{m}\right)\left(C_i^{ph} - C_i^{m}\right)$ with

$$\sum_{i=1}^{2}\left(\partial G^{m}/\partial C_{ie}^{m}\right)\left(C_{ie}^{ph} - C_{ie}^{m}\right). \qquad \text{(A2.2c)}$$

Substituting (A2) into (4b) and taking advantage of the fact that at equilibrium,

$$G_e^{m} - G_e^{ph} + \sum_{i=1}^{2}\left(\partial G^{m}/\partial C_{ie}^{m}\right)\left(C_{ie}^{ph} - C_{ie}^{m}\right) = 0 \text{,allows}$$

rewriting (4b) into:

$$\sum_{i=1}^{2}\left(\partial G^{m}/\partial C_i^{m}\right)_e \Delta C_i^{m-ph} - RT\, v/v_0^{ph} = \left(S_e^{m} - S_e^{ph}\right)\Delta T \ ,$$

here as above $i \in \{1..2\}$, $ph \in \{\alpha, \beta, \gamma\}$.

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