C. R. Mecanique 345 (2017) 56–65

Contents lists available at ScienceDirect

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Eutectic solidification patterns: Interest of microgravity environment

Structures de solidification eutectique : de l'intérêt d'un environnement de micropesanteur

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ARTICLE INFO

Article history:
Received 7 March 2016
Accepted 1 June 2016
Available online 8 November 2016

Keywords:
Solidification
In situ experiments
Phase-field models

Mots-clés :
Solidification
Expériences in situ
Modèles de champ de phase

ABSTRACT

The solidification of binary eutectic alloys produces two-phase composite materials in which the microstructure, that is, the geometrical distribution of the two solid phases, results from complex pattern-formation processes at the moving solid–liquid interface. Since the volume fraction of the two solids depends on the local composition, solidification dynamics can be strongly influenced by thermosolutal convection in the liquid. In this contribution, we review our experimental and numerical work devoted to the understanding of eutectic solidification under purely diffusive conditions, which will soon be tested and extended during the microgravity experiment TRANSPARENT ALLOYS planned by the European Space Agency (ESA).

RÉSUMÉ

La solidification des alliages eutectiques binaires produit des matériaux composites biphasés, dont la microstructure, c'est-à-dire l'arrangement géométrique des deux phases cristallines dans le solide, résulte d'un processus complexe d'auto-organisation à l'interface solide–liquide en cours de croissance. Puisque la fraction volumique des phases solides est une fonction de la composition locale, la dynamique de solidification peut être fortement influencée par des mouvements de convection thermo-solutale dans le liquide. Dans cet article, nous faisons le point sur nos travaux expérimentaux et numériques dédiés à la compréhension de la croissance eutectique en conditions de transport purement diffusif. Ces résultats seront bientôt testés et étendus dans une expérience en micropesanteur TRANSPARENT ALLOYS prévue par l'Agence spatiale européenne (ESA).

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http://dx.doi.org/10.1016/j.crme.2016.10.008
1631-0721/

1. Introduction

Solidification phenomena have played an important role in the history of human civilization, to the point that various epochs are named after solidified materials. Our remote ancestors fought against harsh climatic conditions during the ice age. During the bronze age and the iron age, the mastery of increasingly complex metallurgical techniques was a key ingredient for progress. Later on, the industrial revolution was largely based on the capacity to produce steel in large quantities. Finally, the development of microelectronics was only possible thanks to the progress of solidification-based purification techniques (e.g., zone-refinement) and single-crystal growth for silicon. Thus, solidification has accompanied the progress of human civilization since the dawn of times.

There have also been various links between solidification and geographic exploration. One of the starting points of modern solidification science is the work of Stefan, who formulated in 1889 the mathematical model to describe the growth of an ice layer on water in contact with cold air [1,2]. The field data against which Stefan tested his theory came from several polar expeditions [3]. With various extensions, this type of mathematical formulation has been extensively used later on to describe growth processes, and mathematicians often refer to such free-boundary problems as “Stefan problems” [4].

While the race for the poles, and the struggle to reach the most remote points on the planet, were at the forefront of discovery at the end of the 19th century, today, so to say, space is the final frontier. Quite curiously, there is again a link between exploration and solidification. One of the major assumptions in Stefan’s theory was that heat transport takes place by conduction only. This is true in the setting considered in Stefan’s original work, where heat conduction takes place in the solid ice. However, as soon as heat transport is driven by temperature gradients in the liquid, the resulting density variations trigger convective fluid motion. Density variations are even stronger in crystal growth from a multicomponent liquid mixture, where both heat and chemical components need to be transported. In fact, diffusive conditions during solidification can be realized on earth only in samples in which at least one dimension is in the 10–100 μm range, such that viscous friction at the walls prevents or reduces the fluid motion.

The access to space, and thus to an environment with reduced gravity levels, has offered the possibility to study solidification in macroscopic samples without, or at least with a low level of convection. Solidification experiments in sounding rockets, space vehicles or space stations have a long tradition [5–15]. The main goal of such experiments is to provide reference data and observations against which modern theories and models of solidification can be tested and validated for further refinement and use under terrestrial gravity conditions. As a consequence, contrary to the historic example of the Stefan problem, in which a theory was developed only long after the field data had been retrieved, today modeling accompanies solidification science both in the prematuration of new space experiments and in the interpretation of data obtained in microgravity.

Solidification is a classical example of pattern formation outside of equilibrium, in which a structured final state forms by self-organization processes from a structureless initial state [16,17]. The solidification of metallic alloys results in the spontaneous development of a large variety of *microstructures* [18]: dendrites, cells, multi-phase eutectic or peritectic composites, and multi-scale architectures that are made of combinations of several subunits. These structures are a frozen trace of interfacial patterns that exhibit a complex spatio-temporal dynamics. Although solidification is only the first stage of materials fabrication, and is often followed by heat treatments, rolling, or other processing steps, the material usually keeps a memory of the initial structuration, and therefore the solidification microstructures largely influence materials properties. For a physicist, it is a challenge to understand by which mechanisms these structures form, and how their genesis can be controlled and guided towards desirable target structures.

The study of solidification science from the viewpoint of the modern theory of pattern formation started in the 1980s [19] and has been ongoing ever since. The fundamental processes that shape the microstructures are well known: structures result from a subtle interplay between the transport of heat and chemical components, and the properties of the solid–liquid interfaces. For nonfaceted crystal growth, the most important interfacial effect is the Gibbs–Thomson effect, which originates from capillarity. Since these processes occur at the moving interface of a growing structure, both in experiments and numerical simulations it is necessary to follow the *dynamics* of the solidification front, and access the time evolution of the entire structure. In experiments, this requires an observation *in situ* during growth; in numerical simulations, it is necessary to solve the complete free-boundary, or Stefan problem. A close comparison between experiments and simulations is crucial, both to validate the mathematical and numerical models and to understand the fine details of the pattern formation process.

The French space agency CNES has set up a long-term fundamental research program on solidification in microgravity environments, which supports ground experiments as well as numerical simulations to prepare experiments in space. Here, we will review some aspects of our joint work on the solidification of eutectic alloys. In order to boldly go where no one has gone before we have combined innovative in situ experimental techniques with numerical simulations that use state of the art phase-field methods.

