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Doctor of Technical Sciences V. Mazur, Ph.D. A. Mazur
University «National Metallurgical Academy of Ukraine», Dnipropetrovsk, Ukraine

EUTECTICS: GENESIS AND MORPHOLOGY*

The eutectic spatial structure stages in different systems is studied. The eutectic phase crystals continuity inside eutectic grain has been investigated. The eutectic colony micromorphology elements, which are eutectic cells were described. The base phase relief determining role in cells substructure forming was established. The bicrystal grouth mechanism in screw dislocation of base phase crystal was shown for the first time.

Key words: *B. Grain boundaries; B. optical microscopy; eutectic growth.*

Metal, metal-ceramic and ceramic eutectic alloys are the natural composite materials. Their structure is formed during two- or multiphase crystallization. Level of their mechanical, physical and other service properties depends not only on chemical and phase composition, but also on parameters micro- and macrostructures. The phase structure of alloy is determined by type of the phase equilibria diagram of a given system as well as by chemical compound of a concrete alloy. Parameters of micro- and macrostructures are set by a choice of the process equipment and thermo-kinetic characteristics of eutectic crystallization.

Obtaining of regular eutectic structures is often complicated because of formation of the undesirable structural zones, differing by infringement of periodicity of alternation of phases, coarsening of their crystals, occurrence coarse-crystalline structural anomalies as well.

Elimination of undesirable structural anomalies is possible only on the basis of understanding of genesis and physical processes of formation of various types of eutectic structures and structural transitions between them.

Historically structural models of phase transitions were created on the basis of simple geometric or mathematical models which had certain restrictions, but at the same time allowed to count approximately at least some parameters of eutectic crystallization. In the sequel these restrictions and assumptions were forgotten and the given hypothesis already applied for universality.

Meanwhile now well-known, that maintenance of eutectic structure regularity is a multi-factorial problem.

External factors are set by the process equipment and caused by instability of thermal and rate parameters of the unidirectional crystallization.

Internal factors are connected with non-stationarity of structural transients in eutectic alloys and caused by degree of our misunderstanding of physical essence of these processes. Examples of structural transients are the following:

- Nucleation and growth in a parent liquid of primary crystals;
- Nucleation and growth of the second eutectic phase;
- The beginning of couple bi-phase growth;
- Structural transitions with change of micro-morphology (lamellar – rod-like or on the contrary);
- Formation of cellular structure of eutectics, caused by loss of stability of flat front of crystallization;
-Formation of pyramidal structure eutectics on all faces or basic surfaces of a primary crystal.

Each of these transient processes can be supervised under the stipulation that we understand the nature of its occurrence and development and we select adequate technological influence.

Thus detailed research of genesis and morphology of eutectic colonies is actual problem.

Materials and technique

Eutectic type alloys including metal, inter-metallic, ceramic and covalent phases of eutectic genesis served as object of research.

Ingots of experimental alloys have been prepared in resistance furnaces as well as in induction, plasma beam, electron beam and electric arc furnaces.

The structure, phase composition and certain thermodynamic behaviors of eutectic solidification have been studied with light and electron microscopy, XRD, electron probe microanalysis, DTA, DSC.

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As result the new experimental 3D-models of eutectic colonies in different alloys as well as 3D-models of structural transitions during non-stationary processes have been constructed.

Discussion

The first investigations of eutectic microstructure have been carried out in the eighties of nineteenth century by Gutrie, Osmond, Benediks. During more than 100 years four main hypothesis concerning the nature of eutectics have been formed:

1. Eutectics is mechanical mixture of α- and β-particles. It is formed as result of plural re-nucleation, growth and pinch of α- and β- particles on the eutectic solidification front.
2. Eutectics is arisen by α-matrix and dispersed β-particles. It is formed as result of plural re-nucleation, growth and pinch of α-particles at the solidification front of the a-matrix.
3. Eutectics consists of the α-matrix and branchy dendrite of β-phase. It is formed as result of continuous couple growth of two crystals of α- and β-phases.
4. Eutectics is formed by mutually grown branchy dendrites of α- and β-phases.

An appearance of these four hypothesis was given due to complexity of structural pictures of different eutectic alloys as well as attempts of conclude about 3D-structure on the base of single sections of given eutectics.

An ascertainment of adequate structural model is the important task for eutectic technology because it gives possibility to solve what is a way to control the regularity of eutectics:

- technological influence on *the eutectic phases nucleation* (hypothesis 1 and 2) or
- controlling of *thermo-kinetic parameters of growth* (hypothesis 3 and 4).

Therefore 3D modeling of eutectic structure is actual task.

Eutectic equilibrium and microscopic mechanism of eutectic solidification

Eutectic equilibrium in A-B system is established when chemical potential of given atom kind (A or B) in three phases (L, α and β) $\mu^A_L = \mu^A_\alpha = \mu^A_\beta$ and β $\mu^B_L = \mu^B_\alpha = \mu^B_\beta$ (Fig. 1, c).

Whereas thermodynamic motivity of ato-mic diffusion $\Delta\mu = \mu^B_L - \mu^B_\alpha = 0$ and $\Delta\mu = \mu^B_L - \mu^B_\beta = 0$,

diffusion flows in liquid phase are absent and eutectic solidification is impossible.

Therefore these two conceptions (eutectic equilibrium and eutectic solidification) are mutually excluding.

Eutectic solidification starts when the system is taking away of equilibrium for example when liquid phase is undercooled (Fig. 1, d). In accordance with the principles of local thermodynamic equilibrium of thermodynamics of irreversible processes when $T = T_E - \Delta T$, in spite of absence thermodynamic equilibrium in system in tote, local

