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Estimation of interdendritic undercooling during freezing of ternary and quaternary aluminium alloys

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Expressions have been developed for the maximum interdendritic supercooling during the freezing of ternary and quaternary systems. The actual undercoolings during freezing of several ternary and quaternary aluminium base alloys have been computed. Using available data for the measured diffusion coefficients and assuming reasonable values for other diffusion coefficients, it is shown that the interdendritic supercooling does not exceed one degree centigrade in all the aluminium alloys investigated. In fact, in most of the alloys it is less than a tenth of a degree centrigrade.

1. Introduction

In recent years many attempts have been made to understand the dentritic solidification processes of multicomponent systems through experimental and analytical approaches. The experimental approaches have concentrated [1–4] on measurements of actual dendrite arm spacings as a function of freezing time in a variety of moulds. The analytical approaches have concentrated on the interface stability in ternary systems [5, 6].

Limited computations are available [7] for values of interdendritic supercoolings in ternary and quaternary aqueous solutions where the values of distribution coefficients are very small and have been neglected. In this paper, we have measured the dendrite arm spacings as a function of freezing rate in two ternary and one quaternary aluminium base alloys and have estimated the maximum interdendritic undercooling during solidification.

2. Theoretical analysis

Fig. 1 shows the parallel plate shaped dendrites growing next to each other in the early stages of solidification with the interdentritic liquid being gradually consumed. The concentration gradients and the supercoolings are shown schematically in Fig. 1a and b.

During solidifcation these solutes will be rejected at the interface and will diffuse into the interdendritic liquid. The diffusion of these solutes will be given by

$$J_1 = -D_{11}\frac{\partial C_1}{\partial x} - D_{12}\frac{\partial C_2}{\partial x} - D_{13}\frac{\partial C_3}{\partial x}, \quad (1)$$

$$J_2 = -D_{21}\frac{\partial C_1}{\partial x} - D_{22}\frac{\partial C_2}{\partial x} - D_{23}\frac{\partial C_3}{\partial x}, \quad (2)$$

and

$$J_3 = -D_{31}\frac{\partial C_1}{\partial x} - D_{32}\frac{\partial C_2}{\partial x} - D_{33}\frac{\partial C_3}{\partial x}, \quad (3)$$

where x is the distance from the interface, J_1, J_2 and J_3 are fluxes; C_1, C_2 and C_3 are the concentrations of the solutes in the interdendritic liquid and D_{11}, D_{22} and so on are the diffusion coefficients. The rates of change of solute concentration with temperature, θ, in the interdendritic liquid are given by

$$\frac{\partial C_1}{\partial \theta} = D_{11}\frac{\partial^2 C_1}{\partial x^2} + D_{12}\frac{\partial^2 C_2}{\partial x^2} + D_{13}\frac{\partial^2 C_3}{\partial x^2} \quad (4)$$

$$\frac{\partial C_2}{\partial \theta} = D_{21}\frac{\partial^2 C_1}{\partial x^2} + D_{22}\frac{\partial^2 C_2}{\partial x^2} + D_{23}\frac{\partial^2 C_3}{\partial x^2} \quad (5)$$

$$\frac{\partial C_3}{\partial \theta} = D_{31}\frac{\partial^2 C_1}{\partial x^2} + D_{32}\frac{\partial^2 C_2}{\partial x^2} + D_{33}\frac{\partial^2 C_3}{\partial x^2}. \quad (6)$$

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Furthermore, expressing $\partial C_1/\partial\theta$, $\partial C_2/\partial\theta$ and $\partial C_3/\partial\theta$ analogous to the material balance described in earlier works [7, 8] we find

$$\frac{\mathrm{d}C_1}{\mathrm{d}\theta} = \bar{C}_1(1-k_1)\frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta}, \tag{7}$$

$$\frac{\mathrm{d}C_2}{\mathrm{d}\theta} = \bar{C}_2(1-k_2)\frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta}, \tag{8}$$

and

$$\frac{\mathrm{d}C_3}{\mathrm{d}\theta} = \bar{C}_3(1-k_3)\frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta} \tag{9}$$

where k_1, k_2 and k_3 are distribution coefficients, f_s is the fraction of solid, and $\mathrm{d}f_\mathrm{s}/\mathrm{d}\theta$ is the change in fraction of solid with respect to temperature.