The remainder of this paper is structured as follows. We summarize the general background of our research in Section 2, and briefly introduce our experimental and numerical methods in Sec. 3. In Sec. 4, we review our explorations of patterns beyond simple lamellae and rods, and in Sec. 5 we examine the effects of “deformations” of the thermal field on eutectic solidification patterns. A further discussion of several aspects (Sec. 6) is followed by conclusions and perspectives in Sec. 7.

2. General background

The phase diagram of a eutectic alloy exhibits a particular point, the so-called eutectic point, at which two solid phases of distinct compositions are in equilibrium with the liquid. The composition of the liquid lies in between the compositions of the two solids, and therefore solidification of a liquid of near-eutectic composition yields a two-phase solid. While the global volume fraction of the two phases is fixed by the sample composition, as imposed by mass conservation, their spatial distribution is determined by self-organization processes that take place at the crystallization front. The two solids exchange components by diffusion in the liquid, while diffusion in the solid can usually be neglected. For alloys with non-faceted solid–liquid interfaces, local equilibrium at the growth front fixes the interface shape. In particular, the Gibbs–Thomson effect, which describes the displacement of the local equilibrium temperature by the interface curvature, and the equilibrium at the trijunction points (Young's law) need to be taken into account.

A well-controlled method to study eutectic microstructures is directional solidification: a sample is placed between two furnaces of different temperatures and pulled with controlled velocity V into the colder zone. In steady-state conditions, the crystallization front advances with velocity V. The two kinds of microstructures that are most frequently found in the resulting solid are lamellae and rods, that is, alternating platelets of the two solid phases that grow roughly along the temperature gradient, and cylinders of the minority phase embedded in a matrix of the majority phase, respectively. They correspond to solidification front patterns with banded (or striped) and hexagonal arrangements, respectively. An approximate solution to the mathematical problem of eutectic growth in a steady state was proposed by Jackson and Hunt [20], who calculated the relation between the spacing λ, that is, the spatial period of the pattern, and the average front temperature. They also found that there exists a characteristic scaling length $\lambda_{JH} \sim 1/\sqrt{V}$ which results from a balance between diffusion and capillarity. The spacings found in experiments in bulk samples are usually distributed in a narrow range around λ_{JH} [21].

The Jackson–Hunt analysis makes several simplifying assumptions: (i) "ideal", that is, perfectly periodic patterns, (ii) no convection in the liquid, (iii) a simple thermal field (a constant temperature gradient aligned with the growth direction, with planar isotherms), and (iv) isotropic interface properties. A close inspection reveals that these assumptions are actually not verified in typical bulk-solidification experiments. In recent years, we have examined several of these issues in detail, and we will present here some of our results concerning points (i) and (iii); point (iv) will be briefly commented on as a subject of ongoing work. Point (ii) will be addressed in a forthcoming space experiment (ESA project TRANSPARENT ALLOYS [22]). The main motivation to do space experiments is the dependence of the expected morphology (lamellae, rods, or more complicated patterns) on the alloy composition. If convection is present, this composition is generally not homogeneous, which can explain, for instance, why both lamella and rod morphologies were seen on the same micrograph during studies of the lamella-to-rod transition [23]. A careful exploration of the various structures is thus only possible in the absence of convection. Moreover, as will be detailed below, the configuration of the thermal field can have a dramatic influence on the pattern formation dynamics. An exciting possibility would be to use this property to drive particular transitions between patterns in a controlled way. However, this is severely limited in terrestrial conditions because modifying the thermal field will generally lead to strong convection.

3. Methods

3.1. Experimental

It turns out that there exist several transparent organic alloys, made of small and simple molecules, which freeze like metals [24] – most importantly, they have microscopically rough, nonfaceted solid–liquid interfaces. They can therefore be used as "metal analogs". Directional-solidification studies using thin samples of transparent alloys, initiated by Jackson and Hunt themselves, have led to major advances in our understanding of solidification. In those experiments, a film of the alloy to be solidified of thickness in the 10 μm range is confined between two glass plates (Fig. 1). Since the typical length scales of eutectic patterns are generally larger than the film thickness, the pattern can be considered as two-dimensional. Only the lamellar morphology can exist in this geometry. This allows for an observation of the dynamics in side view. Both the liquid and the two solids are transparent, but since the refraction indices of the three phases are different, the interfaces can be clearly distinguished with an optical microscope.

In order to explore pattern dynamics in three dimensions, a genuinely new setup, called DIRSOL, was developed (see Fig. 2). This represents a considerable challenge: a three-dimensional image of a complex structure consisting of two transparent phases is required. This setup uses (semi-)bulk samples of transparent alloys [25] with inner thickness ranging between 300 and 500 μm, which is much larger than the interphase spacing in eutectic microstructures. Real-time observation is performed with a long-distance microscope that focuses the solid–liquid interface from the exterior in an oblique direction, through the liquid and a glass wall (non-invasive method). Illumination is applied in an oblique way as well, through the solid. By a judicious choice of illumination and observation angles, it was possible to obtain well-focused top-view pictures of the solidification front with a black-and-white contrast between the two solid phases, and a resolution in the micron range [26,27]. Experiments were carried out with alloys of near-eutectic concentration, in which there is no macroscopic diffusion layer in the liquid. By using a vertical directional solidification setup, thermosolutal convection could

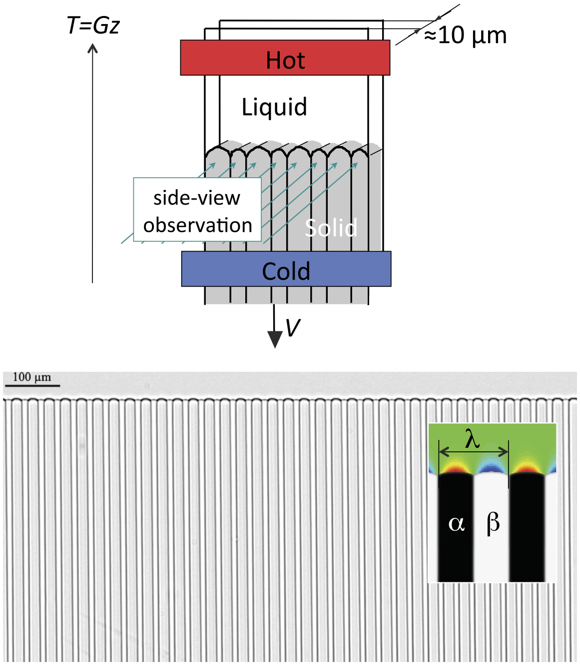

Fig. 1. Top: Principle of thin-sample directional solidification. V: pulling velocity. G: temperature gradient (vertical axis z). Side-view observation: optical microscope. Bottom: Steady periodic (lamellar) eutectic growth pattern in thin-sample directional solidification (slightly hypereutectic CBr_4–C_2Cl_6 transparent alloy; $V = 1\ \mu m\,s^{-1}$; $\lambda \approx 1.2\,\lambda_{JH}$). Liquid and solid–solid interfaces are seen as dark lines. Inset: Two-dimensional phase-field numerical simulation of a periodic lamellar pattern (model symmetric eutectic alloy). α and β: solid phases. Colors in the liquid: solute diffusion field. λ: lamellar spacing.

then be largely avoided on earth. The multi-user TRANSPARENT ALLOYS apparatus has been developed by ESA on the basis of the DIRSOL optical method.