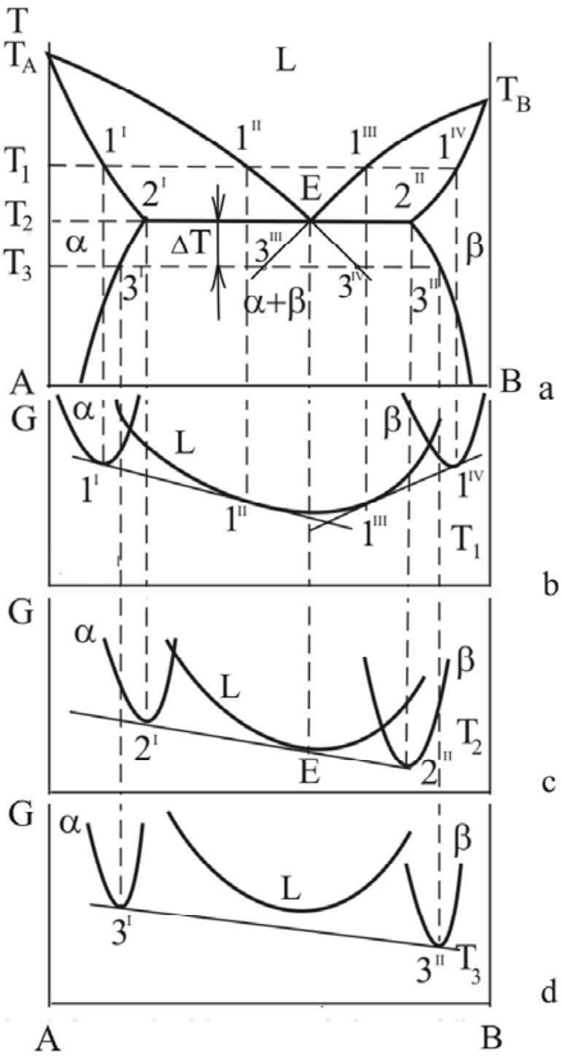


Fig. 1. Eutectic phase equilibrium diagram (a) and Gibbs free energies (b–d)

equilibrium on the interphase boundaries is established. So after nucleation of eutectic phases the local equilibrium concentrations of liquid phase are follows (Fig. 2): c_3^{IV} and c_3^{III} on the boundaries L/α and L/β respectively.

As $c_3^{IV} > c_3^{III}$ (for B atoms) diffusion flow of B atoms originates in liquid phase and it directed from a solidification front to b one. Atoms of A kind move in opposite direction. It is tangential diffusion flow I_t. These flows provides couple (cooperative) growth of eutectic phases.

Normal diffusion flow I_n is stimulated by concentration inequalities $c_3^{IV} > c_E$ and $c_3^{III} < c_E$ where c_E is concentration of the liquid phase far from solidification front.

Diffusion flow of B atoms is directed from outlying liquid to β solidification front. A atoms diffuse from outlying liquid to α solidification front. It provides autonomous growth of eutectic phases.

The degree of cooperativity of eutectic structure is given [1, 2] as $I_t/(I_t+I_n)$.

When ξ=1 cooperative, fine differentiated structure is formed.

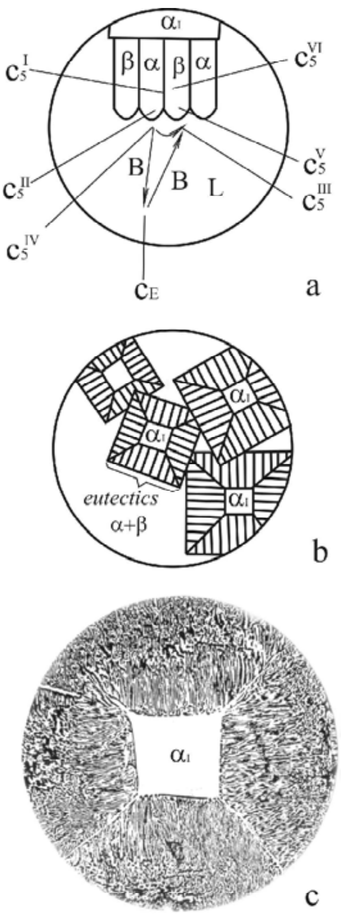


Fig. 2. Diffusion flows in liquid phase during eutectic solidification (a) and eutectic grain formation, b- morphological scheme, c- microstructure. Primary basic crystal is identified as α_1

When ξ=0 coarse conglomeratic structure is resulted.

Controlling of proportion of normal and tangential diffusion flows is important technological problem.

Eutectic solidification proper starts after nucleation of the second eutectic phase on the surface of primary crystal. If given alloy includes eutectic phases with different type of interatomic bonds, as rule the phase of more heterodesmisity of interatomic bonds serves as nucleating. In the pair: metallic solid solution-carbide the last one nucleates the first one.

The relief of primary crystal plays key role in nucleation of the second phase and in further eutectic crystallization. Faceted primary crystals form steps (waves of growth) and terraces on the close packed planes (Fig. 3).

The second eutectic phase is nucleated in cavities between two terraces or near steps of growth waves (Fig. 4).

When slow crystallization is broken by sudden cooling in water it is possible to observe the profile of crystallization front and the initial stages of eutectic transformation (Fig. 5).

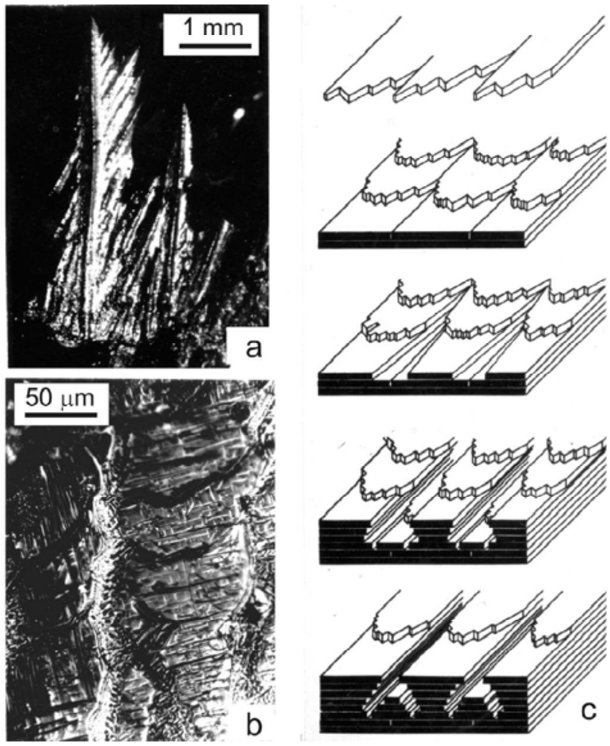


Fig. 3. Relief of primary Fe_3C crystal (a, b) after decantation in eutectic alloy Fe-4.6 % (wt.) C and its formation scheme (c)

Fig. 4. Nucleation and growth the second eutectic γ-Fe phase (austenite) on the terrace of primary Fe_3C crystal

Fine dispersed dark field is quenched liquid phase, white strip is cross section of basic cementite Fe_3C crystal growing left to right in liquid. In the beginning austenite dendrite grows up along free surface of cementite. In result bi-phase grating is formed. Transversal growth of this grating forms the foundation of eutectics. As the primary crystal has the steps on his surface different sites of eutectics have step-like surface of solidification front in transversal direction. A competition between these sites during their growth in the longitudinal direction results to cell formation.

