

Model for calculation of microstructural development in rapidly directionally solidified immiscible alloys^①

ZHAO Jiur-zhou(赵九洲)

(Institute of Metal Research, The Chinese Academy of Sciences, Shenyang 110016, China)

[Abstract] A model has been developed for the calculation of the microstructural evolution in a rapidly directionally solidified immiscible alloy. Numerical solutions have been performed for Al-Pb immiscible alloys. The results demonstrate that at a higher solidification velocity a constitutional supercooling region appears in front of the solid/liquid interface and the liquid-liquid decomposition takes place in this region. A higher solidification velocity leads to a higher nucleation rate and, therefore, a higher number density of the minority phase droplets. As a result, the average radius of droplets in the melt at the solid/liquid interface decreases with the solidification velocity.

[Key words] immiscible alloy; directional solidification; microstructure; theory and modeling

[CLC number] TG 249.7

[Document code] A

1 INTRODUCTION

In order to take the maximum advantage of immiscible alloys with a phase diagram as depicted in Fig. 1 for proposed applications, it is desirable to produce aligned fibrous or dispersed microstructures that contain a high volume fraction of the hypermonotectic immiscible phase. Directional solidification experiments done before showed that although it should, theoretically, be possible to obtain an aligned fibrous microstructure similar in appearance to the structure formed for monotectic composition by establishing steady-state growth conditions using the proper thermal gradient to growth rate ratio $(G/R)^{[1]}$, it seems difficult to succeed in doing so. It was found that the composition of the melt adjusts itself to the monotectic one very quickly as a hypermonotectic sample is placed in a vertical temperature gradient because of the convective instability and, therefore, it is difficult to obtain a composite microstructure^[2,3]. It should be mentioned that the experiments usually were carried out by using low growth velocities to achieve a high G/R ratio which is believed to be beneficial to the stabilization of a planar solidification interface and couple growth. When solidified at a higher solidification rate constitutional supercooling may appear in front of the solidification interface and, therefore, liquid-liquid decomposition takes place in this region. If the solidification velocity is high enough, the spatial separation of the two liquid phases may be restrained and a well dispersed structure can be obtained. The experiments of the melt spun Al-In alloy has proved this^[4]. But till now no theoretical works have been done on the microstructure evolution

in a rapidly directional solidified immiscible alloy. In this paper we present a numerical model describing the microstructure evolution in a rapidly directionally solidified immiscible alloy by taking into account the common action of nucleation, diffusional growth and droplet motion in front of the solidification interface. The model will be used to predict the solidification process of hypermonotectic Al-Pb alloys.

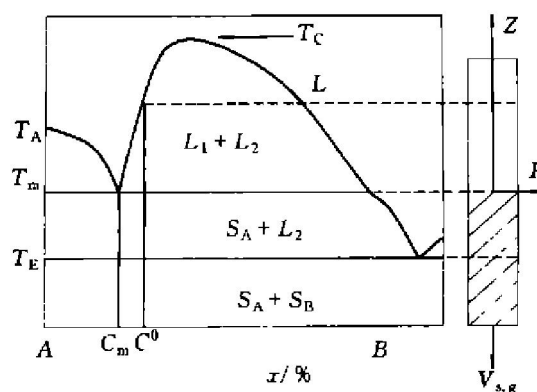


Fig. 1 Schematic phase diagram of alloy with liquid miscibility gap
(u_S is downward and u_M is upward,
 u_S and u_M see Eqn. (1))

2 THEORETICAL MODEL

Supposing a constitutional supercooling region exists in advance of the solidification interface, the nucleation of the minority phase droplets may take place in this region. The nucleated droplets grow by the diffusion of solute in the matrix. They can also settle due to the gravity (Stokes motion) or migrate due to a temperature gradient (Marangoni migration). The author describe the microstructure evolu-

① **[Foundation item]** Project supported by the Hundred Talent Person Plan of China

[Received date] 2001- 09- 11; [Accepted date] 2001- 10- 31

tion of a polydispersed system of droplets by defining a droplet radius distribution function $f(R, z)$. $f(R, z) dR$ is the number of droplets per unit volume at position z in a size class $R, R + dR$. This function obeys a continuity equation as given below under the common action of the nucleation, the diffusional growth and the motion of droplets:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R}(vf) + \frac{\partial(u_M - u_S - R_s)f}{\partial z} = \left. \frac{\partial I}{\partial R} \right|_{R=R^*} \quad (1)$$

where $u_S(R, z)$ and $u_M(R, z)$ are the Stokes and the Marangoni velocities of droplets, respectively, $I(R, z)$ is the nucleation rate which can be predicted with the classical theory of the homogeneous nucleation^[5~7], v is the diffusional growth rate of droplets (for details see Ref. [5] and Ref. [6]). The author neglect in this approximation the collision and coagulation of droplets.