3.2. Numerical

The phase-field method has emerged in recent years as the method of choice for simulations of solidification microstructures and other pattern-formation processes [28–30]. It uses the phenomenological description of first-order phase transitions in terms of a Ginzburg–Landau free energy functional, with order parameters that are called phase fields. The interfaces between phases are localized by rapid but smooth variations of the phase fields, and their motion is given by partial differential equations for the phase field that are obtained from the variational principles of out-of-equilibrium thermodynamics, and that are coupled to the relevant transport equations for heat and/or components.

A major step forward has been made by the development of the thin-interface asymptotics [31], which makes it possible to freely choose the thickness of the diffuse interfaces as long as this thickness remains at least an order of magnitude smaller than any physical scale present in the free-boundary problem. This procedure has made it possible to tremendously increase computational efficiency while keeping the same accuracy. Indeed, the resolution of the numerical grid has to be of the same order of magnitude as the interface thickness to properly resolve the interface dynamics. An upscaling of the interface thickness leads therefore to a dramatic reduction of the number of computational nodes that are required, as well as to larger timesteps. This makes quantitative simulations of solidification microstructures in three dimensions possible on scales that can reach several microstructural units [32]. The accuracy and performance of such methods depend on the formulation of the model equations. Several models for alloy solidification have been developed and thoroughly benchmarked; here, we present results that were obtained using the model of Ref. [33].

4. Eutectic patterns beyond lamellae and rods

As already discussed above, the characteristic spacing of eutectic lamellae is close to the Jackson–Hunt spacing in massive samples [21]. The experiments in thin samples, however, have demonstrated that there is no real selection mechanism for the spacing in two dimensions. Indeed, it is possible to create growth fronts with spacings that are quite different from λ_{JH}. This can be done by increasing or decreasing the pulling velocity in the course of an experiment by a factor that can be as large as two. If the velocity jump is of moderate enough amplitude, the number of lamellae present in the system does not change (and, therefore, the spacing of the pattern is kept constant), whereas λ_{JH} changes (we recall that $\lambda_{JH} \sim 1/\sqrt{V}$). It was found that there is a range of spacings around λ_{JH} that are stable [34]. Inside this stability range, a pattern with a nonuniform spacing profile is driven to a periodic state. For patterns in which the spacing is weakly modulated around an

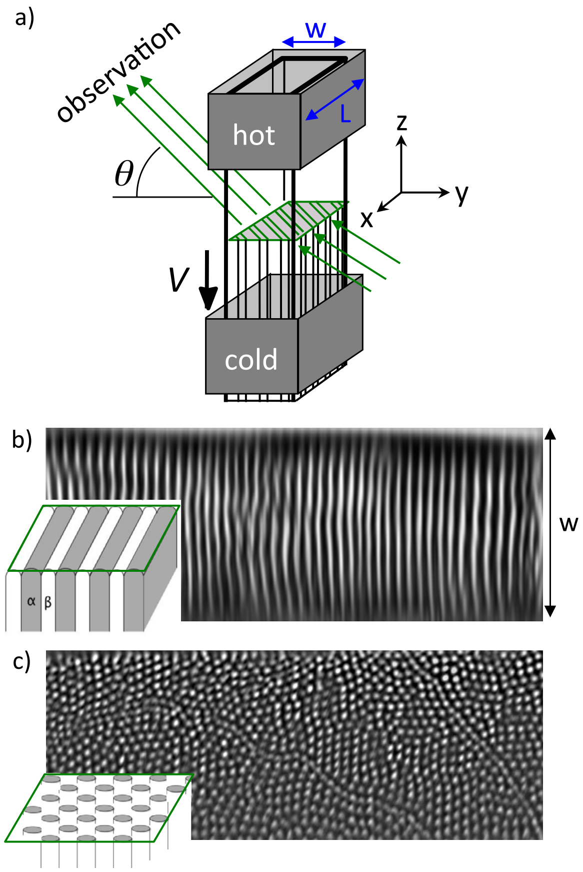

Fig. 2. a) Principle of the DIRSOL apparatus for real-time, oblique-view observation (viewing angle θ) of the solid–liquid interface with a long-distance optical microscope during directional solidification of transparent eutectic alloys. y: normal to the glass walls. w and L: thickness and lateral width of the sample ($L \gg w$). b) Lamellar pattern; near-eutectic CBr_4–C_2Cl_6 alloy ($V = 0.37\ \mu m\, s^{-1}$; $w = 350\ \mu m$). Bright (dark) lamellae: α (β) phase. c) Rod-like pattern in a 350-μm sample of a near-eutectic succinonitrile-(D)camphor alloy ($V = 0.035\ \mu m\, s^{-1}$). Bright spots: (D) camphor fibers in the (dark) succinonitrile matrix. The images have been rescaled numerically to 1:1 aspect ratio. Insets: schematic perspective of the two kinds of growth patterns.

average spacing λ_0, this general smoothing mechanism can be described by a phenomenological diffusion equation, which is conveniently called "spacing diffusion" equation. The corresponding spacing-diffusion coefficient depends on λ_0. The range of stable spacing is bounded for small spacing by a lamella elimination instability, and for large spacings by various oscillatory instabilities. The lamella elimination instability is triggered by an inversion of the spacing-diffusion process, that is, the spacing-diffusion coefficient becomes negative. The threshold spacings at which those instabilities occur, and thus the range of stable spacings, depend on the alloy composition. For the transparent eutectic alloy CBr_4–C_2Cl_6 at the eutectic composition, the upper stability limit is at approximately twice λ_{JH}. All these results are in excellent agreement with numerical calculations [35–37].