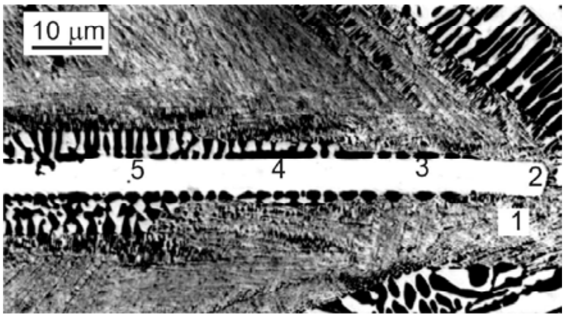


Fig. 5. Transverse cross-section of primary Fe_3C crystal showing the initial stages of eutectic grain growth: 1 – quenched liquid phase; 2 – growth of Fe_3C crystal with free surface; 3 – growth of γ-Fe dendrite branches (dark); 4 – formation of biphasic (γ-Fe + Fe_3C) grating; 5 – transversal growth of (γ-Fe + Fe_3C) eutectics and creation of cellular step on eutectic solidification front

The cellular substructure of (γ-Fe + Fe_3C) eutectics

The analysis of consecutive (001) Fe_3C sections shown an origin of both plate-like and rod-like eutectic structures (Fig. 6).

The sites where austenite forms fine branched dendrite in the future obtain rod-like structure (marked by round).

In the sites, where austenite covers the cementite by continuous layer, the cementite bars grow in [010] Fe_3C direction from adjacent eutectic site. Transversal growth of cementite bars in [001] Fe_3C and austenite plates between them leads to forming of bi-phase plate-like packet.

It is important to note continuity of both eutectic phases during growth of eutectics. Additional nucleation of eutectic phases is absent.

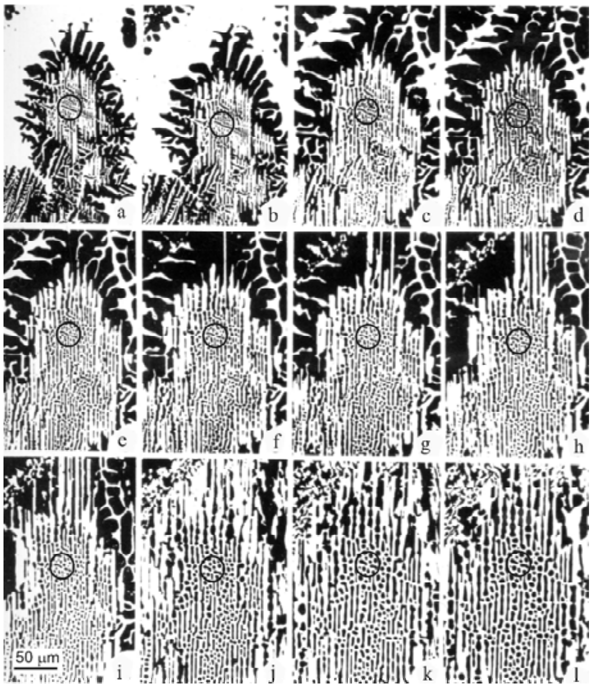
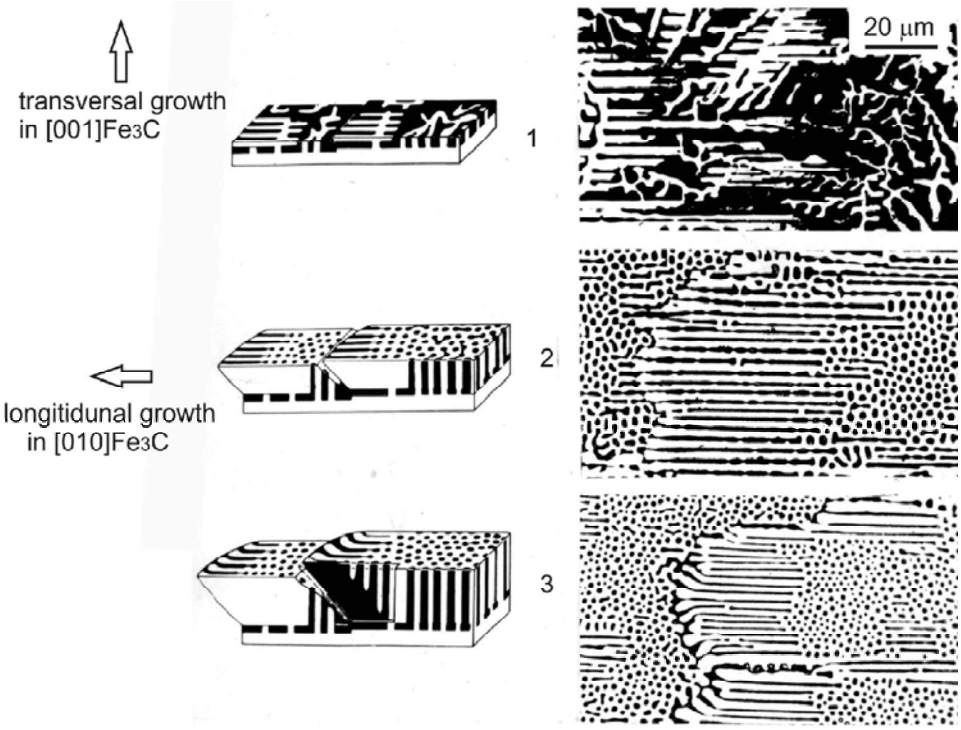


Fig. 6. Consecutive (001) Fe_3C sections of the eutectic cell. Rounded area shows a continuity of both dark austenite γ-Fe and white cementite Fe_3C phases

The found laws in as much as possible concentrated kind are shown on Fig. 7.

Here characteristic micro-photos are compared with the three-dimensional structural models orientated concerning the main crystallographic directions of cementite.



a b

Fig. 7. Stages of eutectic cells formation in (γ-Fe + Fe_3C) eutectics: α – scheme; β – microstructures

Cementite bars grow in the left part of a micro-photos and model 1. The right part is occupied by dendrite austenite branches. This is a stage of forming of eutectic colony base. The second position shows already shaped eutectics. Eutectic site which is based on a biphasic lamellar package continues to grow in plate-like kind while growth of eutectic sites which are based on a biphasic grid leads to formation of rod morphology. During transversal growth the austenite plates turn to rods due to constitutional undercooling of the melt. On the third model and micro-photo the final stage of eutectic growth is shown.

Originally flat front of the cells growing in a longitudinal direction (010) Fe_3C loses stability and gets the wavy form. In these conditions the plates of eutectic phases growing on a normal to front fan-likely turn.

3D-model of ledeburite includes all stages of eutectic solidification (Fig. 8).

The base cementite crystal grows in a liquid from left to right, and the basic stages of colony formation are situated in the opposite direction.