In the two liquid phase region $z_{S/L} < z < z_{L_1+L_2}$ the solute transfers both through the diffusion controlled process and the motion of droplets. The stable state concentration field obeys a partial differential equation:

$$\begin{aligned} \frac{\partial D}{\partial z} \frac{\partial S}{\partial z} + R_s \frac{\partial C_m}{\partial z} - \frac{4}{3}\pi \cdot \\ \left| \int_0^\infty \frac{(\partial u_M - u_S)f(C_\beta - C_m)}{\partial z} R^3 dR \right| = 0 \quad (2) \\ \left. \frac{\partial S}{\partial z} \right|_{z=z_{L/S}} \\ C_m(z > z_{L_1+L_2}) = C_0 \end{aligned}$$

where $S(z) = C_m(z) - C_{m,\infty}$ is the supersaturation with $C_m(z)$ being the mean field concentration in the matrix liquid and $C_{m,\infty}$ the equilibrium composition at a flat interface boundary, $C_\beta(z)$ is the concentration of the liquid within the droplet, C_0 is the initial composition of the alloy.

Coupling a given temperature profile and the concentration field obtained by solving Eqn. (2) with the phase diagram, the droplet distribution function in the melt is determined via a solution of Eqn. (1).

3 NUMERICAL METHOD

The numerical method used in this analysis is based on the finite volume method^[8]. Calculations are performed for hypermonotectic Al-Pb alloys which are of special importance in connection with advanced bearings for automotive applications^[9]. To be accurate the author use a phase diagram calculated directly from the thermodynamic data given by Yu et al^[10]. The interface tension between the droplet and the matrix was taken as^[11] 0.12 J/m^2 at the monotectic reaction temperature $T = 932.6 \text{ K}$ and it was related

with temperature by $\sigma(T) = \sigma_0(1 - T/T_c)^{1.26}$ ^[12, 13] with $T_c = 1695.4 \text{ K}$ being the critical temperature and σ_0 a constant that can be determined from the value of the interfacial tension at the monotectic temperature. The diffusion coefficient of Pb in the matrix is estimated as $5 \times 10^{-9} \text{ m}^2/\text{s}$ at the monotectic reaction temperature. It was related with temperature by $D(T) = D_0 T^{2.9}$ ^[9]. This temperature dependence of the diffusion coefficient might look strange comparing with the often used Arrhenius-type law. For metallic melts, however, there is an increasing amount of data showing that the simple power law is valid. It is at least a good approximation in the temperature range under consideration for immiscible alloys. Recent results confirm this relation for Al-Pb and Al-In alloys^[9].

In this calculation the author assume that at the solid/liquid interface the local monotectic reaction process redistributes the solute in the liquid by forming a lot of very fine droplets which do not interact with the droplets stemming from the liquid-liquid decomposition in the miscibility gap. The droplets of the monotectic reaction are not counted in this calculation.

4 NUMERICAL RESULTS AND DISCUSSION

4.1 Comparison with analytical solution

Assuming that an initially single phase hypermonotectic alloy melt is quenched instantaneously to a temperature below the binodal line and that the dimensionless supersaturation of solute in the matrix $S = C_m - C_{m,\infty}$ is constant during the phase transformation, then the nucleation rate is time independent and any nucleus created has just the critical radius R^* . Eqn. (1) can be solved analytically supposing that the effect of the droplet curvature on the solubility of solute in the matrix be negligible and that the droplets move only according to the well known Stokes motion.

$$f = IR/DS,$$

if

$$R_{\max} \leq [4DS(H - z)/K_S]^{1/4},$$

else

$$f = 0 \quad (3)$$

where $K_S = 2(\rho^d - \rho^m)(\eta^d - \eta^m)g/3\eta^m(2\eta^m + 3\eta^d)$. ρ^d and ρ^m are the viscosities of the droplet and the matrix, respectively, η^d and η^m are the densities and g is the gravity acceleration, H is the height of the sample.

Supposing an Al+ 5% Pb sample of 10 mm in height is quenched from a temperature above the binodal line to 797°C , the steady state distribution of droplet radius at the position $z = 8 \text{ mm}$ is shown in Fig. 2 according to Eqn. (3). The same problem is solved numerically with the method outlined above.

The result is also shown in Fig. 2. The agreement is excellent. There is, however, one important difference. The analytical solution of Eqn. (3) is exact triangle dropping from its maximum value to zero at the biggest droplet radius, while the numerical solution yields a distribution curve which is smeared around this maximum value and is a continuous function of the droplet radius rather than a step function. This is the natural result of the numerical method reflecting the continuous distribution of droplet size.

