Current Opinion in Solid State and Materials Science 20 (2016) 46–54

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cossms

Eutectic and peritectic solidification patterns

Silvère Akamatsu [a], Mathis Plapp [b,*]

[a] Sorbonne Universités, UPMC Univ. Paris 06, CNRS-UMR 7588, Institut des NanoSciences de Paris, F-75005 Paris, France
[b] Condensed Matter Physics, Ecole Polytechnique, CNRS, 91128 Palaiseau, France

ARTICLE INFO

Article history:
Received 5 May 2015
Revised 30 September 2015
Accepted 21 October 2015
Available online 27 October 2015

Keywords:
Solidification
Eutectic alloys
Peritectic alloys
In situ experiments
Phase-field modelling

ABSTRACT

Recent advances in the understanding of eutectic and peritectic two-phase pattern formation under purely diffusive transport are reviewed. The parallel progress of two key techniques, namely, in situ experimentation with model, low-melting transparent and metallic alloys in thin and bulk samples, and numerical phase-field simulations, is highlighted. Experiments and simulations are interpreted in the light of the theory of non-equilibrium pattern formation phenomena. Focus is put on microstructure selection and morphological transitions, multiscale patterns in ternary alloys, and the influence of crystallographic effects on pattern formation. Open problems, for example on crystallographic effects, irregular eutectics, and peritectic solidification, are outlined.

1. Introduction

The solidification of eutectic and peritectic alloys of composition close to a nonvariant point in the phase diagram frequently produces multi-phased microstructures in the bulk. Eutectic or peritectic structures are also frequently found to form during the late stages of a solidification process. Those microstructures are essentially a frozen-in trace of the pattern-formation dynamics at the solidification front [1–3]. The latter is governed by the interplay between solute diffusion in the liquid and the response of the interfaces due to capillary and kinetic effects. We will focus on metallic alloys and organic “metal analogs”, for which the solid–liquid interfaces are non-faceted and kinetic effects can be neglected; irregular eutectics will therefore not be addressed here. We will concentrate on recent developments in this field; earlier works are covered in textbooks [4,5] and previous review articles [6–11].

In recent years, considerable progress on complex morphological features of multiphased solidification microstructures has been made on a fundamental level thanks to the parallel advancement of in situ experimentation and numerical simulations. The rapid development of phase-field modelling [12,13] makes it now possible to perform quantitative simulations of multi-phase solidification in three dimensions for extended systems [14–16]. Experimentally, in addition to major improvements of the classic thin-sample directional solidification technique, novel real-time observation methods have been developed, which allow for the imaging of eutectic front patterns in bulk samples of transparent organic alloys with a micron-scale resolution [17,18]. Moreover, implementing high-resolution X-ray radiography and tomography has brought unprecedented information on solidification microstructures in bulk and thin metallic samples [19].

Theoretical interpretation of the data obtained from experiments and simulations crucially benefits from the concepts and methods of fundamental physics of nonequilibrium pattern formation. The interaction of this field with solidification science started in the 1980s [20] and has been fruitfully pursued since then, thus shedding new light on increasingly complex questions that include microstructure selection and morphological transitions, solute redistribution transients, multiscale patterns in ternary alloys and interfacial-anisotropy (crystallographic) effects. Therefore, in the following, we will seek to establish a close link between experimental and numerical results, and the theory of pattern formation.

To this end, it is useful to concentrate on model (binary and ternary) alloys and investigate them in well-controlled laboratory experiments. In particular, the use of thin samples or microgravity environments can suppress the convective motions in the liquid. This simplifies the numerical treatment, and makes the results directly comparable to theories of diffusion-limited crystal growth. While this approach omits several aspects that are important for practical applications (multiple components, convection), it can validate the theories and models that are needed as a basis for a complete understanding of such situations. Most of the results that are reviewed below have been obtained either by (in situ)

* Corresponding author.
E-mail addresses: silvere.akamatsu@insp.jussieu.fr (S. Akamatsu), mathis.plapp@polytechnique.fr (M. Plapp).

http://dx.doi.org/10.1016/j.cossms.2015.10.002
1359-0286/

directional-solidification experiments, that is, solidification in a fixed temperature gradient of magnitude G, with an imposed velocity V, or by phase-field simulations.

In the following, we will discuss subsequently binary eutectics, with an emphasis on various phenomena that influence the dynamics of two-phase pattern formation, ternary eutectics, in which an entirely new microstructure, namely spiral two-phase dendrites, was discovered, and peritectics. The review will be concluded by a list of what we consider to be important open questions.

2. Binary eutectics

2.1. Background

In a binary eutectic alloy, two distinct solid phases, generically called α and β in the following, coexist with the liquid phase at the eutectic temperature T_E, with the composition C_E of the liquid falling in between the compositions of the two solids. For a range of compositions around C_E, the liquid can solidify into a two-phase composite (coupled growth). For two solid phases with isotropic and nonfaceted solid–liquid interfaces, the theoretical description of this growth mode includes bulk diffusion in the liquid phase, mass conservation at the moving interfaces (Stefan condition), and local equilibrium at interfaces (Gibbs–Thomson equation) and trijunction points (Young's law). The resulting free-boundary problem has been stated in many publications, and can be found for example in Ref. [21].

