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Acta Materialia 60 (2012) 3840–3848

Acta MATERIALIA

www.elsevier.com/locate/actamat

Competition of the primary and peritectic phases in hypoperitectic Cu–Sn alloys solidified at low speed in a diffusive regime

J. Valloton *, J.-D. Wagnière, M. Rappaz

Computational Materials Laboratory, Institute of Materials, Ecole Polytechnique Fédérale de Lausanne, Station 12, CH-1015 Lausanne, Switzerland

Received 18 November 2011; received in revised form 5 March 2012; accepted 17 March 2012
Available online 1 May 2012

Abstract

Directional solidification experiments on hypoperitectic Cu–Sn alloys have been performed at very low velocity in a high thermal gradient to ensure planar front growth of both phases. The diameter of the sample has been reduced to 500 μm to strongly reduce convection. Lamellar and fibrous peritectic cooperative growth of the primary α- and peritectic β-phases has been observed on length spanning several millimeters. For the first time in a high solidification interval peritectic alloy, a quenched interface of both phases in contact with the liquid has been obtained. An unexpectedly high volume fraction of the primary phase, which furthermore fluctuates over time, has been observed. This is attributed to the transient state of the (α + β) growth front to a steady state and the associated evolution of the large diffusion layer ahead of the solid–liquid interface.

Keywords: Peritectic solidification; Directional solidification; Copper alloys; Cooperative growth

1. Introduction

Peritectic phase diagrams are frequently observed in many commercially important alloys, such as steels (Fe–C, Fe–Ni), brasses (Cu–Zn), bronzes (Cu–Sn) and some aluminium alloys (Al–Ti). In such systems, the primary α-phase reacts upon cooling with the liquid phase to yield the peritectic β-phase at the peritectic temperature T_{per}. In the hypoperitectic region of peritectic metallic systems, various new microstructures have been revealed during directional solidification experiments at low growth rates, i.e. where both α- and β-phases would grow independently as planar fronts [1–8]: (i) discrete bands of α- and β-phases; (ii) partial bands or islands of one phase in the matrix of the other phase; and (iii) cooperative growth of both phases with a planar solid–liquid interface. Up to now, cooperative growth of the two phases has only been observed in peritectic alloys with a small solidification interval (a few kelvin) [8–10]. Kohler et al. [11,12] were able to produce recently such microstructure in hypoperitectic Cu–Sn alloys with a high freezing range of ~100 K, but with considerable solutal convection in their samples. In the present work, directional solidification experiments are carried out on Cu–21 wt.% Sn alloys at a high G_l/V_p ratio, but with a diameter of the samples reduced to 500 μm, which strongly limits convection.

2. Theoretical background

The microstructures found in the hypoperitectic region at low growth rates result from the specific shape of the peritectic phase diagrams (Fig. 1). Consider a hypoperitectic alloy of nominal composition C_0 directionally solidified at a low velocity that guarantees planar front growth for both phases. During the initial transient, the solute rejected in the liquid by the primary phase builds up a solute boundary layer. Accordingly, the temperature of the interface decreases from $T^{\alpha}_{liq}(C_0)$ to the steady-state solidus temperature $T^{\alpha}_{sol}(C_0) = T^{\alpha}_{liq}(C_0/k_{\alpha})$, located below T_{per}, where k_{α} is the corresponding partition coefficient. When the composition of the liquid at the α–liquid interface, $C^{*\alpha}_{l}$, exceeds the

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* Corresponding author. Tel.: +41 216933943.
E-mail address: jonas.valloton@epfl.ch (J. Valloton).

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http://dx.doi.org/10.1016/j.actamat.2012.03.030

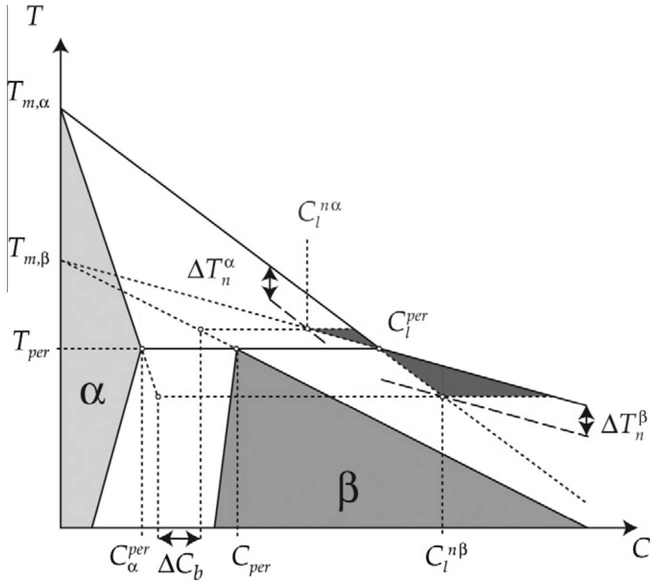

Fig. 1. Schematic peritectic phase diagram with the banding mechanism developed by Trivedi [1] for initial alloy compositions situated in the banding window ΔC_b, for k_α and $k_\beta < 1$. ΔT_n^α and ΔT_n^β correspond to the nucleation undercoolings for the α- and β-phases, respectively.