The experiments in bulk samples and the phase-field simulations have allowed us to explore the stability of eutectic lamellae in three dimensions. A new instability called "zigzag" was found for large spacings ($\lambda \approx 1.2\,\lambda_{JH}$ in CBr_4–C_2Cl_6 at the eutectic composition). This instability leads from straight to wavy or *chevron* patterns (see Fig. 3a), and is one of the generic instabilities that are expected for stripe patterns [38]. To our surprise, in bulk samples, we did not observe the symmetry-breaking instabilities that were found in thin samples at large spacings. Phase-field simulations have clarified this point [39]: other instability modes, which are the three-dimensional extensions of the thin-sample oscillatory modes, do exist but become active at much larger spacings than the zigzag instability. This explains why only the zigzag instability was observed in bulk-sample experiments. On the small-spacing side, we observed a lamella elimination instability involving the migration of half-lamellae. This dynamics, as well as the lamella branching process that occurs well above the zigzag instability [40] still remain to be studied.

The DIRSOL setup also has allowed us to study the rod-eutectic morphology, which only exists in bulk samples (and 3D numerical simulations). A first question of interest was that of the stability diagram of rod eutectics. Our in situ experiments showed that the lower limit corresponds to the elimination of rods, and the upper limit to a splitting of individual rods [44, 45]. The splitting instability limit is close to (and scales with) λ_{JH}, while the elimination instability occurs for spacing values well below λ_{JH}. The stability of eutectic rods has been also addressed in systematic phase-field simulations [43]. It was found that for moderately asymmetric volume fractions (30% of the minority phase), rods undergo a shape bifurcation for

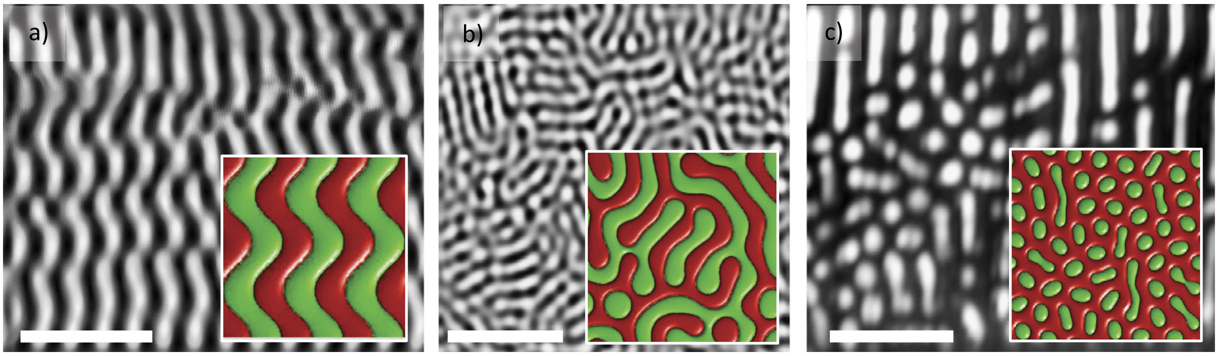

Fig. 3. Eutectic growth patterns in bulk directional solidification. Real-time observations in transparent alloys with the DIRSOL setup. a) Zigzag pattern (CBr_4–C_2Cl_6; $V = 0.39$ μm s^{-1}); note the presence of defects reminiscent of the fault lines commonly observed in bulk metallic eutectics [26]. b) Labyrinth pattern (CBr_4–C_2Cl_6; $V = 1.0$ μm s^{-1}) [41]. c) Coexistence between rods, elongated rods and broken lamellae (succinonitrile-(D)camphor; $V = 0.01$ μm s^{-1}) [42]. Bars: 100 μm. Insets: 3D phase-field calculations (eutectic alloy with symmetric phase diagram) [39,43].

large spacings: their cross-section changes from circular to elongated (towards the first or the second neighbors, depending on the boundary conditions) and then to a dumbbell-like non-convex shape. In partial agreement with this, our real-time experiments revealed the existence of elongated rods during transient stages, as a precursor of rod splitting [45], and in confined geometries [42,46] (Fig. 3c; also see [40,47,23]). However, steady periodic elongated-rod patterns have not been observed experimentally. Finally, for smaller volume fractions of the rod phase, eutectic-rod oscillations occurred. In the simulations, both the rod diameter and the position of the rod centers were observed to oscillate. Rod oscillations have also been observed experimentally, but have not yet been characterized in detail [45]. It is worth mentioning that, in the experiments, the eutectic-rod oscillation dynamics only occurred in highly disordered patterns – in this respect, it is similar to the ones observed under microgravity conditions (in the DSI/DECLIC facility) in cellular patterns in dilute alloys [12,13].

In large isotropic systems, it is actually rare to observe perfectly periodic eutectic patterns. Rod-like eutectics are generally observed to organize into relatively small well-ordered domains separated by disordered areas called dynamic walls. Lamellar eutectics generally form disordered "labyrinth" patterns, in which the local orientation of the lamellae greatly varies from place to place (see Fig. 3b). The same is also true in simulations of large systems that are started from a random arrangement of the two solid phases: in this case, although some of the topological defects of the initial state are eliminated over time, the pattern does not get ordered on a large spatial scale during the time scales accessible in the simulations, which are comparable to time scales reached in experiments.

5. Tilted and non-planar isotherms

In the standard theoretical treatment of directional solidification, an extremely simple temperature field is usually assumed: a constant temperature gradient that is independent of the solid–liquid interface configuration during growth, with planar isotherms perpendicular to the sample pulling axis. This can indeed be a good approximation for thin-sample directional solidification and V of the order of 1 μm/s, but in bulk directional solidification, this assumption is wrong, even in the absence of convection. This comes from the fact that the heat conductivities of the liquid, the growing solid, and the container walls that are in mutual contact are all different. The continuity of the temperature field then necessarily entails a bending of the isotherms, thus "transverse" temperature variations along the directions perpendicular to the growth axis. In addition, latent heat generated by the crystallization of the solid has to be transported away through the container walls. Finally, if the experimental setup is not strictly symmetric, there will be a bias in the thermal field between the opposite sides of the sample. As a practical consequence, the isotherms are generally both tilted and curved. This has several important consequences, two of which will be discussed presently.