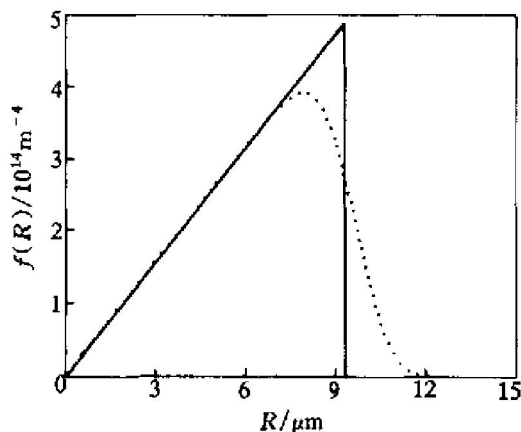


Fig. 2 Droplet size distribution function for Al+5% Pb alloy quenched from 1 000 °C to 797 °C (Solid line represents prediction of analytical solution of Eqn. (1) and dotted line numerical solution)

4.2 Numerical results and discussion

Supposing an Al+ 5% Pb alloy directionally solidify in a temperature gradient of 400 K/cm at a rate of 28 mm/s. Fig. 3 shows the upper consolute temperature of the melt ahead of the solidification interface and the temperature profile in the melt together with the nucleation rate of the minority phase droplets. It indicates that a constitutional supercooling region does appear in advance of the interface. Fig. 4 shows the nucleation of Pb-rich

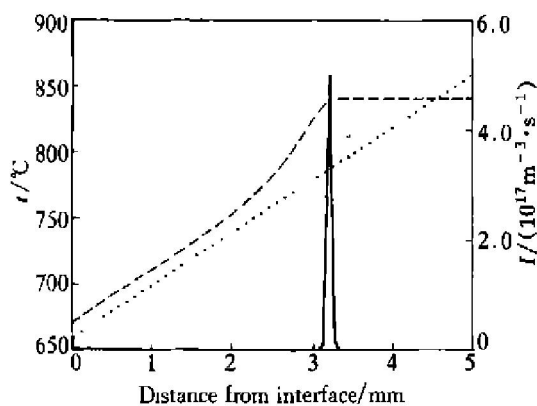


Fig. 3 Temperature profile (dotted line), upper consolute temperature (dashed line) and nucleation rate (solid line) in front of solid/ liquid interface when Al+ 5% Pb alloy solidified at velocity of 28 mm/s in temperature gradient of 400 K/cm

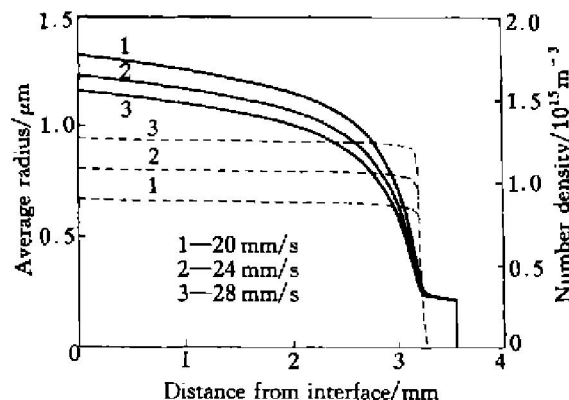


Fig. 4 Average droplet radius (solid lines) and number densities of drops (dashed lines) in front of solidification interface when Al+ 5% Pb alloy solidified at different velocities in temperature gradient of 400 K/cm

phase droplets takes place in a region around the supersaturation peak. The nucleated drops grow as they move towards the solidification interface and, therefore, the average droplet radius increases with approaching the solid/ liquid interface, and the number density of droplets is also shown in Fig. 4. It also increases with approaching the solid/ liquid interface due to the common actions of the Marangoni and Stokes motion of droplets (Fig. 5).

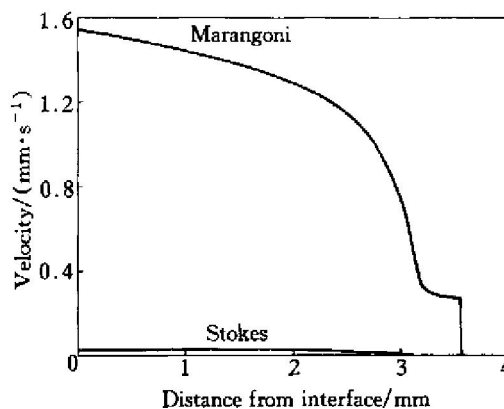


Fig. 5 Stokes and Marangoni velocities of local average size drops in front of solidification interface when Al+ 5% Pb alloy solidified at velocity of 28 mm/s in temperature gradient of 400 K/cm

Fig. 6 shows the results calculated for different solidification velocities. Numerical results show that a higher solidification rate leads to a larger supersaturation and, therefore, a higher nucleation rate. As the result, the number density of droplets increases and the average droplet radius decreases with increasing solidification velocity (Fig. 4).

