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Coupled region and area fraction of primary phases in Sb–InSb eutectic alloys

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Unidirectional solidification of Sb–InSb alloys, 26–34 wt% In, was carried out in the range of growth rate 1.2×10^{-4} to 1.2×10^{-1} cm s^{-1} and with a temperature gradient 57 °C cm^{-1}. An explanation is given which relates the coupled region with quantitative data concerning the primary phases, e.g. the area fraction and the protrusion length ahead of the eutectic interface. The coupled region can be constructed with reasonable accuracy from those quantities measured. The estimated coupled region is in qualitative agreement with the experimental result.

1. Introduction

In off-eutectic alloys it is well known that an abrupt microstructural change occurs across the boundary of the coupled region, i.e. the appearance or disappearance of the primary phase [1–4]. The appearance/disappearance of primary phase across the boundary implies that its amount should vary with the growth rate, once it starts to appear: in the case of the eutectic system with a symmetrical coupled region, when the temperature gradient is positive, the amount of primary phase will increase up to a maximum with an increase of growth rate and then decrease finally to zero with further increasing growth rate. Also the length of the primary phase protruding ahead of the eutectic interface will exhibit the same trend with growth rate as the amount of primary phase, because its appearance essentially accompanies the protrusion ahead of the eutectic interface.

Sharp and Flemings [5] have made a suggestion that the composition of the matrix eutectic should be exactly equivalent to that on the boundary of the coupled region. Since the amount of primary phase can be determined simply by the material balance rule from the composition of the matrix eutectic, it may be possible to estimate the coupled region from the amount of the primary phase. In this sense the variation in the amount of primary phase with the growth rate is of importance for the analysis of the coupled region.

However, little attention was given to the amount of primary phase growing outside the boundary of the coupled region except in a few investigations [6, 7], and furthermore, no attempt was made to relate this amount with the coupled region. In the present work, therefore, the area fraction of the primary phase and its protrusion length in Sb–InSb eutectic alloys were measured in order to provide a definite relationship between those quantities measured and the coupled region, and to compare the estimated coupled region with the experimentally determined one. Sb–InSb eutectic alloys were chosen for the present study because of the negligible intersolubility in each constituent phase, permitting a rather simplified constitutional analysis, and because of their potential importance in electrical application [8].

2. Experimental procedure

Alloys in the range 26–34 wt % In were prepared using 99.999% pure In and Sb which were induction-melted together in evacuated (10^{-3} torr) and a sealed quartz tube (6 mm internal diameter). The alloys were then once again encapsulated in another evacuated quartz tube, and subsequently subjected to unidirectional solidification in a Bridgman-type vertical furnace described elsewhere [9]. The solidified specimens were finally 100 mm long and 6 mm in diameter. The growth rate (actual interface velocity) was varied in the range 1.2×10^{-4} to 1.2×10^{-1} cm s^{-1} by controlling the traction rate of the specimen into the cooling zone. As described elsewhere [10], the growth rates are approximately equal to the traction rates for lower traction rates ($< 3 \times 10^{-3}$ cm s^{-1}), but this is not the case for higher traction rates; in particular, the growth rate was half the traction rate for 2.4×10^{-1} cm s^{-1}.

The temperature gradient was measured within the specimen by a Chromel–Alumel sheathed thermocouple of 1.6 mm (elemental wire: 0.2 mm) and remained constant at 57 ± 7 °C cm^{-1} for the range of growth rates employed in the present experiments. Such a measurement of temperature gradient was carried out only in some selected specimens (about a quarter of the total), but the gradient in the other specimens was taken to be the same as in specimens under identical thermal conditions. Longitudinal and transverse sections taken from the middle of the specimen were examined either unetched or etched with a solution of 70 ml distilled water + 30 ml HCl + 5 ml H_2O_2. The area fraction of the primary phase, which could be assumed to approximate to the volume fraction, was measured on the transverse sections by means of an image-analysing computer (Leco model 2001).

3. Results

A symmetrical coupled region was obtained in the Sb–InSb eutectic system, as indicated in Fig. 1. The boundary line indicated by the broken line for the range of higher growth rates was based on data for the area fraction of primary dendrites, although a transition from eutectic to primary dendrite was never detected in this limited number of specimens. This will be discussed in detail in the next section.