It has been observed in rod eutectics that a slight curvature of the solidification front of characteristic radius larger than the section of the sample, with the solid bulging into the liquid, imposes a continual stretch of the pattern [44]. This is a consequence of the fact that, in the absence of strong crystallographic effects, eutectic structures generally grow approximately in the direction normal to the global crystallization front. After a certain transient time, this curvature-induced stretching is balanced, on average, by rod splittings. As a result, the histogram of rod spacings is peaked close to the rod-splitting threshold, and is essentially independent of the initial conditions. It is worth noting that this long-time solidification dynamics realizes an interesting example of a system driven to operate at a marginal-stability point. More practically, the coupled-growth structures thus produced also present statistical features, namely, sharp selection of the mean spacing, and broad dispersion of the local spacing values, that are clearly reminiscent of those observed in metallic eutectics [21].

What seemed at first sight to be a mere complication of the experiment can actually be used to learn more about the pattern dynamics. In particular, the isotherms can be deliberately tilted by a controlled thermal bias. Then, a finite slant of the solidification front with respect to the main growth axis is fixed experimentally, and the whole pattern globally drifts

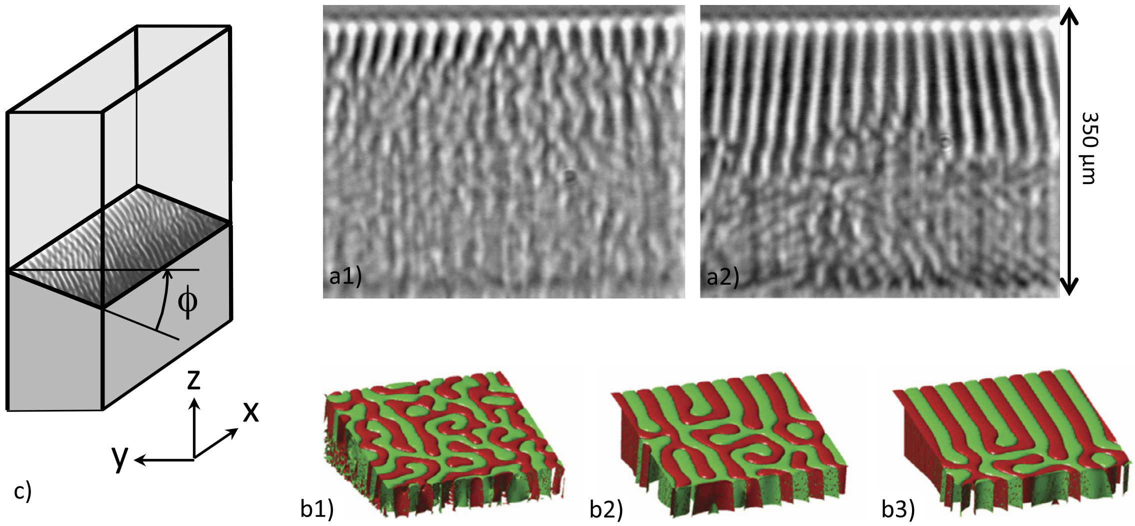

Fig. 4. Real-time observations: a1) and a2) Global drift of a labyrinth pattern and formation of regular lamellae by an invasion process due to a thermal-bias effect. b1) to b3): Phase field simulations of this morphological transition at three successive instants (thermal-bias angle $\phi = 12°$). c) Schematic representation of the thermal bias.

from the "upper" toward the "lower" edge (see Fig. 4). In this way, a labyrinth pattern generated during the first stages of a solidification run is replaced by a lamellar pattern that propagates and "invades" the entire sample. We have incorporated this thermal-bias effect in phase-field simulations, and observed the very same invasion process [41]. We have obtained a good quantitative agreement between experiments and simulations regarding the velocity of the lamellar front.

6. Discussion

One of the most interesting questions we have, and will continue to address, is the coexistence of, or the competition between, ordered and disordered patterns. Ordered lamellar patterns are actually quite frequent in bulk samples of metallic eutectics, where lamellae are often straight and well ordered over considerable distances [48,40]. How such regular patterns are formed is by no means a trivial question. As we have seen above, a possibility is that the process is assisted and guided by the structure of the thermal field. Another alley we currently explore is to exploit the dynamic transitions that occur between different patterns. With this aim in view, we have set up a simulation in which the composition of the liquid varies slowly with time. In the experiments, this could in principle be realized, for instance by using a macrosegregation process to create a large-scale longitudinal composition gradient in the sample, but this remains to be tested in practice. In the simulation in question, the system starts out with a pattern of α rods in a β matrix. Then, the volume fraction of α slowly increases as solidification goes on, and we observe a transition first to a lamellar pattern, and then to a pattern of β rods in an α matrix (see Fig. 8 in Ref. [43] for a sequence of snapshot pictures). Both the patterns (lamellae and rods) that are formed after these dynamic transitions are more regular than the patterns that arise from random initial conditions [43]. According to our previous studies of invasion processes [49], this could be due to the fact that the spatio-temporal dynamics of the transitions between patterns is propagative. For instance, in the simulation the transition from lamellae to rods starts at a lamella termination: rods form by successive pinchoff events from this termination, which creates a row of regularly spaced rods than serves later on as a "template" for a regular rod pattern. This issue needs to be studied in more detail.

Another method of modifying the organization of the patterns is confinement. We have carried out simulations [50] and experiments [42] in confined samples, that is, samples with an intermediary thickness in which a small number of "layers" of rods can form. We found that confinement has a strong effect on the selection of the structures, and helps to establish ordered patterns, probably because it blocks long-wavelength instability modes in the direction normal to the sample.

For the sake of clarity, we have as of yet deliberately ignored crystallographic effects. Before concluding this report, we wish to briefly mention the work we have done to clarify their role in eutectic growth. It is a well-known fact that eutectics are generally made of large "eutectic grains" (that is, regions in which the crystallographic orientation of each crystal phase is uniform) and that the growth pattern may substantially vary from grain to grain during a given experiment [51,52]. We have long advocated that one should distinguish between "floating" grains, which exhibit isotropic (or smoothly anisotropic) behavior, and "locked" grains, in which lamellae tend to grow in certain preferred directions that are fixed by the crystallography (in fact, the entire dataset overviewed in this contribution actually depended on our ability to grow large floating eutectic grains [49]). We have very recently addressed anew the question of how crystallographic anisotropy influences the dynamics of eutectic growth. To achieve this, we have performed experiments using a novel method called *rotating directional solidification* [53], developed an approximate theory of the lateral drift of eutectic patterns induced by anisotropic interphase boundaries [54], and performed numerical simulations of this phenomenon using either a boundary-integral or a phase-field method [55].