The cornerstone for our understanding of eutectic growth fronts is the Jackson–Hunt theory [3] (also see the pioneering works by Zener and Hillert [1,2]), which solves an approximate version of this problem for a steady periodic pattern of spacing (spatial period) λ. The interplay between diffusion and capillarity is characterized by a scaling length λ_m (at which the front undercooling exhibits a minimum in directional solidification), which is proportional to $V^{-1/2}$. Eutectic-growth dynamics essentially depends on a single parameter, λ/λ_m, proportional to $\lambda V^{1/2}$, and is little sensitive to the magnitude of the temperature gradient G [22].

The two morphologies that are most frequently observed in eutectic composites are parallel platelets (lamellae) of the two phases, and fibers (rods) of one phase, located on the nodes of a regular triangular lattice, and surrounded by a matrix of the other phase. Jackson and Hunt have calculated λ_m for these two morphologies. In fact, many other arrangements of the solid phases along the (planar) front are also observed. This morphological "multistability" is a direct consequence of the symmetry properties of the system. The same symmetry elements are also exhibited by many other pattern-forming systems with an axial symmetry, such as Rayleigh–Bénard convection, Faraday surface waves, reaction–diffusion systems, and magnetic thin films. Lamellae and fibers in eutectics correspond to regular stripe and dot patterns that are common in these systems. For the present review, it is useful to take advantage of the knowledge accumulated on generic aspects of these systems in the theories of nonequilibrium pattern formation [23,24].

In nonequilibrium pattern forming systems, steady periodic patterns are generally stable over a finite range of values of the spatial period λ, at fixed control parameters. Inside the region of stability in the space of control parameters (*stability balloon*), pattern uniformization is ensured by a generic relaxation mechanism of diffusive nature ("phase" or "spacing" diffusion). The limits of the stability balloon are set by morphological instabilities (bifurcations), which break one or several symmetries of the underlying regular pattern. Outside the basic-state stability balloon, the system restabilizes into a steady, symmetry-broken periodic pattern or displays a complex spatio-temporal dynamics.

These facts imply that in laboratory experiments, particular attention has to be paid to the preparation of the initial state: which kind of pattern forms depends, in practice, on sample history and boundary conditions. This has been explicitly demonstrated for lamellar patterns in a thin-sample geometry [25]. A common directional-solidification protocol (also see numerical simulations [26]) consists of establishing a steady-state pattern at constant V, and observing the response of the system to successive V jumps.

In this way, many results have been obtained in thin-sample directional solidification of transparent alloys. The stability balloon (stable spacings as a function of alloy concentration) has been determined experimentally and numerically. Its limits are set by various oscillatory instabilities for large spacings, and by lamella elimination for small spacings [25–27]. This constitutes a reference basis for more recent studies on bulk solidification, which are reviewed in the next section. Bulk solidification is a much more challenging subject due to the large number of geometrical degrees of freedom (two-dimensional translational and rotational symmetry) of the ("ideal") system. New real-time experimental methods have been set up, which combine the use of a long-distance optical microscope with subsequent image processing for yielding the equivalent of a "top view" of the growth front in samples of inner thickness reaching 1 mm [17,18]. Due to possible thermo-solutal instabilities, experiments are mostly limited to near-eutectic compositions. Efficient and accurate phase-field models for bulk eutectic growth have been developed [28] that have made it possible to perform three-dimensional simulations on a length scale of several microstructural units [14,15].

In the following, we will review the morphological transformations of lamellar and rod eutectics, as well as space–time dynamical features and topological defects which determine the long-time evolution of extended patterns in directional solidification. Finally, the universality of the above-mentioned phenomenology breaks down in more "realistic" situations, when new physical effects (external or internal) break the symmetries of the ideal system. We will consider two dynamic forcing phenomena: the effect of an imperfectly-shaped temperature gradient, and crystallographic effects.

2.2. Dynamics of patterns with isotropic interfaces

Lamellar eutectics. Lamellar eutectic patterns in bulk-sample solidification have been studied both in experiments and simulations [29,30,14]. A new instability mode was identified in the experiments, namely, the zigzag instability (Fig. 1a), which is a transition from straight to chevron patterns or wavy lamellae (for general bases of the zigzag bifurcation, see Ref. [23]). Phase-field simulations in three dimensions [14] have helped to clarify the connection to the results obtained in thin samples [25,26]. Other instability modes, that extend the known two-dimensional modes to three dimensions, do exist but grow more slowly than the zigzag instability for all parameter sets that were investigated. This explains why in the experiments only the zigzag mode was clearly identified.

Let us now turn to the dynamics of extended systems. In the experiments that revealed the existence of the zigzag instability in lamellar eutectics [29], quite frequently the eutectic fronts did not self-organize into well-ordered lamellar arrays, but remained disordered during the entire time of the experiment (Fig. 1b): while the characteristic spacing is clearly visible, the local orientation of the lamellae varies from point to point in space, and no global ordering emerges. In the simulations, this is actually the generic behavior when a mixture of the two phases with random