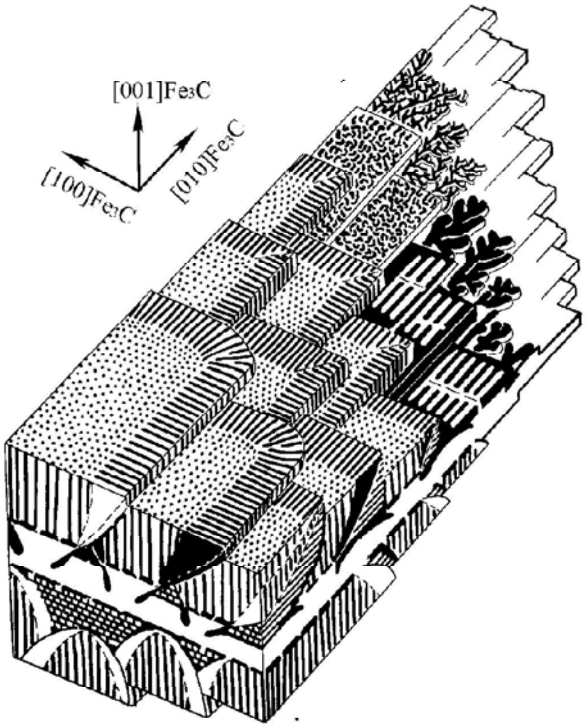


Fig. 8. 3D model of (γ-Fe + Fe_3C) eutectic

Pyramidal structure of eutectic colony

An analysis of the consecutive sections of Bi-Sn eutectic grain (colonies) shown that eutectics grows on all plates of a basic crystal (Fig. 9). As result eutectic grain consists of six identical sites in form of truncated pyramids.

The basic crystal sites of biggest curvature (edges and apexes) lead during growth and form the inter-pyramidal boundaries of eutectic grain (Fig. 10). Near the inter-pyramidal boundaries eutectics grow as plate-like bi-phase packet. Far from them rod-like eutectics is formed in condition of constitutional undercooling of a liquid phase.

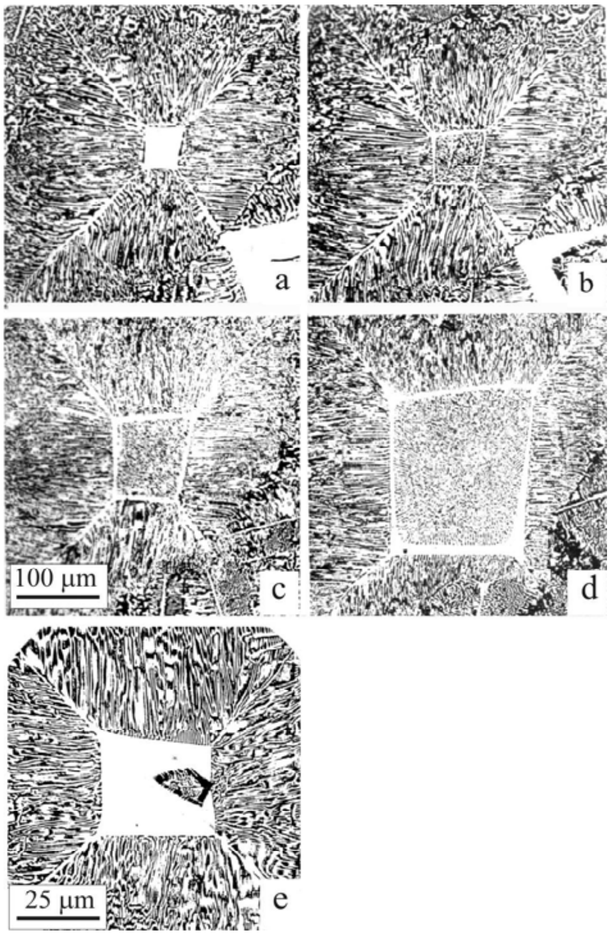


Fig. 9. The consecutive sections of Bi-Sn eutectics: a – the basic primary Bi crystal is located in center of eutectic grain; b-d – sections through five eutectic pyramids; e – growth of Sn dendrite on the plane of Bi crystal

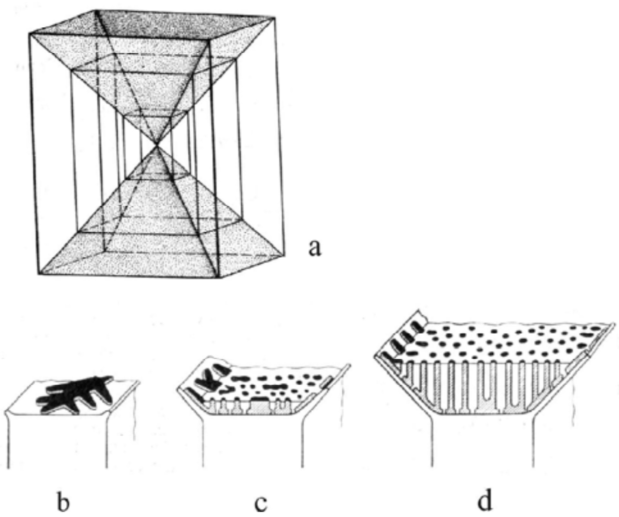


Fig. 10. Inter-pyramidal boundaries (arrowed): in cubic crystal (a); forming of inter-pyramidal boundaries in Bi-Sn eutectics (b-d)

In dependence of crystallographic orientation of secant plane three main type of microstructure: (001)Bi, (110)Bi and (111)Bi can be received (Fig. 11). It is natural that character view of inter-pyramidal boundaries will differ: square, X-like and triangular.

In common case the picture of inter-colonial, intercellular and inter-pyramidal boundaries is very complex and too little understandable. Perhaps Chalmers [3] kept it in mind when he called this structure as «china script».

Intercellular boundaries are noted by coarsening of eutectic phases. Distinction between intercellular boundaries and inter-colonial one consists in degree of coarsening of eutectics on the boundaries and in random misorietation of the next eutectic formations as well. Inter-pyramidal boundaries have mutually parallel contours.

Inter-pyramidal boundaries in eutectics of octahedral faceting divided a colony by 8 pyramids (Fig. 12).