In brief, it is crucial to note that the anisotropy of the interphase boundary enters the theoretical coupled-growth problem in the so-called Young–Herring law which expresses the local equilibrium at the solid–solid–liquid trijunction. Knowing this, and in agreement with in situ observations, our theoretical proposition is that, in steady-state growth, the lamellar tilt angle is fixed at a value for which the shape of the solid–liquid interfaces keeps the same mirror symmetry as in the isotropic case, in spite of the lateral drift of the pattern (*symmetric pattern conjecture*). In the rotating directional solidification method, a (thin) sample is continually rotated with respect to the temperature gradient. The orientation of a given eutectic grain thus changes continuously while it grows, but the relative orientation between the two solid phases does not vary. For a floating, isotropic eutectic grain, the lamellae grow locally perpendicular to the planar coupled-growth isotherm, and the microstructure left in the solid is made of circular lamellae. In an anisotropic eutectic grain, the rotating-solidification microstructure possesses a 2-fold symmetry, which is expected for a crystal–crystal interface [53]. According to the symmetric pattern conjecture, the rotating-solidification microstructure of a given eutectic grain is homothetic to the Wulff-shape of the interphase boundary [54]. We obtained a satisfactory agreement between the experimental, theoretical and numerical results [55], validating the proposed theory and opening the way to new researches on the thorny subject of "preferred orientation relationships" in eutectic growth. The numerical simulations have moreover highlighted crystallographic effects as a major factor in the formation of regular lamellar patterns [56].

As a final remark, we would also like to stress the increasing interest in ternary eutectic patterns that is now developing in industry and research [52]. We have contributed to this movement since the 2000s by clarifying experimentally and theoretically the nature of the formation of eutectic cells or colonies that occurs in dilute ternary eutectics, when a low-concentration impurity is added to a binary eutectic alloy of reference [57,58]. More recently, capitalizing on the work done by the ACCESS team on transparent multicomponent eutectic alloys [59], a new growth structure called "two-phase spiral dendrite" has been discovered experimentally in ternary eutectic alloys containing a large amount of impurity, but in a growth regime where the solid still remains two-phased [60]. A scaling-law theory of the spiral dendrite has been proposed [61], and this structure has been reproduced in phase-field simulations [62]. We have also endeavored a systematic study of the amazing variety of possible three-phase microstructures that are delivered by directional solidification of a ternary-eutectic alloy of concentration near a ternary eutectic point (three different crystals growing together), numerically in two dimensions [63], experimentally in thin samples [64]. The systematic characterization and analysis of these structures is only in its beginnings.

7. Conclusions and perspectives

We have described some aspects of our common research work on the pattern-formation dynamics in eutectic alloys. Whereas the reviewed material is about ground experiments and numerical simulations only, the entire project has been motivated by the planning and preparation of a microgravity experiment, TRANSPARENT ALLOYS, prepared by the European Space Agency, and hopefully to be launched soon for the Materials Science Glovebox on board of the International Space Station. This experiment will allow us to make major progress on several questions that we have been studying for a long time, in particular the dynamics of the lamellae-to-rods transition (triggered in a controlled way by a large-scale composition gradient) and the stability diagram of lamellae and rods (without the uncontrolled variations in composition that are created by convection). The detailed comparison between microgravity experiments and numerical modeling is bound to reveal shortcomings of the model and thus point out future directions of improvement.

The development of this project over such a long time scale owes a lot to a stable funding environment, which was provided by the program on microgravity research in materials science of the CNES under the leadership of Bernard Zappoli. We are happy to contribute to this dossier in his honor.

References

[1] J. Stefan, Über die Theorie der Eisbildung, Insbesondere über die Eisbildung im Polarmeere, Sitz. Ber. - Österr. Akad. Wiss. Math.-Nat.wiss. Kl., II Math. Astron. Phys. Meteorol. Tech. 98 (1889) 965–983.

[2] J. Stefan, Über die Theorie der Eisbildung, Insbesondere über die Eisbildung im Polarmeere, Ann. Phys. Chem. 42 (1891) 269–286.

[3] J. Crepeau, Josef Stefan: his life and legacy in the thermal sciences, Exp. Therm. Fluid Sci. 31 (2007) 795–803, http://dx.doi.org/10.1016/j.expthermflusci.2006.08.005.

[4] A. Visintin, Introduction to Stefan-type problems, in: C. Dafermos, M. Pokorny (Eds.), Handbook of Differential Equations: Evolutionary Differential Equations, vol. IV, North-Holland, Amsterdam, 2008, pp. 377–484.

[5] M.E. Glicksman, M.B. Koss, E.A. Winsa, Dendritic growth velocities in microgravity, Phys. Rev. Lett. 73 (1994) 573–576.

[6] L. Tennenhouse, M. Koss, J. LaCombe, M. Glicksman, Use of microgravity to interpret dendritic growth kinetics at small supercoolings, in: Proc. 10th American Conference on Crystal Growth/9th International Conference on Vapor Growth and Epitaxy, Vail, CO, USA, 4–9 August 1996, J. Cryst. Growth 174 (1997) 82–89, http://dx.doi.org/10.1016/S0022-0248(96)01064-0.

[7] J.C. LaCombe, M.B. Koss, V.E. Fradkov, M.E. Glicksman, Three-dimensional dendrite-tip morphology, Phys. Rev. E 52 (1995) 2778–2786.

[8] M. Koss, J. LaCombe, L. Tennenhouse, M. Glicksman, E. Winsa, Dendritic growth tip velocities and radii of curvature in microgravity, Metall. Mater. Trans. A 30 (1999) 3177–3190, http://dx.doi.org/10.1007/s11661-999-0228-0.

[9] J. Favier, J. Garandet, A. Rouzaud, D. Camel, Mass-transport phenomena during solidification in microgravity – preliminary results of the 1st MEPHISTO flight experiment, J. Cryst. Growth 140 (1994) 237–243, http://dx.doi.org/10.1016/0022-0248(94)90517-7.

[10] B. Drevet, H. Nguyen Thi, D. Camel, B. Billia, M. Dupouy, Solidification of aluminium–lithium alloys near the cell/dendrite transition-influence of solutal convection, J. Cryst. Growth 218 (2000) 419–433, http://dx.doi.org/10.1016/S0022-0248(00)00567-4.