Fig. 2 shows the typical microstructure of alloys grown within the coupled region. The triangular Sb rod embedded in the InSb matrix was shown to

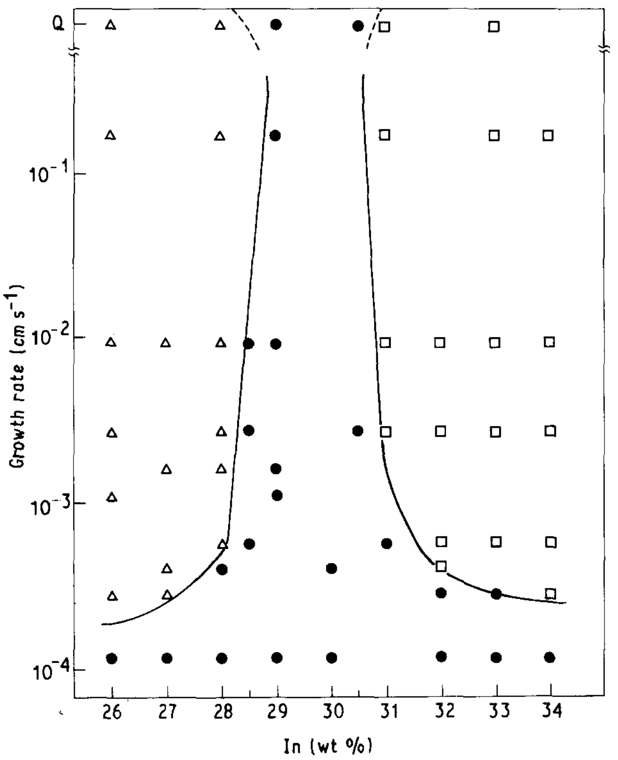

Figure 1 Coupled region in the Sb–InSb eutectic system: (●) eutectic, (△) Sb primary, (□) InSb primary. Q means water-quenched.

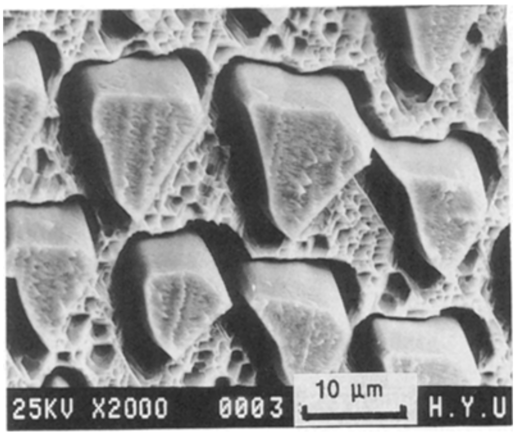

Figure 2 Typical microstructure within the coupled region, showing the regular arrays of Sb rods in the InSb matrix (30 wt % In, $R = 1.2 \times 10^{-4}$ cm s^{-1}).