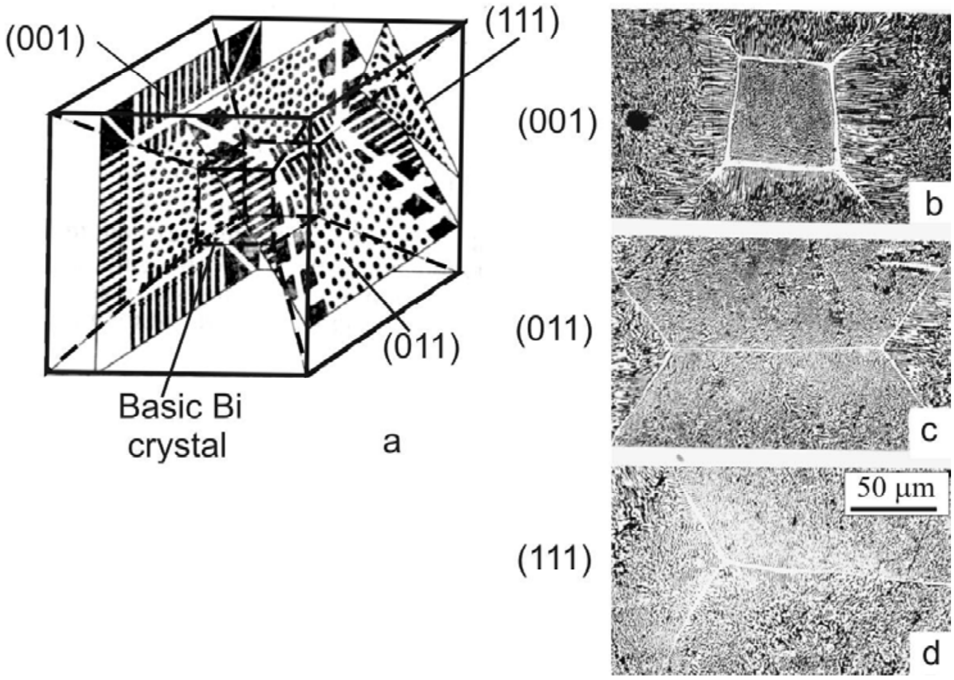


Fig. 11. Three types of inter-pyramidal boundaries in cubic eutectics Bi-Sn

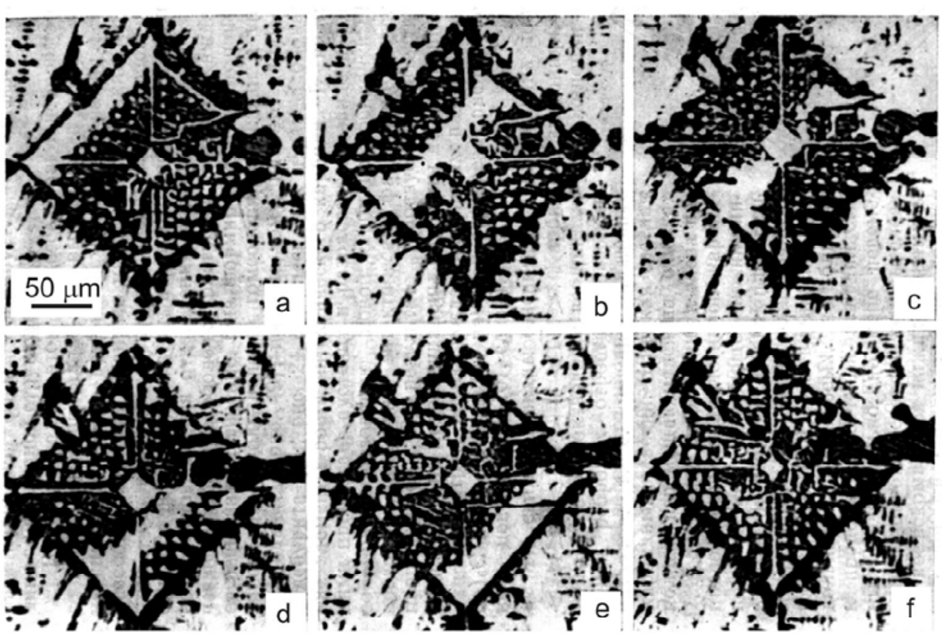


Fig. 12. Consecutive sections of the octahedral eutectic colony in Fe-Mo-C system: dark phase is γ-Fe and white phase is (Mo, Fe)C. The basic carbide crystal is genetic centre of eutectic colony

At transition from one section to another the wide light strip moves from left to right. It is inter-pyramidal boundary of a plane of approximately parallel to plane of the drawing.

Quite often eutectics with faceted matrix phase can grow in dendrite kind with the faceted branches (Fig. 13). Then there is a structural paradox: inter-pyramidal boundaries are formed inside eutectic cells.

Dendrite growth of eutectic colony with a roundish crystal of a matrix phase forms roundish eutectic cells (Fig. 14). Their boundaries are noted by coarsening of eutectic phases and arise as result of a competition of the next sites.

If the primary crystal of a basic phase is discriminated by the big anisotropy of growth rate it is possible creation of very interesting structures (Fig. 15). In (β-Ti) + Ti_5Si_3 eutectics the pyramids grown on the lateral plane of silicide can have a silicide phase as a matrix. Other pyramid growing on the face plane has metallic solid solution matrix. In the last case the structure of a classical composite is formed: the rods of a high-strength silicide phase are distributed in a plastic metal matrix (Fig. 15, d).

Some crystals with a big anisotropy of growth rate grow by means of a screw dislocation. Intermetallide $MgZn_2$ can serve as example (Fig. 16). Crystal of this phase forms a hexagonal prism. It easily branches during growth in a direction (0001)$MgZn_2$ (Fig. 16, e).

The screw dislocation works at the tops of dendrite branches (Fig. 17, a). If the dislocation step is decorated by the second phase, biphasic spiral packet is formed (Fig, 17, b, c). The eutectics of a trivial morphology is formed on lateral sides of a prism as it was considered earlier.

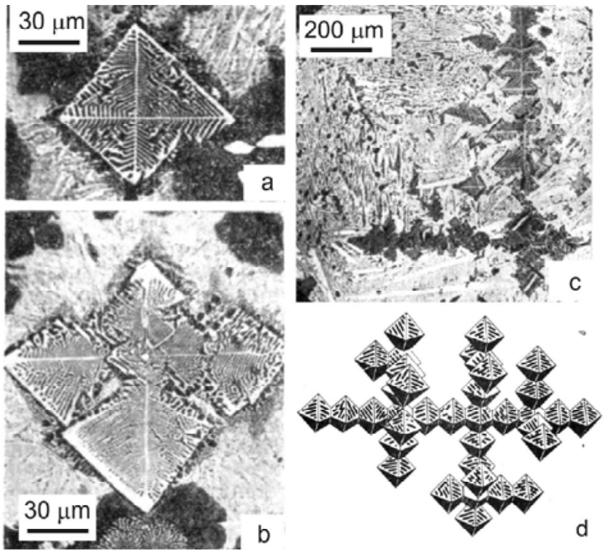


Fig. 13. Dendrite growth of (γ-Fe) + (Mo, Fe)$_6$C eutectic colony: a – start of eutectic solidification; b – intermediate stage; c – biphasic octahedral dendrite colony; d – 3D scheme