[11] J. Garandet, G. Boutet, P. Lehmann, B. Drevet, D. Camel, A. Rouzaud, J. Favier, G. Faivre, S. Coriell, J. Alexander, B. Billia, Morphological stability of a solid–liquid interface and cellular growth: insights from thermoelectric measurements in microgravity experiments, J. Cryst. Growth 279 (2005) 195–205, http://dx.doi.org/10.1016/j.jcrysgro.2005.01.108.

[12] N. Bergeon, D. Tourret, L. Chen, J.-M. Debierre, R. Guérin, A. Ramirez, B. Billia, A. Karma, R. Trivedi, Spatiotemporal dynamics of oscillatory cellular patterns in three-dimensional directional solidification, Phys. Rev. Lett. 110 (2013) 226102, http://dx.doi.org/10.1103/PhysRevLett.110.226102.

[13] D. Tourret, J.M. Debierre, Y. Song, F.L. Mota, N. Bergeon, R. Guerin, R. Trivedi, B. Billia, A. Karma, Oscillatory cellular patterns in three-dimensional directional solidification, Phys. Rev. E 92 (2015) 042401, http://dx.doi.org/10.1103/PhysRevE.92.042401.

[14] D. Jarvis, O. Minster, Metallurgy in space, in: R. Roosz, M. Rettenmayr, Z. Gacsi (Eds.), Solidification and Gravity IV, Proc. 4th International Conference on Solidification and Gravity, Miskolc-Lillafüred, Hungary, 6–9 September 2004, pp. 1–18.

[15] G. Salloum-Abou-Jaoude, H. Nguyen-Thi, G. Reinhart, R.H. Mathiesen, G. Zimmermann, D. Voss, Characterization of motion of dendrite fragment by X-ray radiography on earth and under microgravity environment, Materials Science Forum 790–791 (2014) 311–316.

[16] M.C. Cross, P.C. Hohenberg, Pattern formation outside of equilibrium, Rev. Mod. Phys. 65 (1993) 851.

[17] V. Fleury, J.-F. Gouyet, E.M. Leonetti, Branching in Nature, Les Houches, France, vol. 13, EDP Sciences, Springer, 2001.

[18] W. Kurz, D.J. Fisher, Fundamentals of Solidification, Trans Tech Publications, Zurich, Switzerland, 1998.

[19] J.S. Langer, Instabilities and pattern formation in crystal growth, Rev. Mod. Phys. 52 (1980) 1.

[20] K.A. Jackson, J.D. Hunt, Lamellar and rod eutectic growth, Trans. Metall. Soc. AIME 236 (1966) 1129.

[21] R. Trivedi, J.T. Mason, J.D. Verhoeven, W. Kurz, Eutectic spacing selection in lead-based alloy systems, Metall. Trans. A 22 (1991) 2523–2533, http://dx.doi.org/10.1007/BF02665018.

[22] A. Ludwig, J. Mogeritsch, M. Kolbe, G. Zimmermann, L. Sturz, N. Bergeon, B. Billia, G. Faivre, S. Akamatsu, S. Bottin-Rousseau, D. Voss, Advanced solidification studies on transparent alloy systems: a new European solidification insert for material science glovebox on board the international space station, JOM 64 (2012) 1097–1101, http://dx.doi.org/10.1007/s11837-012-0403-4.

[23] S. Liu, J.H. Lee, R. Trivedi, Dynamic effects in the lamellar-rod eutectic transition, Acta Mater. 59 (2011) 3102–3115, http://dx.doi.org/10.1016/j.actamat.2011.01.050.

[24] K. Jackson, J. Hunt, Transparent compounds that freeze like metals, Acta Metall. 13 (1965) 1212–1215, http://dx.doi.org/10.1016/0001-6160(65)90061-1.

[25] S. Bottin-Rousseau, M. Perrut, C. Picard, S. Akamatsu, G. Faivre, An experimental method for the in situ observation of eutectic growth patterns in bulk samples of transparent alloys, J. Cryst. Growth 306 (2007) 465–472, http://dx.doi.org/10.1016/j.jcrysgro.2007.05.035.

[26] S. Akamatsu, S. Bottin-Rousseau, G. Faivre, Experimental evidence for a zigzag bifurcation in bulk lamellar eutectic growth, Phys. Rev. Lett. 93 (2004) 175701.

[27] S. Akamatsu, S. Bottin-Rousseau, G. Faivre, Stability of lamellar eutectic growth in thick samples, Philos. Mag. 86 (24) (2006) 3703.

[28] W.J. Boettinger, J.A. Warren, C. Beckermann, A. Karma, Phase-field simulation of solidification, Annu. Rev. Mater. Res. 32 (2002) 163–194.

[29] I. Steinbach, Phase-field models in materials science, Model. Simul. Mater. Sci. Eng. 17 (17) (2009) 073001.

[30] N. Provatas, K. Elder, Phase-Field Methods in Materials Science and Engineering, Wiley–VCH, Weinheim, 2010.

[31] A. Karma, W.-J. Rappel, Quantitative phase-field modeling of dendritic growth in two and three dimensions, Phys. Rev. E 57 (4) (1998) 4323–4349.

[32] M. Plapp, Three-dimensional phase-field simulations of directional solidification, J. Cryst. Growth 303 (2007) 49–57.

[33] R. Folch, M. Plapp, Quantitative phase-field modeling of two-phase solidification, Phys. Rev. E 72 (1) (2005) 011602.

[34] M. Ginibre, S. Akamatsu, G. Faivre, Experimental determination of the stability diagram of a lamellar eutectic growth front, Phys. Rev. E 56 (1997) 780.

[35] A. Karma, A. Sarkissian, Morphological instabilities of lamellar eutectics, Metall. Mater. Trans. A 27 (1996) 635.

[36] S. Akamatsu, M. Plapp, G. Faivre, A. Karma, Pattern stability and trijunction motion in eutectic solidification, Phys. Rev. E 66 (2002) 030501(R).

[37] S. Akamatsu, M. Plapp, G. Faivre, A. Karma, Overstability of lamellar eutectic growth below the minimum-undercooling spacing, Metall. Mater. Trans. A 35 (2004) 1815.

[38] P. Manneville, Dissipative Structures and Weak Turbulence, Academic Press, Boston, MA, USA, 1990.

[39] A. Parisi, M. Plapp, Stability of lamellar eutectic growth, Acta Mater. 56 (2008) 1348.

[40] H. Walker, S. Liu, J.H. Lee, R. Trivedi, Eutectic growth in three dimensions, Metall. Mater. Trans. A 38A (7) (2007) 1417–1425.

