



COMPETITIVE GROWTH AND COUPLET GROWTH ZONE IN EUTECTIC ALLOYS IN DIRECTIONAL SOLIDIFICATION

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Abstract

Although significant studies on eutectic systems have been carried out in the past, some critical fundamental questions still remain unanswered. The following several critical aspects of coupled growth are being examined in this study: (a) the influence of interface energy and its anisotropy on the lamellar to rod transition; (b) the ability to form coupled (or cooperative) growth of the two phases in eutectic systems; (c) the stability of eutectic structure under rapid solidification conditions.

Keywords: eutectic, kinetics, solidification, competitive growth, couplet zone

1. Introduction

Basic concepts of the theory of eutectic alloys are a small but theoretically and practically important part of the science of metals. In accordance with the old and universally accepted ideas the components of eutectic systems, which are almost insoluble (in many systems) in solid state, are infinitely miscible in the liquid state, i.e., at a temperature above the liquidus line on the phase diagram alloys are treated as liquid solutions of components. When cooled to the eutectic temperature T_e , a solution becomes supersaturated with both components; its crystallization occurs by diffusion decomposition into a mixture of crystals of almost pure components (solid solutions on their base, i.e., α and β). Eutectic equilibrium is described as $L = \alpha + \beta$.

In a melt of eutectic components, which is represented by double-phase dispersion, the dispersed particles and the dispersion medium form a solvate complex with eutectic composition, which is preserved in crystallization. This composition corresponds to a specific (for the given dispersion) proportion of components at which the entire dispersion medium is in a bound state (as a result of salvation) of interatomic interaction with the force field of the dispersed particles. The eutectic solvate complex crystallizes and melts completely at a constant temperature the lowest for the given dispersion [1].

2. The kinetics of eutectic solidification

The concepts of the mechanism of eutectic crystallization, of the structure and formation of main units of the macroscopic structure of a casting (ingot), i.e., eutectic grains (macrograins), have changed substantially from the beginning of the study of the topic. At first, a eutectic structure was often treated as a mechanical mixture of fine crystals not connected with each other.

Such a eutectic grows due to alternate nucleation and growth of crystals of both eutectic phases. This approach makes the search for any structural component (eutectic grain) other than fine crystals of eutectic phases in a casting senseless [2].

The linear rate of growth of the eutectic is specified by the expression $V_E = K_{VE} (\Delta T)^2$, where K_{VE} is a constant for the given alloy. This expression is a result of the solution of the two-dimensional problem on the distribution of the dissolved component in the melt in front of the double-phase crystallization front of the eutectic. It should be noted that strictly speaking, its use is not justified for growth stages accompanied by variation of the temperature. Such variation of the temperature is observed in the initial stage of formation of eutectic grains and during hardening of the last portions of the melt. However, the duration of these processes is very short relative to the duration of the EC as a whole, which allows us to use this expression [2,3].

Kinetics of eutectic transformation leads to additional deviation from equilibrium, because melting of extremely non-uniform eutectic system requires mass transfer of eutectic components through liquid phase. Atoms of eutectic alloy are transferred for distances comparable to structural parameters of solid eutectic. That is many times as much as for melting transition in pure metal where only minimal displacements of atoms from crystal lattice nodes are required [4].

The mentioned difference in the crystallization of alloys with nearly eutectic concentration and primary crystals belonging and not belonging to the base phase is representable by the diagram given in Fig. 1a. When the second phase of the eutectic nucleates on a primary crystal of the base phase, it rapidly covers the entire surface of the primary crystal; the independent growth of the primary crystal stops, and the EC begins. Geometrically this situation is describable by a ring model (Fig. 1a). When the first crystal does not belong to the base phase, its growth does not stop

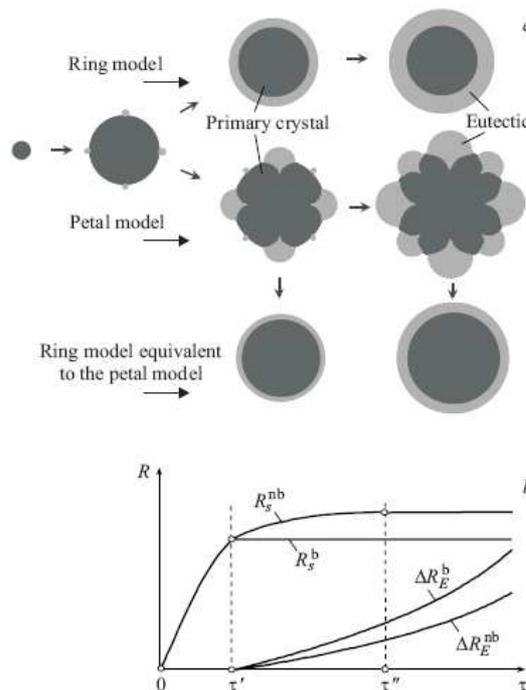


Fig. 1. Ring and petal models of eutectic crystallization (a) and difference in the kinetics of their growth (b): τ' and τ'' are moments of nucleation of second phase on the surface of the first phase and of enclosure of the surface of the primary crystal by eutectic, respectively; R_s^b and R_s^{nb} are radii of primary crystals of the base and nonbase phases; ΔR_E^b and ΔR_E^{nb} are thicknesses of eutectic shells on primary crystals of the base and nonbase phases [2]

