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Dendritic Growth in the Carbon Tetrabromide and Hexachlorethane System

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Dendritic microstructures are the most frequently observed solidification microstructures in metallic alloys. In addition, the evolution of the steady-state dendritic structures with well-developed sidebranches is one of the complex and fascinating problems in our understanding of pattern formation in physical and biological systems.[1] Consequently, a significant number of theoretical and experimental studies have been carried out to understand precisely how the microstructural scales of dendrites, *viz.*, dendrite tip radius, primary spacing, and secondary arm spacing, are related to the driving force. Often it is rationalized that the microstructural scales of dendritic morphology become finer with the increasing driving forces, because a finer scale can efficiently dissipate the latent heat of fusion or can readily redistribute solute with the increase in the solidification rate. However, it has been recognized for a long time that for a given driving force, an infinite number of solutions are possible, which is consistent with the latent heat removal or with the solute redistribution. A mathematical solution of this problem was first obtained by Ivantsov.[2] In contrast, experimental studies show a unique selection of dendrite tip radii for a given driving force. Thus, one of the challenging problems in the theory of dendritic growth has been to understand the criterion that the system follows in selecting the unique dendrite tip radius from an infinite set of solutions of the thermal and mass transport equations.

For a number of years, it was assumed that the dendrite in an undercooled melt selects the tip radius which corresponds to the maximum in the growth rate. The invalidity of such an assumption was documented by Glicksman and co-workers[3,4,5] by their very careful and thorough experimental studies in a well-characterized system of pure succinonitrile. In an analogous problem of directional solidification, the experimental studies by Trivedi and co-workers[6,7,8] and Esaka and Kurz[9] have shown the invalidity of the criterion based on the minimum undercooling at the interface. Langer and Müller-Krumbhaar[10] subsequently examined the selection criterion based on the stability of the dendrite tip. They carried out a linear stability analysis of the Ivantsov parabola and showed that of all possible solutions of the transport equations, only a finite number of solutions give rise to a stable tip radius. The largest stable radius was found to agree remarkably well with the experimental results of Glicksman *et al.*[3] Consequently, Langer and Müller-Krumbhaar[10] proposed the *marginal stability* criterion in which the system selects the dendrite tip radius that is just stable with respect to the tip-splitting phenomenon. The marginal stability criterion was also found to explain the experimental results on the directional solidification of the succinonitrile-acetone system.

One of the drawbacks of the marginal stability criterion is that there is no rationale for the selection of the marginally stable state over all other stable states. Furthermore, Langer and Müller-Krumbhaar[10] carried out the linear stability analysis of an isothermal paraboloid, which is not the self-consistent shape, when surface energy effects are present in the system. Although the surface energy effect is small, it is nevertheless very important, since it must be present to stabilize the dendrite tip with respect to the tip-splitting instability. Several self-consistent models of dendritic growth have recently been developed.[11-16] They show that no self-consistent steady-state dendrite growth is possible when the effects of isotropic surface energy or interface kinetics, however small, are included in the model. It is only when the anisotropy in the interface energy is taken into account that a self-consistent steady-state dendrite growth is possible. Furthermore, they find that there is only one solution that is stable with respect to the tip-splitting phenomenon.[17,18] This unique dendrite tip selection criterion is called the solvability approach, which for small Peclet number conditions, gives the result

$$m_L G_C - G = \Gamma/\sigma^* R^2 \qquad [1]$$

where G_C is the concentration gradient at the unperturbed interface being considered, m_L is the slope of the liquidus, R is the radius of the dendrite tip, and Γ is the ratio of surface energy to the entropy of fusion per unit volume. The value of $G = (K_S G_S + K_L G_L)/(K_S + K_L)$. Thus, for systems with $K_S = K_L$, $G = (G_L + G_S)/2$. The term σ^* is a constant which depends on the surface energy anisotropy parameter, ε, and the solvability criterion predicts that $\sigma^* \sim \varepsilon^{1.75}$, for $\varepsilon \ll 1$. It should be noted that Eq. [1] also precisely describes the prediction of the marginal stability criterion, except that the value of σ^* is predicted to be a numerical constant, equal to $\sim$0.025, for all systems. In succinonitrile, where the anisotropy in the surface energy is small, both the marginal stability and the solvability criteria predict the value of σ^* to be around 0.02. Thus, it has not been possible to test these theories from the results in the succinonitrile

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system, so it is necessary to examine other systems where the anisotropy parameter is slightly higher. Therefore, the major aim of this work is to present directional solidification results in the carbon tetrabromide and hexachlorethane system. Both hypoeutectic and hypereutectic compositions were studied so that dendrites of carbon tetrabromide as well as of hexachlorethane could be examined. For both these cases, VR^2 was found to be constant, and from these results, the values of σ^* were determined.

