Unidirectional solidification of a Zn-rich Zn–2.17 wt%Cu hypo-peritectic alloy

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Abstract

Unidirectional solidification of a Zn-rich Zn–2.17 wt%Cu hypo-peritectic alloy has been carried out to investigate the microstructure evolution over the growth velocity range 0.02–4.82 mm/s at a temperature gradient of 15 K/mm by means of the Bridgman technique. Regular and plate-like two-phase cellular structures were observed in samples grown at growth velocities \( V \) above 0.48 and 2.64 mm/s, respectively. The dominant microstructure in samples grown below 0.22 mm/s was dendrites of primary \( \varepsilon \) in a matrix of secondary \( \eta \). Intercellular spacing \( \Lambda \) decreased with increasing growth velocity \( V \) such that \( \Lambda V^{1/2} \) is a constant of 316 ± 55 \( \mu \text{m}^{3/2}/\text{s}^{1/2} \). Secondary dendrite arm spacing \( \lambda_2 \) of primary \( \varepsilon \) decreased with increasing \( V \) such that \( \lambda_2 V^{1/3} \) is a constant of 14.9 ± 0.9 \( \mu\text{m}^{2/3}/\text{s}^{1/3} \). The observed transition from regular cells to plate-like cells of \( \eta \) is discussed on the basis of competitive growth and crystallographic effect. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

Peritectic solidification involves one solid phase reacting with a liquid phase on cooling to produce a second solid phase, e.g. \( \varepsilon + L \rightarrow \eta \) in the Zn–Cu peritectic system [1]. Studies on unidirectional solidification of peritectic alloys have been carried out on Zn–Ag [2], Sn–Cd [3,4], Pb–Bi [5], Ni–Al [6], Ti–Al [7] and Zn–Cu [8] over the past four decades. However, all of these investigations were conducted at lower growth velocity, i.e. \( V < 0.5 \text{ mm/s} \). In the present studies on the solidification of peritectic Zn-rich Zn–Cu alloys, the growth velocity \( V \) has been extended to 4.82 mm/s. The authors’ earlier results showed the formation of a eutectic-like lamellar structure with non-aligned dendrites of primary \( \varepsilon \) in a Zn–3.37 wt%Cu hyper-peritectic alloy [8]. In the present paper, the authors report the microstructure evolution of a Zn-rich Zn–2.17 wt%Cu hypo-peritectic alloy over the growth velocity range 0.02–4.82 mm/s at a temperature gradient of 15 K/mm by means of the Bridgman technique.

2. Experimental

Zn–2.17 wt%Cu alloy was prepared from high-purity Zn (99.999%) and Cu (99.99%) melted by induction heating in air in a high-purity graphite crucible. The prepared alloy was then cast into rods of 1.1 or 2.5 mm diameter and up to 100 mm length by vacuum injection into quartz tubes. These rods were remelted for Bridgman solidification at withdrawal velocities of between 0.02 and 0.5 mm/s for the larger rod diameter and 0.5–4.82 mm/s for the smaller rod diameter, in equipment described elsewhere [9]. The operative temperature gradient during solidification was 15 K/mm. Longitudinal and transverse sections of the solidified samples were prepared for optical microscopy and for microstructure length scale measurement. X-ray diffraction using CuK\( \alpha \) radiation was carried out on powder obtained from the samples by filing. Measurements of secondary dendrite arm spacing (\( \lambda_2 \)) and \( \eta \) intercellular spacing (\( \Lambda \)) were made on longitudinal and transverse sections, respectively, by the linear intercept method, taking at least eight readings per condition.

3. Results

Fig. 1(a)–(c) shows the optical micrographs of longitudinal
and transverse sections from Zn–2.17 wt%Cu grown at 0.16, 1.52 and 4.15 mm/s, respectively, showing the microstructure evolution from typical peritectic to regular cells and to plate-like cells with increasing V. The microstructure was typically peritectic with dendrites of primary ε in a matrix of η when the growth velocity was below 0.22 mm/s (as shown in Fig. 1(a)). The microstructure became regular cellular η plus intercellular ε without primary dendrites of ε when the growth velocity V was between 0.48 and 2.06 mm/s (Fig. 1(b)). The microstructure of samples grown at a velocity of between 2.64 and 4.82 mm/s exhibited plate-like cellular η plus intercellular ε without primary dendrites of ε (Fig. 1(c)). For fully regular cellular structure of η with intercellular ε, it should be noted that there were some very small primary dendrites in some samples grown at growth velocity <0.75 mm/s, but the number was extremely small (less than 10 in the cross-section). Therefore, this structure was designated as a fully cellular structure, in which the volume fraction of the intercellular ε is about 30%. For the fully plate-like cellular structure, the cells of η were parallel to the growth direction and the volume fraction of the intercellular ε was about 13%, being lower than that for regular cellular structure. The ε intercellular spacing A and ε secondary dendrite arm spacing λ₂ are listed as functions of V in Table 1 and plotted in Fig. 2. The ε intercellular spacing A decreases from 16.3 to 4.3 μm with increasing growth velocity V from 0.48 to 4.82 mm/s such that \( A V^{1/2} \) is a constant of 316 ± 55 μm\(^{3/2}/s^{1/2}\). The secondary dendrite arm spacing λ₂ of primary ε decreases from 6.0 to 2.5 μm with increasing V from 0.02 to 0.22 mm/s such that \( λ₂ V^{1/2} \) is a constant of 14.9 ± 0.9 μm\(^{3/2}/s^{1/2}\).