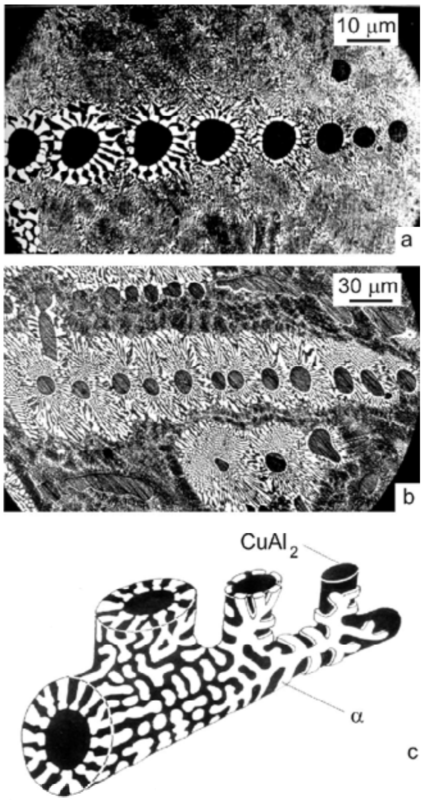


Fig. 14. Growth of eutectics (a-Al) + $CuAl_2$ on a base crystal of the roundish form of growth: a – an initial stage; b – formation cellular boundaries; c – 3D scheme

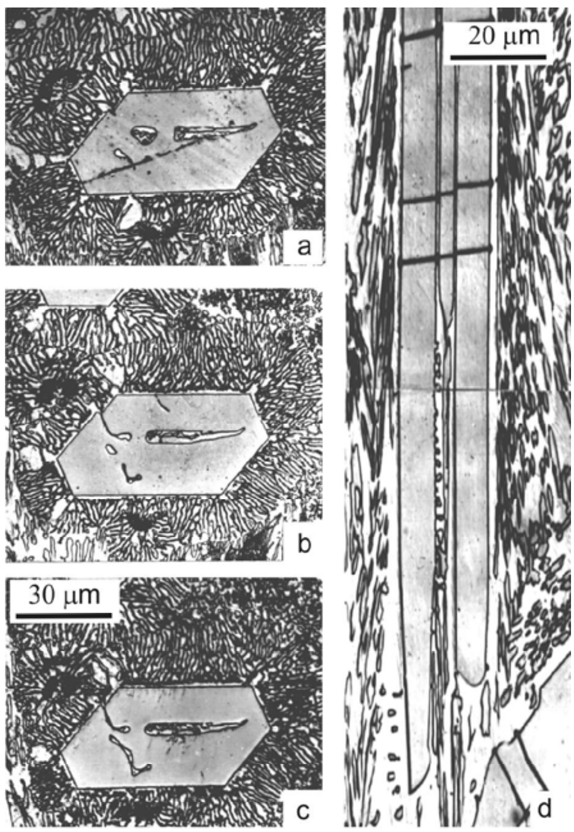


Fig. 15. The morphology of the (b-Ti) + Ti_5Si_3 eutectics [2]: a – c –consecutive transversal sections; the basic silicide crystal is in centre of eutectics; d – longitudinal section

Thus if eutectics is formed on various sides of base crystals with the big anisotropy physical and crystal-chemical properties the micro-morphology of its various sites can essentially differ. It is not structural anomaly but the natural phenomenon. It cannot be eliminated neither by stabilization of fusion thermo-kinetic parameters, nor by compulsory hashing of the melt.

Influence of growth rate

Differentiation eutectic structure λ is the distance between the next rods or plates of the branched out phase. It is defined by linear speed of eutectic crystallization front. If linear speed has changed, structural reorganization of eutectics brings parameter λ into accord with new conditions of growth. An example of the structural transformation during quenching of semi-solid Fe-C alloy is presented on Fig. 18.

The part of eutectics with differentiation λ_1 which grew with small speed V_1 occupies the bottom part of a micro-picture and the scheme. The moment of sudden cooling of a semi-solid alloy in water is marked by line (in a micro-picture) or by plane (on the scheme) on which the differentiation of eutectics decreases sharply from λ_1 to λ_2. Reduction of eutectic differentiation is reached by a branching of solid solution cores (a dark phase) to size λ_2. It provides diffusion transfer of atoms of components on the front of growth for creation of liquid phase supersaturation sufficient for coupled growth of both phases in new conditions. This circumstance defines rigid functional dependence of a differentiation of eutectics from linear speed of advance-ment of biphasic crystallization front

$$\lambda^n V = K,$$

where n is an indicator taking into account the crystal-chemistry nature and atomic mechanism of growth of eutectic phases, K is a constant. For many systems $K = 10^{-10} - 10^{-11}$ sm^3/c.

Well known parallelism of lines on the schedule $\lambda = f(V)$ for different systems speaks about identity of the atomic mechanism of eutectic growth in various eutectics.

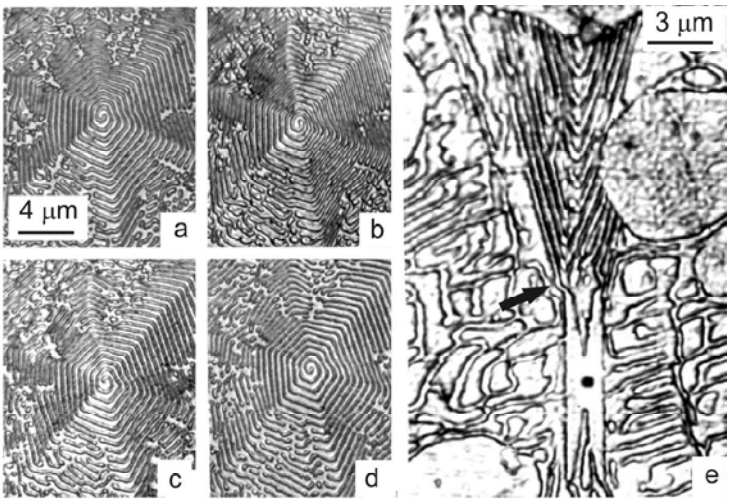


Fig. 16. Spiral conical eutectics Zn + $MgZn_2$ [2]: on the consecutive transversal sections (a–d) the initial spiral turn revolves on its axis; e – longitudinal section through primary prismatic $MgZn_2$ crystal. Spiral conical eutectics springs from vertex of the branch of hexagonal prism (arrowed)