[41] M. Perrut, A. Parisi, S. Akamatsu, S. Bottin-Rousseau, G. Faivre, M. Plapp, Role of transverse temperature gradients in the generation of lamellar eutectic solidification patterns, Acta Mater. 58 (2010) 1761–1769.

[42] M. Serefoglu, S. Bottin-Rousseau, S. Akamatsu, G. Faivre, Dynamics of rod eutectic growth patterns in confined geometry, in: Proc. 3rd International Conference on Advances in Solidification Processes, Aachen, Germany/Rolduc, The Netherlands, 7–10 June 2011, in: IOP Conference Series – Materials Science and Engineering, vol. 27, 2012.

[43] A. Parisi, M. Plapp, Defects and multistability in eutectic solidification patterns, Europhys. Lett. 90 (2010) 26010.

[44] M. Perrut, S. Akamatsu, S. Bottin-Rousseau, G. Faivre, Long-time dynamics of the directional solidification of rodlike eutectics, Phys. Rev. E 79 (2009) 032602.

[45] M. Perrut, S. Bottin-Rousseau, G. Faivre, S. Akamatsu, Dynamic instabilities of rod-like eutectic growth patterns: a real-time study, Acta Mater. 61 (2013) 6802–6808, http://dx.doi.org/10.1016/j.actamat.2013.07.054.

[46] R.E. Napolitano, M. Serefoglu, Control and interpretation of finite-size effects and initial morphology in directional solidification of a rod-type eutectic transparent metal-analog, JOM 64 (2012) 68–75, http://dx.doi.org/10.1007/s11837-011-0214-z.

[47] V. Trnovcová, P.P. Fedorov, C. Bàrta, V. Labas, V.A. Meleshina, B.P. Sobolev, Microstructure and physical properties of superionic eutectic composites of the $LiF–RF_3$ (R = rare earth element) system, Solid State Ion. 119 (1999) 173–180.

[48] U. Hecht, V. Witusiewicz, A. Drevermann, S. Rex, Orientation relationship in univariant Al–Cu–Ag eutectics, Trans. Indian Inst. Met. 58 (2005) 545–551.

[49] S. Akamatsu, S. Moulinet, G. Faivre, The formation of lamellar-eutectic grains in thin samples, Metall. Mater. Trans. A 32 (2001) 2039–2048, http://dx.doi.org/10.1007/s11661-001-0016-y.

[50] M. Şerefoğlu, R.E. Napolitano, M. Plapp, Phase-field investigation of rod eutectic morphologies under geometrical confinement, Phys. Rev. E 84 (2011) 011614, http://dx.doi.org/10.1103/PhysRevE.84.011614.

[51] L. Hogan, R. Kraft, F. Lemkey, Eutectic grains, Adv. Mater. Res. 5 (1971) 83–216.

[52] U. Hecht, L. Gránásy, T. Pusztai, B. Böttger, M. Apel, V. Witusiewicz, L. Ratke, J. De Wilde, L. Froyen, D. Camel, B. Drevet, G. Faivre, S. Fries, B. Legendre, S. Rex, Multiphase solidification in multicomponent alloys, Mater. Sci. Eng., R Rep. 46 (2004) 1–49, http://dx.doi.org/10.1016/j.mser.2004.07.002.

[53] S. Akamatsu, S. Bottin-Rousseau, M. Şerefoğlu, G. Faivre, Lamellar eutectic growth with anisotropic interphase boundaries: experimental study using rotational directional solidification, Acta Mater. 60 (2012) 3206–3214.

[54] S. Akamatsu, S. Bottin-Rousseau, M. Şerefoğlu, G. Faivre, A theory of thin lamellar eutectic growth with anisotropic interphase boundaries, Acta Mater. 60 (2012) 3199–3205.

[55] S. Ghosh, A. Choudhury, M. Plapp, S. Bottin-Rousseau, G. Faivre, S. Akamatsu, Interphase anisotropy effects on lamellar eutectics: a numerical study, Phys. Rev. E 91 (2015) 0022407, http://dx.doi.org/10.1103/PhysRevE.91.022407.

[56] S. Ghosh, M. Plapp, Influence of interphase anisotropy on lamellar eutectic growth patterns, Trans. Indian Inst. Met. 68 (2015) 1235–1238, http://dx.doi.org/10.1007/s12666-015-0711-9.

[57] S. Akamatsu, G. Faivre, Traveling waves, two-phase fingers, and eutectic colonies in thin-sample directional solidification of a ternary eutectic alloy, Phys. Rev. E 61 (2000) 3757–3770.
[58] M. Plapp, A. Karma, Eutectic colony formation: a phase-field study, Phys. Rev. E 66 (2002) 061608.
[59] V.T. Witusiewicz, L. Sturz, U. Hecht, S. Rex, Phase equilibria and eutectic growth in quaternary organic alloys amino-methyl-propanediol–(D)camphor–neopentylglycol–succinonitrile (AMPD–DC–NPG–SCN), J. Cryst. Growth 297 (2006) 117–132, http://dx.doi.org/10.1016/j.jcrysgro.2006.09.004.
[60] S. Akamatsu, M. Perrut, S. Bottin-Rousseau, G. Faivre, Spiral two-phase dendrites, Phys. Rev. Lett. 104 (2010) 056101, http://dx.doi.org/10.1103/PhysRevLett.104.056101.
[61] S. Akamatsu, S. Bottin-Rousseau, G. Faivre, E.A. Brener, Scaling theory of two-phase dendritic growth in undercooled ternary melts, Phys. Rev. Lett. 112 (2014) 105502, http://dx.doi.org/10.1103/PhysRevLett.112.105502.
[62] L. Rátkai, A. Szállás, T. Pusztai, T. Mohri, L. Gránásy, Ternary eutectic dendrites: pattern formation and scaling properties, J. Chem. Phys. (2015) 1.
[63] A. Choudhury, M. Plapp, B. Nestler, Theoretical and numerical study of lamellar eutectic three-phase growth in ternary alloys, Phys. Rev. E 83 (2011) 051608, http://dx.doi.org/10.1103/PhysRevE.83.051608.
[64] S. Bottin-Rousseau, M. Şerefoğlu, S. Yücetürk, G. Faivre, S. Akamatsu, Stability of three-phase ternary-eutectic growth patterns in thin sample, Acta Mater. 109 (2016) 259–266, http://dx.doi.org/10.1016/j.actamat.2016.01.065.