Directional solidification experiments were carried out, using a Hele-Shaw cell in a temperature gradient stage that is described by Mason and Eshelman.[19] The velocity with which the cell was driven externally was first calibrated by using a linear variable differential transformer and periodically checked by observing the motion of a micrometer slide under the microscope. A steady-state interface motion was ensured by examining the location of the dendrite tip with time under the microscope, which remained unaltered under steady-state growth conditions. The temperature gradient at the interface was measured by a calibrated thermocouple which was placed inside the cell.

The carbon tetrabromide and hexachlorethane system was chosen for the present study since all relevant physical properties of this system have been measured.[20] Also, the value of the diffusion coefficient has been determined from detailed experimental studies to characterize the smallest stable eutectic spacing.[21] The values of the parameters for this system are given in Table I. The materials were first purified by the procedure described earlier by Seetharaman and Trivedi.[21] The carbon tetrabromide (CBr_4)-hexachlorethane (C_2Cl_6) system has a eutectic at 8.4 wt pct hexachlorethane. Consequently, we selected two compositions, a hypoeutectic composition with 7.9 wt pct hexachlorethane and a hypereutectic alloy containing 10.5 wt pct hexachlorethane. During the solidification of the hypoeutectic alloy, the solidification structure consists of carbon tetrabromide dendrites with interdendritic eutectic. On the other hand, the hypereutectic alloy exhibits primary dendrites of hexachlorethane with interdendritic eutectic behind the front. Typical dendritic structures for these two compositions are shown in Figure 1.

Directional solidification experiments were carried out over the velocity range of 0.2 to 20.0 μm/s, and the temperature gradient was maintained at 3.0 K/mm. The steady-state dendritic structures were photographed, from which the dendrite tip radius, R, primary spacing, λ_1, and the initial secondary arm near the dendrite tip, λ_2, were measured. The results for CBr_4 and C_2Cl_6 are shown in Figure 2. Both R and λ_2 were found to decrease with the increase in velocity, whereas λ_1 exhibited a maximum. These results show the same behavior as that found in the succinonitrile-acetone system.[6] The dendrite tip radii in the CBr_4 and C_2Cl_6 systems were found to vary as $V^{-0.53+0.03}$ and $V^{-0.47\pm0.03}$, respectively. Thus, the values of VR^2 in these two systems were found to be nearly constant. The least-squares line for VR^2 equal to constant gave the following relationships:

$$VR^2 = 978 \pm 8\ \mu\text{m}^3/\text{s} \quad \text{for } CBr_4 \qquad [2]$$

$$VR^2 = 124 \pm 13\ \mu\text{m}^3/\text{s} \quad \text{for } C_2Cl_6 \qquad [3]$$

The initial secondary spacing near the dendrite tip was found to vary with velocity as $V^{-0.44+0.11}$ and $V^{-0.45\pm0.025}$ for CBr_4 and C_2Cl_6 systems, respectively. These relationships also show that $V\lambda_2^2$ is nearly constant for these two systems.

We shall first compare our results with the theoretical predictions of Eq. [1]. For dendritic structures under directional solidification conditions, the temperature gradient term in Eq. [1] is generally negligible. Also, the value of G_C can be obtained from the solute flux balance at the dendrite tip, *viz.*, $G_C = VC_t(k - 1)/D$, where C_t is the composition in the liquid at the dendrite tip, k is the solute distribution coefficient at the dendrite tip temperature, and D is the interdiffusion coefficient in the liquid. Equation [1] can thus be simplified to the form

$$VR^2 = \Gamma D/\sigma^* \Delta T_S \qquad [4]$$

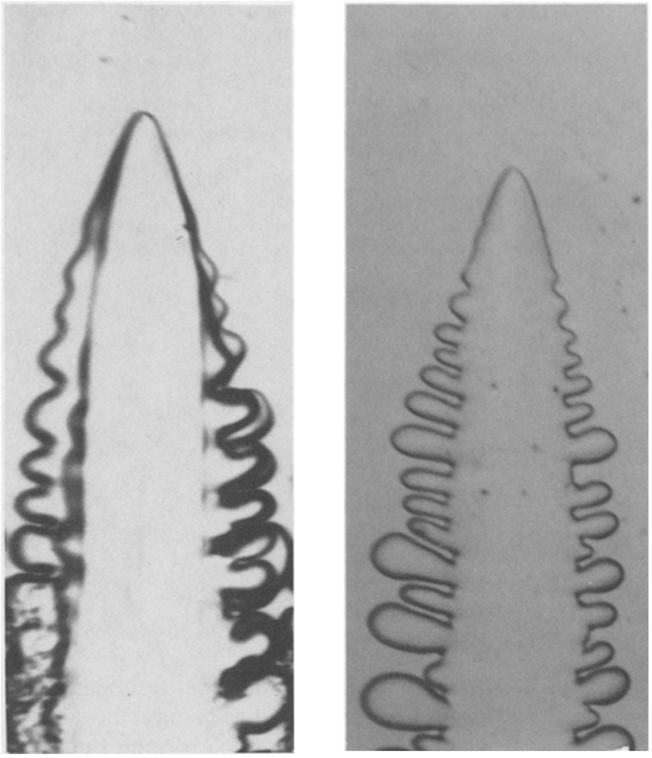

(*a*) (*b*)