upon the nucleation (inoculation) of crystals of the second phase. The primary crystal continues to grow until the eutectic grains, the linear rate of growth of which exceeds that of the primary

crystal, close around it. This kind of structure is known as a petal one. Since the mapping of a petal model is difficult to obtain, we use an equivalent model for geometric representation. The difference in the growth kinetics of the ring and petal models is shown in Fig. 1b [2].

3. Competitive growth of different phases in eutectic alloys

A competitive growth mechanism of eutectic has been suggested by Tammann and Botschwar [5] from a study of formation ability of eutectic structures. That is to say, the microstructure of alloys near the eutectic point is determined by competition between the eutectic structure and the primary phase. Only when the growth of phases takes precedence over that the primary phase, the eutectic-like microstructure can be produced. Otherwise, the primary phase is dominant.

In directional solidification, the interface growth temperature of the primary phase at different growth rates can be described by [6]:

$$T_j^i = T_L^i - \frac{G_L D_L}{V} - A_j V^{1/2}, \quad j = \alpha, \beta \quad (1)$$

where:

T_L^i - the liquidus temperature at the alloy composition C_o ,

V - the growth rate,

G_L and D_L - the temperature gradient and diffusion coefficient in liquid, respectively.

The parameter A_j in eq. (1) is given as:

$$A_j = \left[-\frac{8\Gamma_j m_j C_o (1-k_j)}{D_L} \right]^{1/2}, \quad j = \alpha, \beta \quad (2)$$

where:

Γ_j , m_j and k_j - Gibbs-Thomson coefficient, slope of j -phase liquidus and solute distribution coefficient, respectively.

For eutectic solidification, the interface growth temperature of coupled eutectic in directional solidification can be calculated using the model described by Magnin and Trivedi [7] as:

$$T_e^i = T_E - (\phi + 1/\phi)(K_1 K_2)^{1/2} V^{1/2} = T_E - B V^{1/2}, \quad (3)$$

where $B = (\phi + 1/\phi)(K_1 K_2)^{1/2}$,

$$K_1 = \frac{\bar{m} C_e^o P}{D_L f_\alpha f_\beta}, \quad (4)$$

$$K_2 = 2\bar{m}\delta \left(\frac{\Gamma_\alpha \sin \theta_\alpha}{|m_\alpha| + m_\beta} + \frac{\Gamma_\beta \sin \theta_\beta}{m_\beta f_\beta} \right), \quad (5)$$

$$\bar{m} = \frac{|m_\alpha| m_\beta}{|m_\alpha| + m_\beta}, \quad (6)$$

$$C_e^o = C_\beta^o - C_\alpha^o. \quad (7)$$

For lamellar eutectic growth, the parameters P and δ can be written in simplified forms as:

$$P \cong 0,3383(f_\alpha f_\beta)^{1,661}, \quad (8)$$

$$\delta = 1. \quad (9)$$

For rod eutectic growth, the parameters P and δ can also be simplified as:

$$P \cong 0,167(f_\alpha f_\beta)^{1,25}, \quad (10)$$

$$\delta = 2\sqrt{f_\alpha}, \quad (11)$$

where:

T_E - the equilibrium solidification temperature of eutectic,

\bar{m} - the average slope of eutectic defined in eq. (4),

f_α, f_β - the volume fractions of α phase and β phase respectively,

C_e^o - the composition difference between the solubility limits of β phase (C_β^o) and α phase (C_α^o) defined in eq. (7) at the eutectic solidification temperature [7].

A methodology of competitive growth outlined above provides an adequate framework to understand the major features of the transition from eutectic to dendritic growth. However more subtle variations in eutectic microstructure occur under conditions close to the transition that require a more complete analysis of interface stability [9].

4. Prediction of eutectic coupled zone

The argument in this respect is whether the thermal undercooling ΔT_t and kinetic undercooling ΔT_k can be omitted when dealing with the lamellar eutectic growth within an undercooled alloy melt. The bulk undercooling ΔT of a liquid alloy is usually divided into four parts [10,11]:

$$\Delta T = \Delta T_c + \Delta T_r + \Delta T_t + \Delta T_k, \quad (12)$$

where:

ΔT_c and ΔT_r - the solute undercooling and curvature undercooling.