4. Discussion

Two-phase regular [3,4,6] and plate-like [7,8] cellular growth have been reported for various peritectic systems. Boettinger [3] and Brody and David [4] observed that at a value of \( G/V \) slightly below that determined by constitutional supercooling, two-phase Sn–Cd hyper-peritectic alloys with compositions between 1.0 and 1.3 wt%Cd solidified as coarse cells of α (primary phase) and intercellular β (secondary phase). Lee and Verhoeven [6] reported a two-phase cellular structure of cellular γ' and intercellular γ in Ni–Al peritectic alloys with compositions between 23 and 24 at.%Al involving the reaction γ + L → γ'. The presently observed plate-like cellular structure with Zn–2.17 wt%Cu is similar to that in peritectic Ni–Al and different from that in peritectic Sn–Cd because the dominant cells were formed by the secondary phase (or peritectic phase) and not the primary phase (or peritectic phase). Meissen and Busse [7] found that the microstructure of hyper-peritectic Ti–53.4 at.%Al directionally solidified at a very low growth velocity of 0.05 mm/min was plate-like, and consisted of two phases (primary α and secondary γ) parallel to the growth direction. However, the plate-like growth for the present alloy occurred at a velocity 1000 times that for Ti–53.4 at.%Al. The volume fraction of minor phase in the present samples was about 13%, much less than that of about 50% for the Ti–53.4 at.%Al sample [7]. Formations of plate-like cellular structure were also observed in Zn-rich Zn–2.5 at.%Cd and Cd-rich Cd–2.5 to 4.2 at.%Zn off-eutectic alloys grown at velocities below 0.1 mm/s [10].

Factors such as crystallography and competitive growth are expected to affect the transition from regular to plate-like cellular growth of η. The cell configuration may be determined by crystallographic orientation, particularly for a strongly hexagonal system such as that with the present alloy. Regular and plate-like cells grow in different orientations
| V (mm/s) | Structure  | \(A\) (of \(\eta\)) (\(\mu\)m) | \(\Delta V^{[2]} \) (\\mu\text{m}^{1/2}s^{-1/2}) | \(\lambda_2\) (of \(\epsilon\)) (\(\mu\)m) | \(\lambda_1 V^{[2]} \) (\\mu\text{m}^{1/2}s^{-1/2}) |
|----------|------------|-------------------------------|---------------------------------|-----------------|---------------------------------|
| 4.82     | \(\epsilon M_{\eta}^a\) | 4.3 ± 0.7                     | 299                             | 2.5 ± 0.2       | 15.0                             |
| 4.15     | \(\epsilon M_{\eta}^b\) | 4.1 ± 0.3                     | 264                             | 2.7 ± 0.2       | 14.7                             |
| 3.54     | \(\epsilon M_{\eta}^c\) | 4.5 ± 0.4                     | 268                             | 2.9 ± 0.2       | 13.5                             |
| 2.98     | \(\epsilon M_{\eta}^d\) | 5.0 ± 0.4                     | 273                             | 3.6 ± 0.3       | 15.2                             |
| 2.64     | \(\epsilon M_{\eta}^e\) | 6.3 ± 0.2                     | 324                             | 4.1 ± 0.3       | 14.6                             |
| 2.06     | \(\epsilon M_{\eta}^f\) | 6.3 ± 0.3                     | 286                             | 6.0 ± 0.4       | 16.3                             |
| 1.52     | \(\epsilon M_{\eta}^g\) | 7.2 ± 0.9                     | 280                             | 316 ± 55 (mean) | 14.9 ± 0.9 (mean)                |
| 1.00     | \(\epsilon M_{\eta}^h\) | 13.5 ± 1.6                    | 427                             | 0.22            | 14.9 ± 0.9 (mean)                |
| 0.75     | \(\epsilon M_{\eta}^i\) | 13.9 ± 1.8                    | 380                             | 0.16            | 14.9 ± 0.9 (mean)                |
| 0.48     | \(\epsilon M_{\eta}^j\) | 16.3 ± 2.7                    | 357                             | 0.10            | 14.9 ± 0.9 (mean)                |
| 0.22     | \(\epsilon M_{\eta}^k\) | 2.5 ± 0.2                     | 15.0                             | 0.075           | 14.9 ± 0.9 (mean)                |
| 0.16     | \(\epsilon M_{\eta}^l\) | 2.7 ± 0.2                     | 14.7                             | 0.045           | 14.9 ± 0.9 (mean)                |
| 0.10     | \(\epsilon M_{\eta}^m\) | 2.9 ± 0.2                     | 13.5                             | 0.020           | 14.9 ± 0.9 (mean)                |