Substituting values of $\mathrm{d}C_1/\mathrm{d}\theta$, $\mathrm{d}C_2/\mathrm{d}\theta$ and $\mathrm{d}C_3/\mathrm{d}\theta$ into Equations 4, 5 and 6 and double integrating between the limits of the problem, results in

$$\frac{\bar{C}_1\ (1-k_1)L^2}{8}\ \frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta} = D_{11}\Delta C_1 + D_{12}\Delta C_2 + D_{13}\Delta C_3, \tag{10}$$

$$\frac{\bar{C}_2\ (1-k_2)L^2}{8}\ \frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta} = D_{21}\Delta C_1 + D_{22}\Delta C_2 + D_{23}\Delta C_3, \tag{11}$$

and

$$\frac{\bar{C}_3\ (1-k_3)L^2}{8}\ \frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta} = D_{31}\Delta C_1 + D_{32}\Delta C_2 + D_{33}\Delta C_3, \tag{12}$$

where L is the dendrite arm spacing. Equations 10, 11 and 12 can be solved for ΔC_1, ΔC_2 and ΔC_3 giving

$$\Delta C_1 = \frac{L^2}{8}\ \frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta} \times \frac{[\bar{C}_1\ (1-k_1)(D_{22}D_{33} - D_{23}D_{32}) + \bar{C}_2\ (1-k_2)(D_{13}D_{32} - D_{12}D_{23}) + \bar{C}_3\ (1-k_3)(D_{12}D_{23} - D_{13}D_{32})]}{(D_{11}D_{22}D_{33} - D_{11}D_{23}D_{32} - D_{12}D_{21}D_{33} + D_{12}D_{23}D_{31} + D_{13}D_{21}D_{32} - D_{13}D_{31}D_{22})} \tag{13}$$

$$\Delta C_2 = \frac{L^2}{8}\ \frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta} \times \frac{[\bar{C}_1\ (1-k_1)(D_{21}D_{33} - D_{23}D_{31}) + \bar{C}_2\ (1-k_2)(D_{13}D_{31} - D_{11}D_{33}) + \bar{C}_3\ (1-k_3)(D_{11}D_{23} - D_{13}D_{21})]}{(D_{11}D_{22}D_{33} - D_{11}D_{23}D_{32} - D_{12}D_{21}D_{33} + D_{12}D_{23}D_{31} + D_{13}D_{21}D_{32} - D_{13}D_{31}D_{22})} \tag{14}$$

$$\Delta C_3 = \frac{L^2}{8}\ \frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}\theta} \times \frac{[\bar{C}_1\ (1-k_1)(D_{21}D_{32} - D_{22}D_{31}) + \bar{C}_2\ (1-k_2)(D_{12}D_{31} - D_{11}D_{32}) + \bar{C}_3\ (1-k_3)(D_{11}D_{22} - D_{12}D_{21})]}{(D_{11}D_{22}D_{33} - D_{11}D_{23}D_{32} - D_{12}D_{21}D_{33} + D_{12}D_{23}D_{31} + D_{13}D_{21}D_{32} - D_{13}D_{31}D_{22})} \tag{15}$$

The total interdendritic supercooling can be approximated to

$$\Delta T = \frac{\partial T}{\partial C_1}\Delta C_1 + \frac{\partial T}{\partial C_2}\Delta C_2 + \frac{\partial T}{\partial C_3}\Delta C_3, \tag{16}$$

where $\partial T/\partial C_1 = m_1$, $\partial T/\partial C_2 = m_2$ and $\partial T/\partial C_3 = m_3$ are slopes of the binary liquidus approximated to the same as in quaternary system. The expression for the total undercooling developed in the interdendritic region would be

$$\Delta T = m_1\Delta C_1 + m_2\Delta C_2 + m_3\Delta C_3. \tag{17}$$

The expressions for ternary systems can be derived using a similar procedure considering diffusion of only two solutes. The final expression for ΔT in a ternary system would be

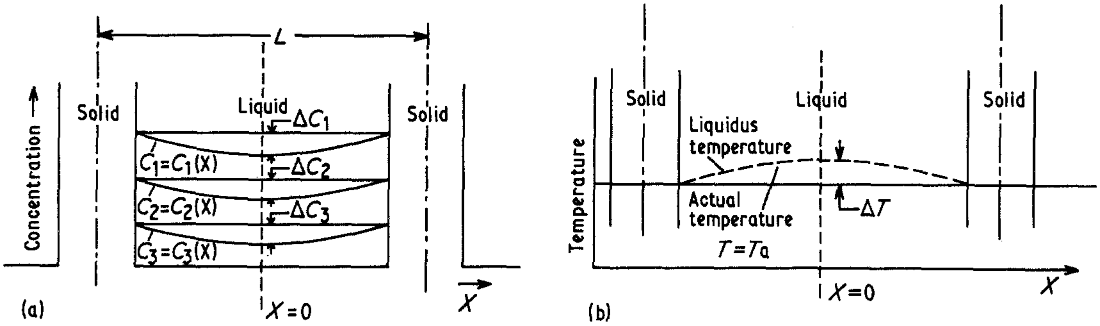

Figure 1 Concentration and temperature profiles in the interdendritic liquid.