Fig. 1 — The shape of the dendrite tip region for (*a*) CBr_4 dendrite grown directionally in CBr_4-7.9 wt pct C_2Cl_6 at V = 5.0 μm/s and G = 3.0 K/mm and (*b*) C_2Cl_6 dendrite grown directionally in CBr_4-10.5 wt pct C_2Cl_6 at V = 1.0 μm/s and G = 3.0 K/mm. Magnification 128.5 times.

Table I. Properties of CBr_4 and C_2Cl_6

Parameter	CBr_4 Dendrites in CBr_4-7.9 Wt Pct C_2Cl_6	C_2Cl_6 Dendrites in CBr_4-10.5 Wt Pct C_2Cl_6
γ, mJ/m^2	9.5	14.5
ΔS, J/m^{3}K	0.09	0.085
Γ, mK	1.06×10^{-7}	0.47×10^{-7}
D, m^2/s	0.8×10^{-9}	0.8×10^{-9}
ΔT_S, K	3.7	15.9

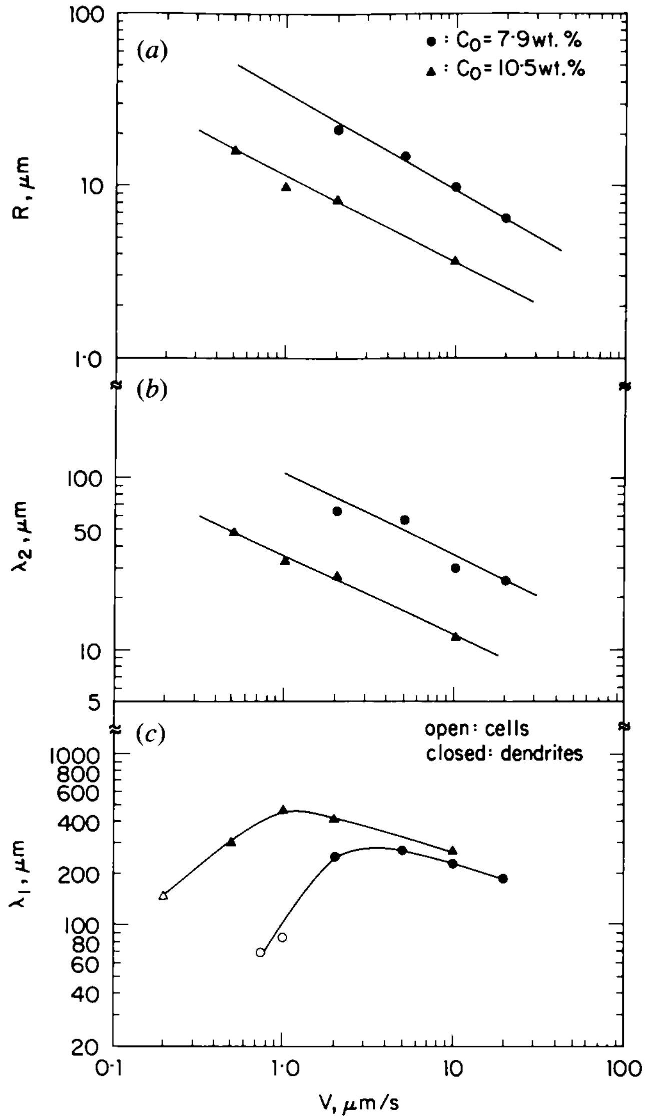


Fig. 2—The variation in the (*a*) dendrite tip radius, (*b*) initial secondary arm spacing near the dendrite tip, and (*c*) primary dendrite spacing, with velocity for CBr_4 and the C_2Cl_6 dendrites.

where $\Delta T_S = m_L C_t(k - 1)$. Note that for a constant value of m_L, ΔT_S is equal to the freezing range of the alloy whose composition corresponds to the solute concentration in the *solid* at the dendrite tip. For the low velocities used in the present study, the dendrite tip temperature will be close to the liquidus temperature of the alloy. Consequently, the values of ΔT_S can be directly obtained from the phase diagram. By substituting the experimental values of VR^2 and the constant values of Γ, D, and ΔT_S, the values of σ^* were evaluated from Eq. [6], and the following results were obtained:

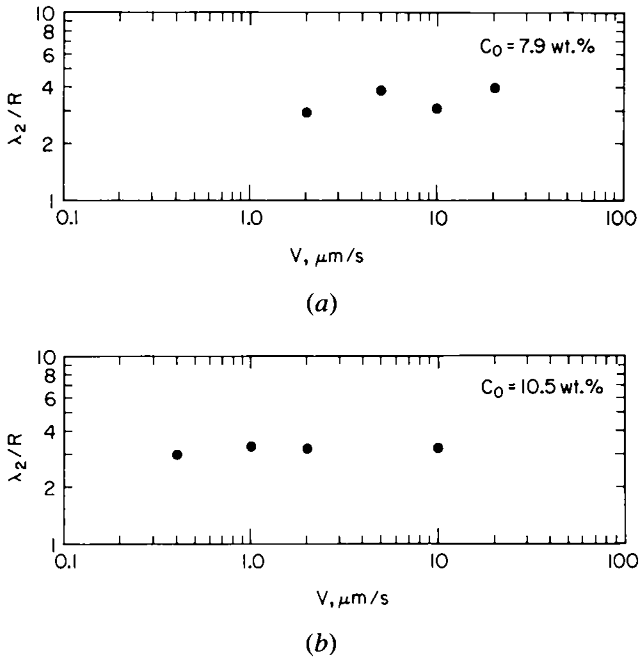
$$\sigma^* = 0.022 \quad \text{for } CBr_4 \qquad [5]$$

and

$$\sigma^* = 0.019 \quad \text{for } C_2Cl_6 \qquad [6]$$

The values of σ^* for CBr_4 and C_2Cl_6 agree with the prediction of the marginal stability criterion. The precise values of the surface energy anisotropy parameter for these materials are not known. However, the shape of the dendrite tip region and the distance between the dendrite tip and the first sidebranch perturbation show that the anisotropy in the interfacial energy is somewhat larger in these systems than in succinonitrile. Thus, according to the solvability approach, the values of σ^* should be higher than the 0.02 that is found for the nearly isotropic succinonitrile dendrites. Thus, our results are not in conformity with the solvability approach, but they do agree remarkably well with the prediction of the marginal stability criterion.

Glicksman *et al.*[3] first discovered the scaling law between λ_2 and R for dendritic growth in a pure undercooled succinonitrile. Subsequently, Glicksman and Singh[22] also reported a similar scaling law for pure pivalic acid dendrites. However, the magnitude of the scaling law constant was found to be significantly higher in the latter system, and this was attributed to the greater anisotropic properties in the pivalic acid system. Similar scaling laws have also been observed in directional solidification studies.[6,23] In these studies, the ratio λ_2/R was found to be 2.0 in the succinonitrile-acetone system, whereas a value of 3.8 was found in the pivalic acid-ethanol system. An examination of our present experimental results (Figure 2) clearly shows that similar scaling law behavior is exhibited by both the CBr_4 and the C_2Cl_6 dendrites. Figures 3(a) and (b) show the value of λ_2/R as a function of velocity. The values of the scaling factors are found to be 3.18 and 3.47 for the CBr_4 and the C_2Cl_6 systems, respectively. These values are between those for a nearly isotropic succinonitrile and a very anisotropic pivalic acid. Since the values of the ratios are found to be very close for the CBr_4 and the C_2Cl_6 dendrites, the anisotropic parameter in both these systems appears to be similar. Thus, we can now make a qualitative correlation that the value of the scaling law



(*a*)

(*b*)

Fig. 3—The value of the ratio λ_2/R as a function of velocity for (*a*) CBr_4 and (*b*) C_2Cl_6 dendrites.

constant increases with the increase in the anisotropic interface properties of the system.

Directional solidification studies have been carried out in the transparent CBr_4-C_2Cl_6 system to examine the variations in the dendrite tip radius, the primary spacing, and the secondary dendrite arm spacing near the tip as a function of velocity. Two different compositions were selected for the study so as to obtain dendrites of CBr_4 and of C_2Cl_6. The value of VR^2 was found to be constant for both these systems. Using these values, the magnitudes of the dendrite tip operating parameters, σ^*, were obtained for these two systems. The values of σ^* for the CBr_4 and C_2Cl_6 dendrites were found to be equal to 0.022 and 0.019, respectively, which are in good agreement with the marginal stability theory. Although the anisotropy in these systems is larger than that in the succinonitrile system, the value of σ^* is found to be the same in three systems, which tend to support the result of the marginal stability theory.

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