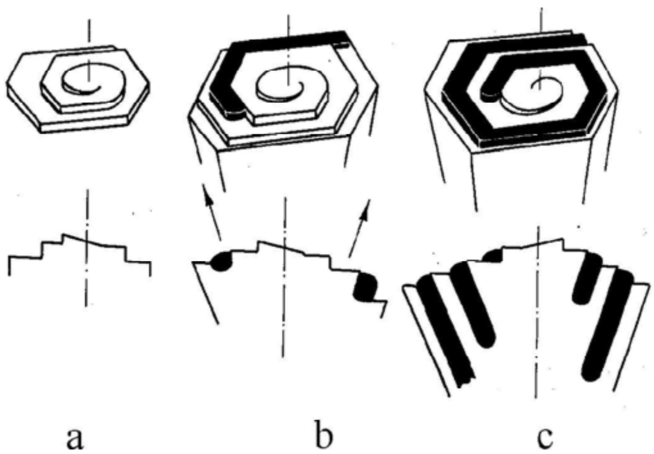


Fig. 17. The model of biphasic growth on the screw dislocation [2]: a – dislocation hill on the vertex of dendrite branch of primary $MgZn_2$ crystal; b – the dislocation decorated by second eutectic Zn phase (dark); c – coupled growth of eutectic phases

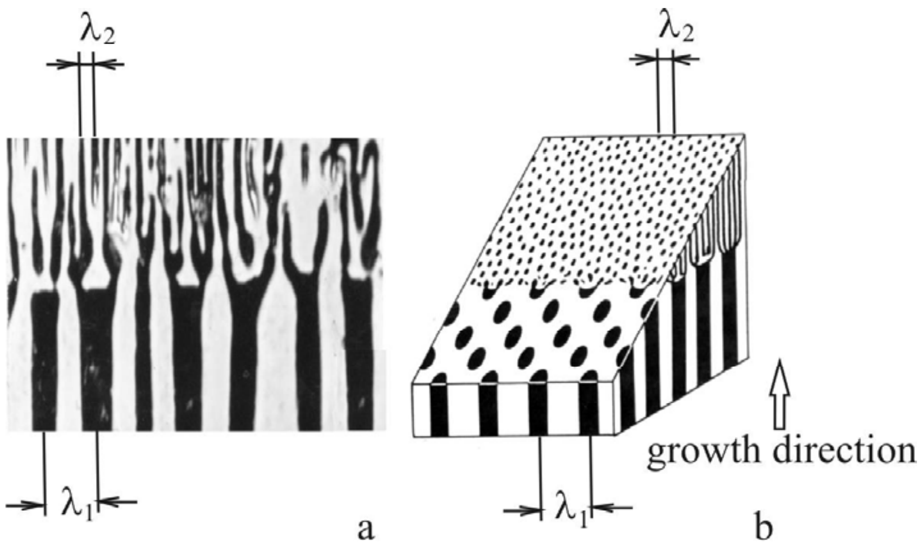


Fig. 18. The branching of rods of γ-Fe (dark) in moment of quenching of semi-solid (γ-Fe) + Fe_3C eutectic alloy in water

Increase of a cooling rate to 10^6 K/s produces formation thin differentiated structures. Thin bridges in both eutectic phases show genetic connections between ellipsoidal parts and dendrite branch of given phases (Fig. 19, a, b). At excess of this rate in Al+$CuAl_2$ eutectics independent nucleation of eutectic phases is noted (Fig. 19, c, d).

Influence of undercooling

Undercooling of the melt is one of the most important technological factors of a structure control.

Usually undercooling ΔT is connected with linear speed of crystallization V by dependence $\Delta T^2/V=K$, where K is a constant [4].

If undercooling is increased the contribution of the distant (or normal, see Fig. 2) diffusion increases and eutectics is formed with smaller degree of cooperativity.

On the other hand it is known that deactivation of nucleating impurities increases an undercooling of a melt. It provides solidification of eutectics with coarser micro-morphology (Fig. 20).

It is interesting to note the invariable form of dendrite growth of non-nucleating γ-Fe phase (dark).

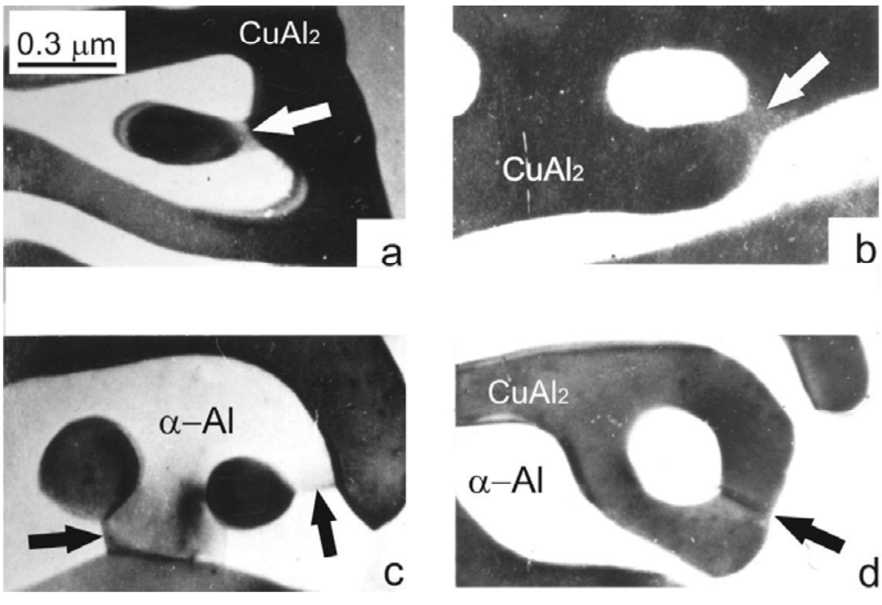


Fig. 19. TEM of thin Al+$CuAl_2$ film without additional thinning: a, b – extremely great rate at which else remains a genetic connection between an elliptic islet and dendrite branch of the given phase (white arrows); c, d – nucleation of the islets of the one phase on the crystallization front of the second one; sub-boundaries (black arrows) show intergrowth of the branches of one phase after environment of the islet of another one

