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Stability of three-phase ternary-eutectic growth patterns in thin sample

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ABSTRACT

Near-eutectic ternary alloys subjected to thin-sample directional solidification can exhibit stationary periodic growth patterns with an ABAC repeat unit, where A, B, and C are the three solid phases in equilibrium with the liquid at the eutectic point. We present an in-situ experimental study of the dynamical features of such patterns in a near-eutectic In–In_2Bi–Sn alloy. We demonstrate that ABAC patterns have a wide stability range of spacing λ at given growth rate. We study quantitatively the λ-diffusion process that is responsible for the spacing uniformity of steady-state patterns inside the stability interval. The instability processes that determine the limits of this interval are examined. Qualitatively, we show that ternary-eutectic ABAC patterns essentially have the same dynamical features as two-phase binary-eutectic patterns. However, lamella elimination (low-λ stability limit) occurs before any Eckhaus instability manifests itself. We also report observations of stationary patterns with an $[AB]_m[AC]_n$ superstructure, where m and n are integers larger than unity.

1. Introduction

The solidification microstructures of ternary eutectic alloys take many different forms depending on the composition and grain structure of the alloy, the geometrical and thermal features of the solidification device, and the solidification history. The most important of these factors are the number of growing phases and the dimensionality of the samples. We are concerned here with two-dimensional three-phase microstructures. These are typically observed in near-eutectic ternary alloys subjected to thin-sample directional solidification (thin-DS). Solidification microstructures are, we recall, nothing else than the trace left behind in the solid by out-of-equilibrium self-organized patterns formed during solidification. At constant solidification rate V and applied thermal gradient G, these patterns generally reach, or, at least, asymptotically tend towards a steady-state. The most well-known example of a steady-state eutectic growth pattern is the two-phase periodic (lamellar) solidification pattern of near-eutectic binary alloys analyzed by Jackson and Hunt (JH) a long time ago [1]. The repeat unit of such a pattern is an AB pair of lamellae, where A and B are the two solid phases in equilibrium with the liquid at the eutectic point. These AB patterns have mirror symmetry with respect to the mid-plane of the lamellae, which is actually a condition for their steadiness. Regarding ternary eutectic alloys, the basic repeat unit of stationary thin-DS patterns is ABAC, where A, B and C are the three eutectic solid phases. It has mirror symmetry with respect to the mid-plane of the B and C lamellae (Fig. 1). This was previously highlighted by Witusiewicz and coworkers in the In–In_2Bi–Sn alloy [2] and a transparent organic alloy [3], and numerically demonstrated by Choudhury et al. [4] (also see Refs. [5,6] regarding bulk solidification). However, the large-scale dynamics of the ABAC patterns has not yet been studied.

Here we present an experimental study of the morphological stability of ABAC growth patterns during directional solidification of a near-eutectic In–In_2 Bi–Sn alloy. We used very thin (≈ 13 μm thick) samples in order for the system to be quasi two-dimensional and rid of convection flows in the liquid. Quantitative results that are presented below were obtained by studying in real time the dynamic response of pre-uniformized ABAC patterns to upward or downward V-jumps. Qualitatively, the results may be best

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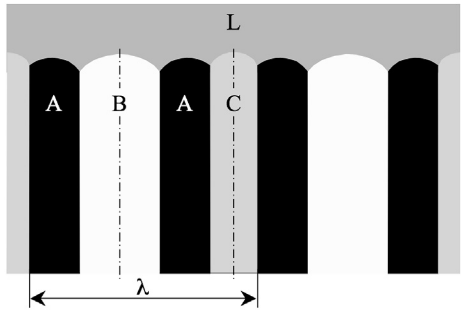

Fig. 1. Sketch of the three-phase ABAC repeat unit of a ternary-eutectic directional-solidification pattern. The thermal gradient is oriented vertically. In a thin sample of the eutectic In–In_2Bi–Sn alloy, the letters A, B, and C refer to the In_2Bi, β-In, and γ-Sn crystal phases, respectively. L: liquid. λ: local spacing value.

understood through a comparison with the known dynamical features of the binary AB patterns [1,7–10]: (i) binary AB patterns have a wide stability range of spacing λ at given V; (ii) any spatial variation of λ that is confined within the stability interval is damped out over time through a long-range process called spacing-diffusion or λ-diffusion, which leads asymptotically to a perfectly periodic (uniform) pattern; (iii) the upper limit of the λ-range of stability (λ_{sup}) is due to the onset of oscillations leading, at still larger λ-values, to lamella splitting; (iv) the lower stability limit (λ_{inf}) corresponds to an instability of the λ-diffusion process, namely, a change of sign of the λ-diffusion coefficient (sometimes referred to as an Eckhaus instability [11]), which leads to lamella elimination; (v) λ_{sup} varies with V as $V^{-1/2}$ and is independent of G; in other words, it obeys the well-known JH scaling law $\lambda_{sup} \propto \lambda_m$, where λ_m is a scaling length that varies with V as $V^{-1/2}$; (vi) λ_{inf} does not obey the JH scaling law, but depends on both V and G in such a way that, at fixed G, the width of the stability range relative to λ_m, i.e. $(\lambda_{sup} - \lambda_{inf})/\lambda_m$, increases as V decreases. In the following, we shall call spacing, and denote it by λ, the width of an ABAC repeat unit in a three-phase eutectic-growth pattern. Which of the features listed above hold true for ternary-eutectic ABAC patterns? The main results of this study may be summed up as follows: ternary ABAC patterns have the same dynamical features as binary AB patterns, except for one significant aspect, namely, lamella elimination is not provoked by an Eckhaus instability but by a qualitatively different phenomenon, most probably, some short-wavelength instability of the ABAC pattern.