liquid composition at the peritectic temperature $C_l^{per} = C_l(T_{per})$, it becomes undercooled with respect to the β-phase. Thus, β can nucleate heterogeneously if its corresponding nucleation undercooling, ΔT_n^β, is reached. Once the peritectic phase has nucleated, growth competition between the two phases is initiated. Assuming infinitely fast lateral spreading of the newly nucleated phase (or, equivalently, infinitely high nucleation density) [1], the β-phase blocks any further growth of the primary α-phase. As the solute boundary layer decreases, i.e. less solute rejected by the β-phase since $k_\beta > k_\alpha$, the temperature of the interface increases and tends to reach $T_{sol}^\beta(C_0) = T_{liq}^\beta(C_0/k_\beta)$, the steady-state temperature of the β-planar interface. However, for alloy compositions in the hypoperitectic range, $T_{sol}^\beta(C_0)$ is located above T_{per}. Then, as the composition $C_l^{*\beta}$ at the β–liquid interface falls below C_l^{per}, the liquid becomes now undercooled with respect to the α-phase. Similarly, when the undercooling reaches a critical value, ΔT_n^α, the primary phase can nucleate and cover the peritectic phase and this banding cycle can then start over again. Knowing the nucleation undercoolings of the two phases, a banding window for stable cycles, ΔC_b, can be determined, as shown in Fig. 1 [1]. For hypoperitectic compositions below this range, the primary phase is at a steady state before ΔT_n^β is reached, whereas alloys with a composition above ΔC_b exhibit a single α-to-β transition, with the peritectic phase reaching a steady state before any new nucleation of the primary phase.

In order to explain the formation of islands rather than bands, the above approximation of infinitely fast lateral spreading must be relaxed. Indeed, while the newly nucleated phase spreads laterally, the first phase continues to grow along the thermal gradient and, depending on the growth conditions, it might engulf the forming band. Using a multi-phase field, Lo et al. [7] showed that island growth occurs for internuclei distances below a critical distance, while band growth is expected above this distance.

Finally, another interesting microstructure that can form in peritectic alloys at low growth rate is the simultaneous growth of α- and β-lamellae. Although similar to eutectic coupled growth, the α- and β-lamellae of peritectic alloys both reject solute elements ahead of the interface. Predicted in 1959 by Chalmers [13], coupled growth was first observed in 1994 in Ni–Al by Lee and Verhoeven [9], and then in Fe–Ni by Vandyoussefi et al. [10] and Dobler et al. [8]. Directional solidification experiments and multiphase field simulations [7,8,14,15] showed that lamellar structures can start growing from islands, providing the distance separating the islands falls within a range of stable lamellar spacings [7].

The observations of bands, islands and cooperative lamellar growth in peritectics has been limited up to now to small solidification interval alloys, typically with $\Delta T_0 = \left(T_{liq}^\alpha(C_0) - T_{per}\right) \simeq 5\,\text{K}$. Recently, Kohler et al. [11,12] investigated peritectic solidification in the Cu–Sn system, an alloy with a solidification interval ΔT_0 nearly 20 times that of Fe–Ni in the hypoperitectic region (around 100 K). Using a liquid metal cooling (LMC) Bridgman solidification setup with quench, these authors observed all three of the peritectic microstructures discussed above – lamellae, bands and islands – but their sample showed appreciable convection. Using synchrotron-based X-ray microtomography, Rappaz et al. [16] confirmed a new growth mechanism of bands: α- and β-phases can be totally interconnected in three dimensions and bands (or islands) can result from an overlay mechanism, rather than from subsequent nucleation events. When the lateral growth of a new layer is too fast, an instability can lead to the formation of a lamellar structure as for eutectic alloys.

3. Experimental method

Many Cu–Sn phase diagrams are available in the literature, and most often these diagrams differ slightly from each other. Notably, the reported peritectic temperature T_{per} varies from 795.7 to 798 °C, and the equilibrium concentrations C_α^{per}, C_{per} and C_l^{per} are not defined accurately. The most widely used Cu–Sn phase diagram, shown in Fig. 2, comes from the Metals Handbook, Metallography, Structures and Phase Diagrams from the American Society for Metals (ASM) [17]. Recently, Liu et al. [18] reinvestigated this phase diagram (see the enlargement in Fig. 2) and showed that the $\beta - \gamma$ domain is actually a succession of second-order ordering transitions and that the $\beta \rightarrow \alpha + \gamma$ and $\beta + \text{liquid} \rightarrow \gamma$ invariant reactions are nonexistent. β and γ are thus considered to be one and the same phase.

In practice, two solid-state transformations within the β-phase can complicate the analysis of the resulting micro-