$$\Delta T = \frac{L^2}{8}\,\frac{\mathrm{d}f_s}{\mathrm{d}\theta}\,\frac{\{m_1\,[\bar{C}_1\,(1-k_1)D_{22}-\bar{C}_2\,(1-k_2)D_{12}]+m_2\,[\bar{C}_2\,(1-k_2)D_{11}-\bar{C}_1\,(1-k_1)D_{21}]\}}{D_{11}D_{22}-D_{12}D_{21}} \tag{18}$$

3. Experimental work

Cylindrical moulds of 100 mm diameter and 150 mm height were prepared using CO_2 sand, and cast iron chills of different volumetric heat capacities were placed at the bottom of the mould cavity during moulding to obtain varying freezing rates.

Melting was carried out using pure constituents in a salamandar plumbage crucible using a resistance furnace. After taking the melt to the required superheat of 80° C, it was degassed by a N_2 + Cl_2 mixture. Cooling curves at different locations along the length of the castings were obtained using thermocouples located at 3, 6 and 12 cm from the top of the mould and connected to a high speed single point recorder. Final dendrite arm spacings were measured on samples sliced at fixed locations at room temperature. The cooling curves obtained were used to compute the freezing range and the total solidification time. The average freezing rate, $\mathrm{d}f_s/\mathrm{d}\theta$ was computed as inverse of total freezing time.

4. Results and conclusions

The values of $L^2/8\,(\mathrm{d}f_s/\mathrm{d}\theta)$ corresponding to various experimentally determined values of L, the final dendrite spacing observed after complete solidification, and $\mathrm{d}f_s/\mathrm{d}\theta$, the average freezing rate (inverse of total freezing time) are given in Table I. Values of available diffusion coefficients, (measured by other workers), estimated values of those not available and the computed values of ΔT are shown in Table II [9, 10]. The values of ΔT in Table II indicates that even if the assumed values of the main diffusion coefficients are varied between 10^{-5} and 10^{-6} and the cross-diffusion coefficients between 10^{-6} to 10^{-9}, the calculated values of ΔT lie in the range 0.004 to 0.1° C. In fact, the diffusion coefficients will vary in a much narrower range within these limits and the range of supercoolings will be further narrowed down within the range 0.004 to 0.1° C. The values of ΔT for these ternary and quaternary systems are of the same order of magnitude as those cal-

TABLE I Variation of L with $L^2/8\,(\mathrm{d}f_s/\mathrm{d}\theta) \times 10^{-9}$

System	$\mathrm{d}f_s/\mathrm{d}\theta$ (sec^{-1})	L (10^{-5} m)	$\frac{L^2}{8}\frac{\mathrm{d}f_s}{\mathrm{d}\theta} \times 10^{-9}$
Al–10.8 wt % Mg–0.35 wt % Fe	0.85	3.10	1.02
	0.84	3.15	1.04
	0.83	3.20	1.06
Al–12 wt % Si–0.6 wt % Fe	2.08	7.88	12.14
	1.39	9.00	14.05
	1.04	11.00	15.73
Al–8 wt % Si–3.1 wt % Ni–1 wt % Mg	3.30	6.10	15.35
	2.80	6.60	15.24
	1.45	8.80	14.04

TABLE II Calculations of interdendritic supercoolings in ternary and quaternary systems