So far, there has been no analytical model to specify the thermal undercooling for eutectic growth. If the bulk undercooling is not very large, ΔT_c and ΔT_r play the dominant roles, whereas ΔT_t and ΔT_k only make minor contributions.

This has been confirmed by the experimental work of many investigators. In fact, there exist two undercooling thresholds for the “lamellar eutectic–anomalous eutectic” structural transition

[10]. Below the lower undercooling threshold ΔT_1^* of about 30–60 K, lamellar eutectic is the unique growth morphology. Above the upper undercooling threshold ΔT_2^* of about 150–200 K, only anomalous eutectic can grow. In the intermediate undercooling regime of $\Delta T_1^* - \Delta T_2^*$, both lamellar eutectic and anomalous eutectic coexist. Metallographic analyses demonstrate that anomalous eutectic is the product of rapid solidification during recalescence, while lamellar eutectic forms in the slow period of solidification after recalescence. Because the remnant undercooling at the end of recalescence becomes quite small, lamellar eutectic growth corresponds to the small undercooling condition even within the intermediate undercooling regime.

As a first order approximation, it is reasonable to neglect the influences of thermal undercooling ΔT_t and kinetic undercooling ΔT_k on lamellar eutectic growth. Consequently, eq. (1) leads to the following approximate relation [10,11]:

$$\Delta T \approx \Delta T_c + \Delta T_r \tag{13}$$

5. Coupled growth zone

The couplet growth zone marks the range of the chemical composition, the growth rate and the temperature gradient, which assure the obtainment of the exclusively eutectic structure (without hypoeutectic phase). Way of marking couplet zone on the basis of the theory of the competitive growth was showed on the Fig. 2 [11, 12].

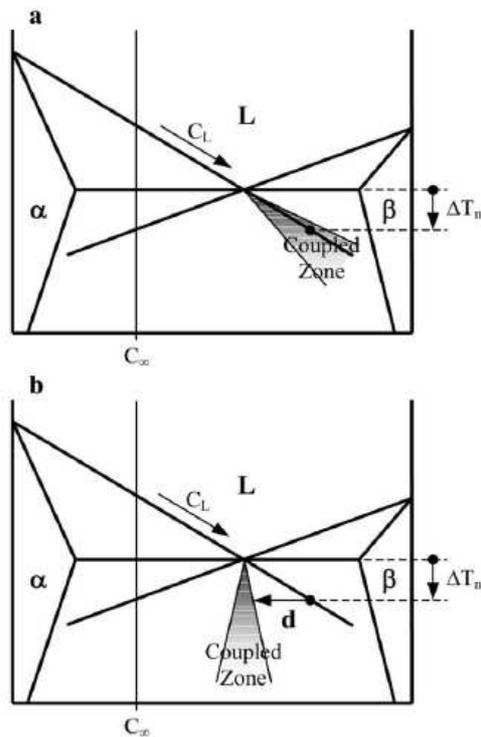


Fig. 2. (a) The coupled zone encompasses the α liquidus extension: coupled eutectic growth occurs directly from the primary α dendrites. (b) The coupled zone does not encompass the α liquidus extension: haloes of β form around the primary α dendrites for any significant β nucleation undercooling ΔT_n [11,13]

Figure 3 is a kind of phase diagram in eutectic systems that the coupled zone encompasses the α liquidus extension. Interface growth temperatures of the single α phase, single β phase and coupled eutectic ($\alpha+\beta$) calculated by eq. (1) and eq. (3) are illustrated schematically as a function of growth rates at a given composition C_o in hypereutectic alloy on the right side of Fig.3.

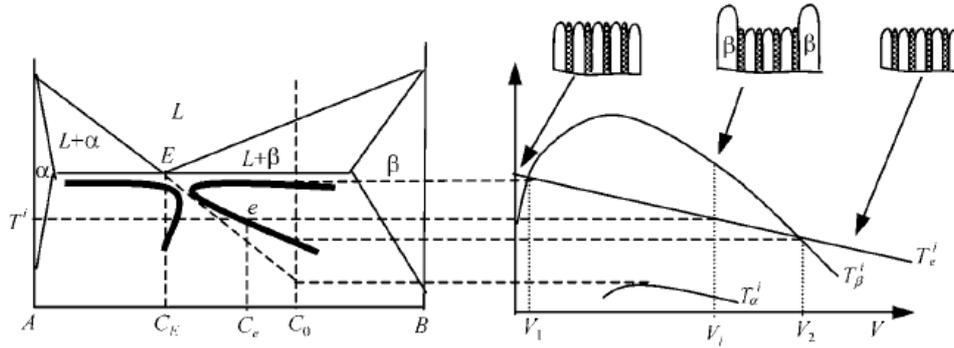


Fig. 3. Coupled zone encompasses the α liquidus extension in eutectic systems and interface growth temperatures of the single α phase, single β phase and coupled eutectic ($\alpha+\beta$) are calculated by eq. (1) and eq. (3) as a function of growth rates at a given composition C_0 in a hypereutectic alloy [8]

