by roughly a kilocalorie or more. This line of reasoning dictates that the correct value of Q_c^* is at least -18 kcal instead of the value of -14.1 as reported by the authors.

Authors' Reply

J. G. SHAW AND W. A. OATES

We were aware of Dr. Shewmon's earlier result concerning the temperature gradient redistribution of cementite in α -iron and agree that this requires that Q_c^* shall be greater than the heat of solution of Fe_3C in α -Fe, $\Delta H_{\text{Fe}_3\text{C}}$. It was because of the disagreement between Shewmon's and our result for Q_c^* and the apparent discrepancy now raised by Dr. Shewmon that considerable effort was expended in the establishment of the reported value for Q_c^* . Since we are fairly confident of this result we are led to believe that $\Delta H_{\text{Fe}_3\text{C}}$ may be less than the 17 to 18 kcal quoted by Dr. Shewmon. Since values for this quantity lying between about 10 and 20 kcal have been reported in the past we do not feel this unreasonable. Doubts about the indirect calculation of $\Delta H_{\text{Fe}_3\text{C}}$ must continue in the absence of knowledge concerning any nonstoichiometry in Fe_3C . The "direct" methods of obtaining $\Delta H_{\text{Fe}_3\text{C}}$ must also still remain questionable when internal friction methods are used in which the peak height-concentration proportionality constant is not truly constant. It is interesting to note that the only calorimetric study of the reaction gave $\Delta H_{\text{Fe}_3\text{C}} = 12.4$ kcal. The present value of Q_c^* tends to support a value for $\Delta H_{\text{Fe}_3\text{C}}$ of about this magnitude.

40. P. G. Shewmon: *Trans. TMS-AIME*, 1958, vol. 212, p. 642.

41. J. C. Swartz: *Trans. TMS-AIME*, 1969, vol. 245, p. 1083

The Structure of Directionally Solidified Pb-Sn Eutectics Containing Antimony and Zinc Additions

G. GARMONG

THE directional solidification of binary eutectic alloys containing ternary additions may result in a breakdown of the regular plane-front structure into cells or dendrites.¹ There have been two approaches to the problem of predicting the growth conditions of the breakdown of plane front growth. One is a direct extension of the Rutter-Chalmers constitutional supercooling model to multiphase alloys.² With this model, the criterion of breakdown is given by³

$$G/R = - \left(\frac{m}{D} \frac{1 - K_0}{K_0} \right) C_0 \quad [1]$$

where G is the liquid-solid temperature gradient, R

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the growth rate, m the slope of the liquidus, D the diffusion coefficient, K_0 a mean distribution coefficient, and C_0 the impurity content. In a second approach, Cline⁴ and Hurle and Jakeman⁵ independently applied perturbation analysis to the liquid-solid interface. Cline⁴ derived an expression for the breakdown criterion as

$$G/R = \frac{1}{2} \left(\frac{K_s}{K_L} + 1 \right) \left[\frac{C_0 - C_i}{D} m^* + B \bar{C}_0 \right] \quad [2]$$

where K_s is solid thermal conductivity, K_L liquid thermal conductivity, m^* the effective binary liquidus slope, $C_0 - C_i$ the difference in binary initial and interface composition, B a positive constant, and $\bar{C}_0$ the ternary impurity content.

Little direct data are available for evaluation of the merits of the two approaches in ternary systems. Diffusion coefficients are not accurately known in many cases, for instance. However, certain qualitative observations may be made. For example, Cline has shown that Eq. [2] may predict a range of stability wider than predicted by Eq. [1]. That is, in certain cases the melt composition may deviate from the binary eutectic and still produce a regular structure even with zero temperature gradient. The present work utilizes two systems, Pb-Sn + Sb and Pb-Sn + Zn, in order to investigate the effects of ternary additions to eutectics. A series of melts was made for each ternary addition. The compositions chosen were such that each alloy was situated on the monovariant line departing the Pb-Sn eutectic.

High-purity materials were used in the production of alloys: 99.999 pct pure Pb, Sn, and Zn, and 99.99 pct pure Sb. Furnace charges of approximately 150 g were weighed to the nearest 0.01 g and melted in a closed graphite crucible under 1 atm of argon. The melts were heated to approximately 450°C, stirred briefly with a stainless steel rod, held for 3 min, and cast directly into quartz tubes. After cooling, each tube was inserted into a larger diameter quartz tube, and the assembly was evacuated, back-filled with 0.5 atm argon, and sealed. Up to six specimens at a time were directionally solidified vertically at rates of 0.4, 0.7, 1.1, 2.2, or 4.4 cm per hr by withdrawing them from a furnace whose center temperature was 400°C. The temperature gradient at the melting point of the specimens was determined by thermocouples sealed into several specimens and was found to be ~18°C per cm, independent of solidification velocity at the low velocities used.

The resulting specimens were circular cylinders 0.8 cm in diam and 20 cm long. Transverse sections for metallography were taken at 4, 10, and 16 cm from the end first solidified. These sections were mechanically polished to Linde A and electropolished in a solution of 2 parts (by volume) perchloric acid, 1 part butyl cellosolve, and 7 parts ethyl alcohol. Polishing voltages ranged from 12 to 18 v, and no subsequent etching was required. Every specimen examined showed no significant microstructural differences in the three sections taken, and it was concluded that steady state had been realized over at least the central portions of each specimen.

The type of structure observed in each alloy is indicated on a plot of G/R vs impurity content for antimony and zinc additions in Figs. 1 and 2, respectively. In