During directional solidification. If the crystal grows in a (1120) direction with three planes (0001), (1101) and (1110) containing the cell boundary, sixfold asymmetrical cells of \(\eta\) will form [11]. On the other hand, if the crystal grows in a (2110) direction with basal plane (0001) containing the cell boundary [10,12], plate-like cells of \(\eta\) will grow while the crystallographic c-axis of \(\eta\)(Zn) is perpendicular to the direction of growth and to the long axis of the cells [10]. The velocity-dependent transition from regular to plate-like cellular growth of \(\eta\) is also affected by competitive growth during solidification. As will now be shown, the plate-like cells grow at larger undercooling at low \(V\) and at relatively lower undercooling at high \(V\) compared with regular cells. The tip undercooling \(\Delta T\) for plate-like cells was given by Hunt [12] as

\[
\Delta T = \frac{GD}{V} + \frac{\sqrt{2GVl}}{D} + \frac{(1 - k)VT}{D} - \frac{\Gamma}{\sqrt{2G}} \left[ m(1 - k)C_0 + \frac{kGD}{V} \right]
\]

(1)

where \(G\) is the temperature gradient, \(D\) the solute diffusion coefficient in the liquid, \(\Gamma\) the Gibbs–Thomson coefficient, \(m\) the liquidus slope, \(k\) the equilibrium distribution coefficient, \(C_0\) the initial alloy concentration and \(l\) the half width of the cells, given by

\[
l = \left\{ \frac{-F_D [m(1 - k)C_0 + kGDV^{-1}]}{G^2V} \right\}^{1/2}
\]

(2)

By fitting part of a sphere to the derived cell tip, the tip undercooling for hexagonal cells was also given by Hunt [12] as

\[
\Delta T = \frac{GD}{V} + \frac{G\lambda^2}{\sqrt{2D}} + \frac{2(1 - k)VT}{D} - \frac{2\sqrt{2\Gamma}}{G\lambda^2} \left[ m(1 - k)C_0 + \frac{kGD}{V} \right]
\]

(3)
where

\[ \lambda = \left\{ \frac{4TD[m(1-k)C_0 + kGDV^{-1}]}{G^2V} \right\}^{1/4} \] (4)

Based on the hemispherical cell-tip approximation, the tip undercooling for cylindrical cells was also given by Kurz and Fisher [13] as

\[ \Delta T = mC_0 \left[ 1 - \frac{1}{1 - (1-k)P_c} \right] \] (5)

where

\[ P_c = \pi \left( \frac{VT}{m(k-1)C_0D} \right)^{1/2} \] (6)

The actual interface temperature \( T_i \) is then calculated as

\[ T_i = T_0 - \Delta T \] (7)

where \( T_0 \) is the equilibrium temperature of the interface. Taking \( m = 3.19 \text{ K/ wt\%} \) [14], \( k = 1.62 \) [14], \( D = 2.04 \times 10^{-3} \text{ mm}^2/\text{s} \) [9], \( \Gamma = 1.1 \times 10^{-4} \text{ K mm} \) [9], \( G = 15 \text{ K/mm} \), \( C_0 = 2.17 \text{ wt\% Cu} \), and \( T_0 = 426.4 ^\circ\text{C} \) for Zn–2.17 wt% Cu alloy, the interface temperature of regular and plate-like cells of \( \gamma \) can be calculated using Eqs. (1)–(7). Fig. 3 shows the interface temperature \( T^H \) of plate-like cells for Zn–2.17 wt% Cu as a function of \( V \) calculated by the Hunt model [12] compared with \( T^K \) of regular hexagonal cells evaluated from the Kurz and Fisher model [13], which indicates two transition velocities between regular and plate-like cellular growth, i.e., \( V_a \) and \( V_b \). If \( V < V_a \) or \( V > V_b \), regular cells dominate; but if \( V_a < V < V_b \), plate-like cells are more stable. For peritectic Zn–2.17 wt% Cu, the calculated \( V_a \) and \( V_b \) are about 0.2 and 10 mm/s, respectively. \( V_a \) is thus smaller by a factor of 10 than the presently observed transition velocity, i.e., 2.64 mm/s. \( V_b \) is not observed in the present case since the velocity is beyond the upper limit of the Bridgman equipment employed. Nevertheless, as for \( T^H \) and \( T^K \) obtained by Hunt model [12] on the same assumptions, Fig. 3 shows that the growth of plate-like cells are more stable than regular cells at growth velocities of above 0.04 mm/s but at \( V < 0.04 \text{ mm/s} \), both regular and plate-like cellular growth are possible.

5. Conclusions

Fully regular and plate-like cellular growth have been observed in a peritectic Zn-rich Zn–2.17 wt% Cu alloy with one of the phases in a low volume fraction. Inter cellular spacing decreases with increasing growth velocity \( V \) such that \( AV^{1/2} \) is a constant of 316 ± 55 \( \mu \text{m}^{3/2}/\text{s}^{1/2} \). The transition from regular to plate-like cellular growth of \( \gamma \) is possibly interpreted primarily as an effect of competitive growth.

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