5 CONCLUSION

A numerical model has been presented describing

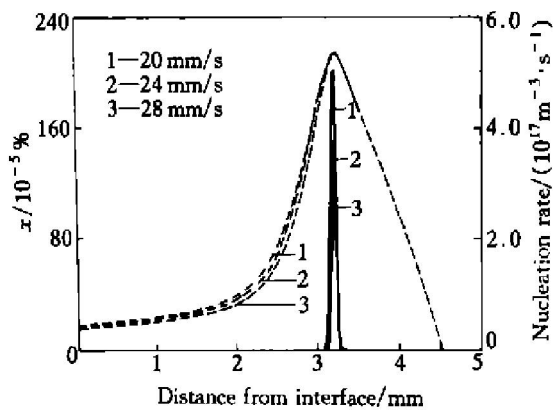


Fig. 6 Supersaturation (dashed lines) and nucleation rate (solid lines) in front of solidification interface when Al+ 5% Pb alloy solidified at different velocities in temperature gradient of 400 K/cm (x represents mole fraction)

the microstructural evolution in a rapidly directionally solidified immiscible alloy. With this model the microstructural evolution of the Al-Pb bearing alloys solidified under the conditions of a vertical Bridgman-Stockbarger-type directional solidification is investigated by coupling a given temperature field and a calculated concentration field with the phase diagram. The numerical results show that at a larger solidification velocity a constitutional supercooling region appears in front of the solid/liquid interface and the liquid-liquid decomposition takes place in this region. At a constant temperature gradient, a higher solidification velocity leads to a higher nucleation rate and, therefore, a higher number density of the minority phase droplets. As a result, the average radius of droplets in the melt at the solid/liquid interface decreases with the solidification velocity.

[REFERENCES]

[1] Andrews J B. Solidification of immiscible alloys [A].

- Ratke L. Immiscible Liquid Metals and Organics [C]. Germany: DGM-Informationsgesellschaft, 1993, 199– 222.
- [2] Grugel R N, Angus H. Alloy solidification in systems containing a liquid miscibility gap [J]. Metall Trans A, 1981, 12A: 669– 681.
- [3] Grugel R N, Lograsso T A, Hellawell A. Directional solidification of alloys in systems containing a liquid miscibility gap [A]. Rindone G E. Materials Processing in the Reduced Gravity Environment of Space [C]. Elsevier Science Publishing Company Inc, 1982. 553– 561.
- [4] LIU Y, GUO J J, SU Y Q, et al. Microstructure of rapidly solidified Al-In immiscible alloy [J]. Trans Non-ferrous Met Soc China, 2001, 11(1): 84– 89.
- [5] Zhao J Z, Ratke L. Microstructure evolution of immiscible alloys during cooling through the miscibility gap [J]. Modelling Simul Sci Eng, 1998, 6: 123– 139.
- [6] Zhao J Z, Ratke L. Kinetics of phase separation in immiscible alloy [J]. Z Metallkd, 1998, 89: 241– 246.
- [7] Granasy L, Ratke L. Homogeneous nucleation within the liquid miscibility gap of Zr-Pb alloys [J]. Scripta Metall Mater, 1993, 28: 1329– 1334.
- [8] Patankar S V. Numerical Heat Transfer and Fluid Flow [M]. New York: McGraw-Hill, 1980.
- [9] Ratke L, Diefenbach S. Liquid immiscible alloys [J]. Mat Sci Eng, 1995, R15: 263– 343.
- [10] Yu Surr-Keun, Sommer F, Predel B. Isopiestic measurements and assessment of the Al-Pb system [J]. Z Metallkd, 1996, 87: 574– 580.
- [11] Eustathopoulos N, Chatain D, Vahlas C. Tensions interfaciales et mecanismes de croissance monotectique des alliages immiscibles binaires [J]. Scripta Metall, 1984, 18: 1– 6.
- [12] Falk F. Interface tension in partially miscible liquid [A]. Ratke L. Immiscible Liquid Metals and Organics [C]. Germany: DGM-Informationsgesellschaft, 1993, 93– 100.
- [13] Falk F, Langbein D, Heide W. Miscibility diagram and interface tension of the binary liquid system hexane-dione-heptane [A]. Ratke L. Immiscible Liquid Metals and Organics [C]. Germany: DGM-Informationsgesellschaft, 1993, 111– 118.

(Edited by HUANG Jin-song)