Coupled growth zone can be outlined with the same interface growth temperature and composition for the single phase and coupled eutectic. From Fig. 3, at lower growth rate V_1 and higher growth rate V_2 , the interface temperature of the single β phase T_β^i and coupled eutectic T_e^i , are equal at the given composition C_0 . When the imposed growth rate V_i is below V_1 , coupled eutectic ($\alpha+\beta$) becomes stable due to the sharp drop in the single-phase temperature, which contributes to the presence of the positive gradient through the term, $G_L D_L / V$ in eq. (1). Thus for finite G_L , the single-phase interface temperature is given by eq. (1) in which the contribution from the third term on the right hand side is negligible. Eq. (1) and eq. (3) can be simplified at low growth rate V_1 as:

$$T_\beta^i \approx T_L^\beta - \frac{G_L D_L}{V} - A_\beta V^{1/2} \approx T_E + m_\beta (C_0 - C_E) - \frac{G_L D_L}{V}, \quad (14)$$

$$T_e^i = T_E - B V^{1/2} \approx T_E, \quad (15)$$

where:

C_E - the eutectic composition, by equating eqs. (14) and (15), the value of the growth rate V_1 , at which the primary β phase-coupled eutectic ($\alpha+\beta$) transition occurs at low undercoolings can be derived as:

$$V_1 = \frac{G_L D_L}{m_\beta (C_0 - C_E)}. \quad (16)$$

At high growth rate, the term $G_L D_L / V$ in eq. (1) is small and can be neglected. Under this assumption, eq. (14) can be approximated as:

$$T_\beta^i \approx T_L^\beta - \frac{G_L D_L}{V} - A_\beta V^{1/2} \approx T_E + m_\beta (C_0 - C_E) - A_\beta V^{1/2}. \quad (17)$$

Equating eq. (3) and eq. (17), the value of the high growth rate V_2 at which the primary β phase coupled eutectic ($\alpha+\beta$) transition occurs at high undercoolings shown in Fig. 2 can be written as:

$$V_2^{1/2} = \frac{m_\beta(C_0 - C_E)}{A_\beta - B} \quad (18)$$

The right hand side of eq. (18) should be positive and values of A_β and B can be calculated using eq. (2) and eq. (3), respectively. From eq. (16) and eq. (18), with the composition C_0 approaching the eutectic composition C_E , the value of the low growth rate V_1 increases and the value of the high growth rate V_2 decreases. If V_1 is equal to V_2 , the alloy composition C_0 corresponding to coupled eutectic ($\alpha+\beta$) growth at any growth rates can be obtained in directional solidification. Moreover, with the increasing growth rate, coupled eutectic ($\alpha+\beta$) will be refined as shown in Fig. 3. In addition, if the imposed growth rate is very large, it should be noted that the directional heat flux would be destroyed and the solidified microstructure would not be the directionally coupled eutectic and it may be the equiaxed eutectic [8].

6. Discussion and conclusion

The study of eutectic growth characteristic has shown that the shape and size of the eutectic couplet zone is determined by growth features and solidification conditions. For example, to obtain a proper eutectic growth in the eutectic system containing a pair of faceted/non-faceted phases, the growth of non-faceted phase should be suppressed (or promoted), due to the strong growth anisotropy of the faceted phase.

The undercooling range for the coupled eutectic growth enlarges due to the kinetic effect. The kinetic effect is dependent not only on the growth velocity, but also on the type of phase diagram. As the crystallization temperature range of eutectic phases at the eutectic composition decreases, the kinetic effect is enhanced.

The significant difference in linear kinetic coefficient of non-faceted and a faceted phase results in a remarkable difference in kinetic undercooling that plays an important role in influencing the shape of the couplet zone in rapid solidification. To maintain the couplet growth of eutectic phase, the solute undercooling of the faceted phase is weakened in comparison with that of the non-faceted phase by shifting the eutectic composition to the faceted phase side and thus leading to the formation of a skewed locus of eutectic composition in rapid processing. The symmetrical couplet zone with a non-faceted/non-faceted reaction can also be well clarified when their comparable contribution in kinetic undercooling are taken into account.

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