In the remainder of the text, we first present the experimental methods (Section 2). We then give some important details about the preparation of extended ABAC lamellar patterns in large eutectic grains (Section 3). The main results (stability diagram, instability mechanisms, and complex patterns) are presented and discussed in Section 4. A conclusion is proposed in the last section.

2. Experimental methods

The In–Bi–Sn ternary phase diagram has a nonvariant eutectic point at the temperature of 332 K (T_E) and the composition of In-20.7 at% Bi-19.1 at% Sn (C_E) [12]. The solid phases in equilibrium with the liquid at this point are the intermetallic compound In_2Bi, the β-In phase and the γ-Sn phase. For brevity, we will generally call these phases A, B, and C, respectively. In_2Bi has a hexagonal structure; β-In and γ-Sn have body-centered tetragonal structures. An alloy of nominal composition C_E was prepared by weighting the appropriate quantities of 99.999% pure indium, bismuth and tin (Goodfellow), and mixing them in the liquid state under a primary vacuum. The actual composition was within less than 0.05 at% of C_E. Glass-wall samples with inner dimensions of $4 \times 50 \times 0.013$ mm^3 were filled with molten alloy using a vacuum-suction method.

Details about the thin-DS stage and the method of observation used can be found elsewhere [10,13]. Let us simply mention that the thin-DS stage is basically made of two temperature-regulated copper blocks separated by a 5-mm gap. The thermal gradient in the region of the solidification front is $G = 8 \pm 0.9$Kmm^{-1}. The growth direction **z** is parallel to the thermal gradient and opposite to the pulling direction. The **y**-axis is perpendicular to the sample plane, whereas the **x**-axis is parallel to the isotherms. The V-range explored is 0.01–0.8 μms^{-1}. The solidification front is observed in real time in the **y** direction (side view) with a reflected-light optical microscope (Leica DMI 5000) equipped with a monochrome digital camera (Scion), connected to a PC for image capturing, processing and analysis. With this method, what is actually observed is the surface of contact between the metallic film and a flat glass wall. After contrast enhancing, the β-In/glass surfaces appeared white and the In_2Bi/glass surfaces black; both the γ-Sn/glass and the liquid/glass surfaces appeared light-grey (Fig. 1). We also performed ex-situ metallographic observations of transverse cross-sections in some samples. These showed that the interphase boundaries were perpendicular to the glass walls, as expected, validating the use of side-view images for dynamical studies of isotropic grains, as we explain shortly.

3. Extended ABAC lamellar patterns

Concerning binary AB eutectic patterns, it is known that near-uniform eutectic patterns can only be grown in samples consisting of “floating” eutectic grains with a size much larger than the spatial average of λ. To explain the origin for this requirement, we must recall the following facts [14,15]: (i) a (eutectic) grain is a portion of the solid, inside which the crystal-lattice orientation of each of the eutectic phases is uniform; (ii) eutectic growth patterns are sensitive to the degree of anisotropy of the surface energies of the various interfaces present, especially, AB interphase boundaries; this degree of anisotropy depends on the orientation of the different phases with respect to one another and the sample, and therefore varies from grain to grain; (iii) eutectic grains can be classified into two broad categories called “floating” and “locked”. The floating grains are those in which anisotropy effects are sufficiently weak for the dynamical features of the eutectic patterns to be those that are reviewed in the Introduction (including, in particular, uniformisation over time by λ-diffusion). In locked grains, on the contrary, surface tension anisotropy has dramatic effects on the pattern formation. These grains most probably have a special orientation relationship between A and B, and low-energy planes for the AB boundaries. The interphase boundaries become locked onto these low-energy directions entailing that λ-diffusion is blocked; (iv) the boundaries between floating eutectic grains are a source of perturbations (lamella terminations, long-range spacing gradients) preventing the growth pattern to approach a fully steady state [14]. The same considerations apply to ternary ABAC patterns. In this case, however, three different orientation relationships (AB, BC, CA) come into play. The floating grains are those, in which the AB, BC and CA boundaries have weak anisotropy.

A large floating ABAC grain in near-eutectic In–In_2Bi–Sn is shown in Fig. 2. The experimental procedure used to create such grains was as follows. After partial directional melting, the system was maintained at rest ($V = 0$) in order to let it return to equilibrium. During this period, two thin solid layers progressively formed between the liquid and the unmelted part of the solid: a polycrystal layer of C (i.e. γ-Sn) in equilibrium with the liquid, and, immediately below it, a two-phase layer of AC (i.e. In_2Bi+γ-Sn). This indicated that the actual composition of the alloy was slightly off-