Alloy system	$\frac{L2}{8} \frac{df_S}{d\theta}$ (10^{13} m^2 sec^{-1})	Diffusion coefficients (m^2 sec^{-1})									ΔT (° C)
		D_{11}	D_{22}	D_{12}	D_{21}	D_{33}	D_{13}	D_{23}	D_{31}	D_{32}	
Al–10.8 Mg* 0.35 Fe	1.04	10^{-9}	10^{-9}	10^{-10}	10^{-10}						0.0042
		10^{-9}	10^{-9}	10^{-11}	10^{-11}						0.0043
		10^{-9}	10^{-9}	10^{-13}	10^{-13}						0.0043
		10^{-10}†	10^{-9}	10^{-10}	10^{-10}						0.0420
		10^{-9}	10^{-10}	10^{-10}	10^{-10}						0.0420
		10^{-10}†	10^{-10}	10^{-11}	10^{-11}						0.0421
Al–12 Si–‡ 0.6 Fe	13.97	10^{-9}	10^{-9}	10^{-10}	10^{-10}						0.0132
		10^{-9}	10^{-9}	10^{-11}	10^{-11}						0.0130
		10^{-9}	10^{-9}	10^{-13}	10^{-13}						0.0132
		10^{-10}	10^{-9}	10^{-10}	10^{-10}						0.0135
		10^{-9}	10^{-10}	10^{-10}	10^{-10}						0.1280
		10^{-9}	10^{-10}	10^{-11}	10^{-11}						0.1310
Al–8 Si 3.15 § Ni–1 Mg	14.88	10^{-9}	5×10^{-9}†	10^{-11}	5×10^{-12}	10^{-10}†	10^{-12}	5×10^{-12}	10^{-12}	10^{-12}	0.0949
		10^{-9}	10^{-9}	10^{-10}	10^{-10}	10^{-9}	10^{-10}	10^{-10}	10^{-10}	10^{-10}	0.0670
		10^{-9}	10^{-9}	10^{-11}	10^{-11}	10^{-9}	10^{-11}	10^{-11}	10^{-11}	10^{-11}	0.07130
		10^{-9}	10^{-9}	10^{-13}	10^{-13}	10^{-9}	10^{-13}	10^{-13}	10^{-13}	10^{-13}	0.0708

†Measured values reported for binaries.

*Binary slopes $m_1 = -5.00$, $m_2 = -0.36$ and distribution coefficients $k_1 = 0.375$, $k_2 = 0.00$

‡Binary slopes $m_1 = -1.00$, $m_2 = -0.36$ and distribution coefficients $k_1 = 0.125$, $k_2 = 0.00$

§Binary slopes $m_1 = -0.75$, $m_2 = -3.50$ and $m_3 = -6.00$ and distribution coefficients $k_1 = 0.17$, $k_2 = 0.00$ and $k_3 = 0.20$

culated for binary Al–Cu alloys [8]. This indicates that even when two or three atomic species are simultaneously being redistributed at the solid–liquid interface the interdendritic supercoolings in aluminium alloys do not exceed one degree centigrade.

Since it was not possible to observe the dendrite spacings during solidification, the final dendrite spacings, L at $f_s \rightarrow 1$, observed after the completion of solidification have been related to the average freezing rate. The dendrite spacings measured at any other fraction of solid are also likely to relate to the freezing rate in the same fashion. In any case, the solidification times are reasonably small to have significant dendrite coarsening.*

The cooling rate $df_s/d\theta$ will change during the freezing cycle. This phenomenon was analysed for unidirectional freezing of aqueous solution by Rohatgi and Adams [11]. Such an analysis has not been carried out for the present alloy systems due to lack of thermophysical data, instead average freezing rates have been rated to final dendrite spacings.

The basic expression developed in this paper can be used to calculate interdendritic undercooling in any ternary and quaternary systems, provided the values of diffusion coefficients, distribution coefficients, slopes of liquidus and relationship between dendrite arm spacings and freezing time are known.

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References

1. G. E. NEREO, R. F. POLICH and M. C. FLEMINGS, *Mod. Castings* February (1965) 57.
2. R. F. POLICH and M. C. FLEMINGS, *Mod. Castings* February (1965) 84.
3. M. C. FLEMINGS, D. R. PIORIER, R. V. BARONE and H. D. BRODY, *J. Iron Steel Inst. (Lond.)* April (1970) 371.
4. J. K. McCAULEY and F. C. LANGENBERG, *J. Metals* March (1965) 318.
5. D. E. COATES and J. S. KIRKALDY, *J. Crystal Growth,* **3–4** (1968) 549.
6. D. E. COATES, S. V. SUBRAMANIAN and G. R. PURDY, *Trans. AIME* **242** (1969) 800.
7. P. K. ROHATGI, E. J. BRUSH, S. M. JAIN and C. M. ADAMS, Jr, *Mater. Sci. Eng.* **13** (1974) 3.
8. P. K. ROHATGI and C. M. ADAMS, Jr, *Trans. AIME* **239** (1967) 1737.
9. M. C. FLEMINGS, "Solidification Processing" (McGraw-Hill, USA, 1974).
10. TAYLOR LYMAN (ED.), "Metals Hand-Book–Phase Diagrams" ASM, Vol. 8, 8th Edition.
11. P. K. ROHATGI and C. M. ADAMS, Jr, *Trans. AIME* **239** (1967) 850.

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*N.B. Dendrite coarsening implies even smaller ΔT at the beginning of solidification.