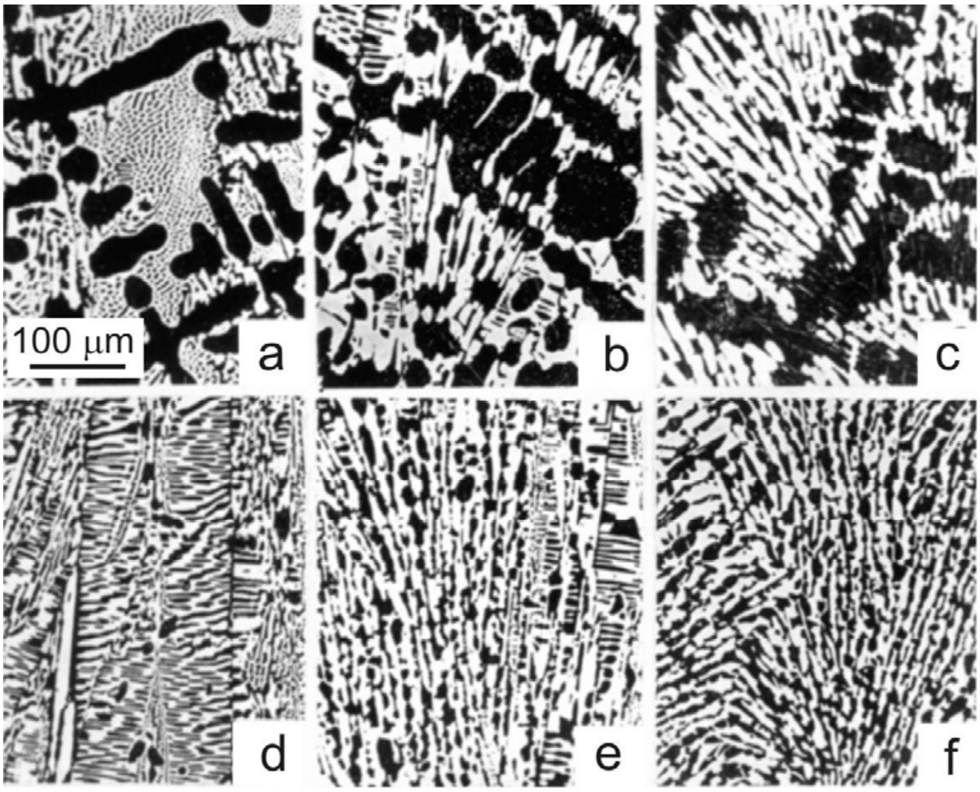


Fig. 20. Influence of a melt undercooling ΔT on a degree of cooperativity of (γ-Fe) + Fe_3C eutectics in hypoeutectic (a-c) and hypereutectic (d-f) alloys: a, d – ΔT = 5 °C; b, e – ΔT = 25 °C; c, f – ΔT =3 5 °C

Conclusion

1. Thus detailed studying of a microstructure of eutectic alloys in various systems has shown that generally structural hypotheses are described by the third and fourth hypotheses. The mechanism of independent nucleation of eutectic phases is possible at extremely big cooling rates on the board with amorphisation. The widespread hypothesis about eutectics as mechanical mixes is erroneous and represents historical interest only.

2. Laws of nucleation and growth of eutectic phases are defined both by their crystal chemistry nature and thermo-kinetic parameters of crystallization front.

3. Nucleation of the second eutectic phase is initiated by a phase with greater degree of covalency of interatomic bonds. This phase differs both by greater entropy of fusion and greater Jackson criterion.

4. Couple growth of eutectic colonies occurs in various crystallographic directions of a base crystal. The next eutectic sites, grown on adjacent planes of a base crystal, are divided by inter-pyramidal boundaries.

5. Cellular structure of eutectics is caused not only by loss of stability of flat crystallization front in the conditions of constitutional under-cooling, but also by relief of a base crystal and distinction in time of nucleation of various sites eutectic on a base crystal.

6. The transients occurring at various stages formation of eutectic colony influence both on a degree of cooperativeness and a morphological regularity of eutectics.

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Мазур В.И., Мазур А.В. Генезис и морфология эвтектики
Исследована пространственная структура эвтектик в различных системах. Выявлена непрерывность кристаллов эвтектических фаз. Описаны микроморфологические элементы эвтектической колонии – эвтектические ячейки. Установлена определяющая роль рельефа базовой фазы в формировании ячеистой субструктуры. Впервые показан механизм роста эвтектического бикристалла на винтовой дислокации в кристалле базовой фазы.
Ключевые слова: *эвтектика, пространственная структура, непрерывность фаз, микроскопическая кинетика.*

Мазур В.І., Мазур О.В. Генезис та морфологія евтектики
Досліджено просторову структуру евтектик в різних системах. Виявлено безперервність кристалів евтектичних фаз. Описані мікроморфологічні елементи евтектичної колонії, якими є евтектичні комірки. Встановлено визначальну роль рельєфу базової фази при формуванні комірчаної субструктури. Вперше показано механізм росту евтектичного бікристалу на гвинтовій дислокації в кристалі базової фази.
Ключові слова: *евтектика, просторова структура, безперервність фаз, мікроскопічна кинетика..*

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Канд. техн. наук С. А. Беженов

Национальный технический университет, г. Запорожье

МЕТОДИЧЕСКИЕ АСПЕКТЫ ПРОБЛЕМЫ ОЦЕНКИ ХАРАКТЕРИСТИК СОПРОТИВЛЕНИЯ УСТАЛОСТИ МЕТАЛЛИЧЕСКИХ МАТЕРИАЛОВ

Предложена методика ускоренного определения характеристик сопротивления усталости конструкционных металлических материалов, основанная на структурно-детерминистской концепции усталости.

Ключевые слова: *многоцикловая усталость, долговечность, предел выносливости, кривая усталости, вероятность разрушения.*

Введение

Основным фактором воздействия на материал инженерных конструкций является внешняя нагрузка, в подавляющем большинстве случаев действующая циклически и вызывающая в материале процесс усталости. Способность материала сопротивляться усталости оценивают по зависимости числа циклов до разрушения N от действующего в материале уровня напряжения σ_a, графическое изображение которой называют кривой усталости. По указанной зависимости производят оценку работоспособности материала на основе тех или иных параметров, называемых характеристиками сопротивления усталости. Проблема низкой эффективности существующих методик определения характеристик сопротивления усталости, основанных на разработанных к настоящему времени теориях усталости, имеет много аспектов, каждый из которых характеризуется своими целями и требует отдельного исследования. Одним из них является методический аспект, которому в последнее время уделяется все большее внимание.

Постановка задачи

В настоящее время определение характеристик сопротивления усталости регламентируется государственными стандартами [1–5]. Одной из основных характеристик согласно [2] является медианное значение предела выносливости $\overline{\sigma}_{-1}$. Для построения кривой распределения предела выносливости образцы испытываются на шести уровнях напряжении. Причем на каждом уровне испытывается не менее 15 образцов и более половины из них испытываются до базы испытаний, что требует больших затрат времени, материальных и трудовых ресурсов. Кроме того, существенным недостатком является то, что медианное значение предела выносливости неоднозначно определяет сопротивление усталости материала, так как не менее важным фактором при этом выступает степень