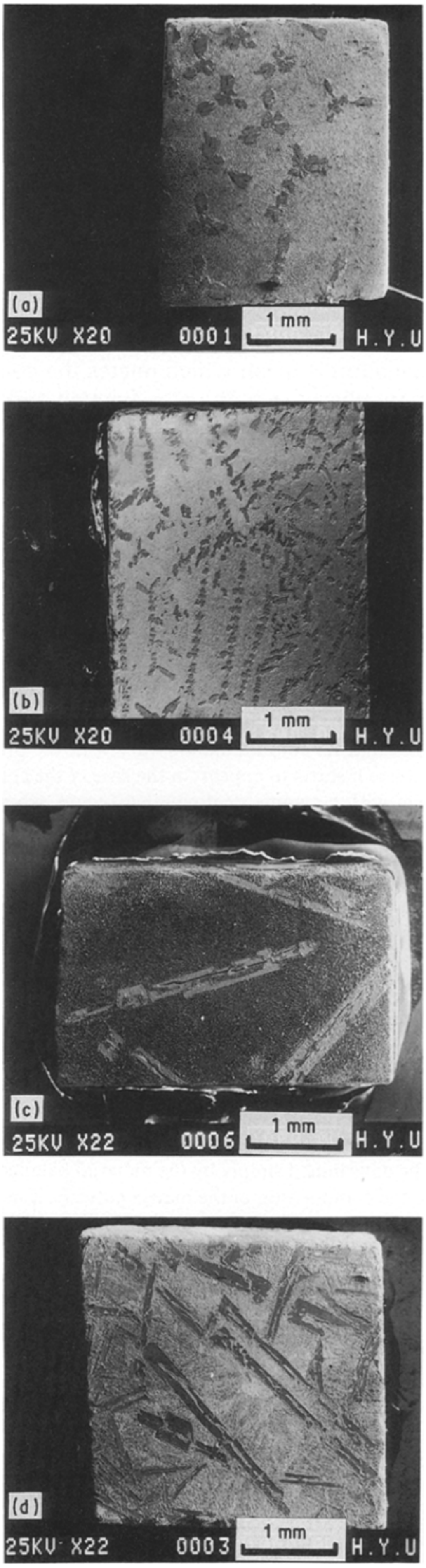

Figure 3 (a, b) Sb and (c, d) InSb primary phases formed in alloys with compositions 26 and 33 wt % In, respectively. Values of R (cm s^{-1}): (a) 1.1×10^{-3}, (b) 9.4×10^{-3}, (c) 5.6×10^{-4}, (d) 1.2×10^{-1}.

protrude upward with the matrix deeply etched away. A gradual increase of the primary phase with increasing growth rate is illustrated in Fig. 3 for hypo- and hyper-eutectic compositions. These photographs were taken on square transverse sections cut from the 6 mm diameter rod, but the quantitative measurement of the area fraction was made on the entire transverse section (6 mm circle) of the rod (in most cases three sections taken at 10 mm interval).

The dependence of the area fraction of primary phase on growth rate is plotted in Figs 4 and 5 for hypo- and hyper-eutectic compositions, respectively. A consistent relationship between the area fraction and the growth rate was obtained for all alloy compositions investigated.

A series of specimens containing 26 and 34 wt % In were quenched during the unidirectional solidification process, thereby preserving the shape of primary dendrites at the instant of quenching. Fig. 6 shows the shape of Sb primary dendrites protruding ahead of the eutectic interface at different growth rates. The dependence of protrusion length on the growth rate is shown in Fig. 7 for both primary Sb and InSb phases. As shown in this figure, the protrusion length of the primary phase increased with the growth rate. The measurement of the length was only possible up to 9.4×10^{-3} cm s^{-1} in the present experiments, because for growth rates greater than the above value it is difficult to obtain a sufficiently well-defined interface to allow an accurate measurement, due to the disturbances in unidirectional heat transfer.

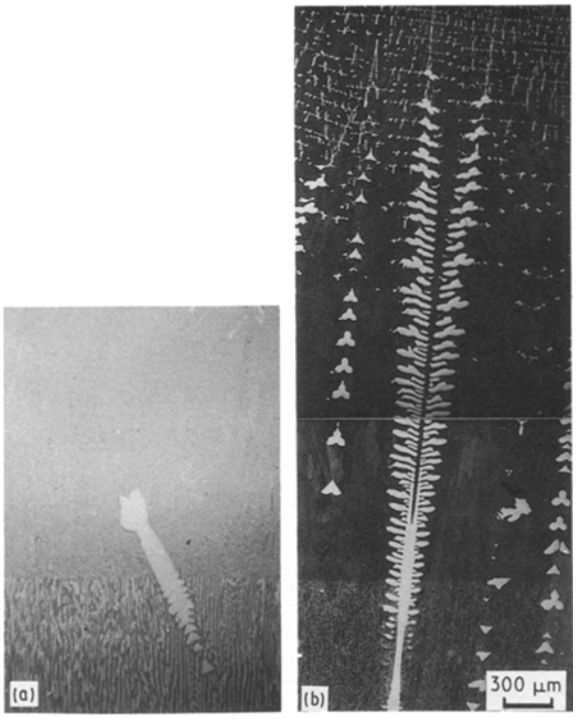

Figure 6 Sb primary dendrite protruding ahead of the eutectic interface (26 wt % In): (a) $R = 2.8\times10^{-4}$ cm s^{-1}, (b) $R = 2.7\times10^{-3}$ cm s^{-1}.

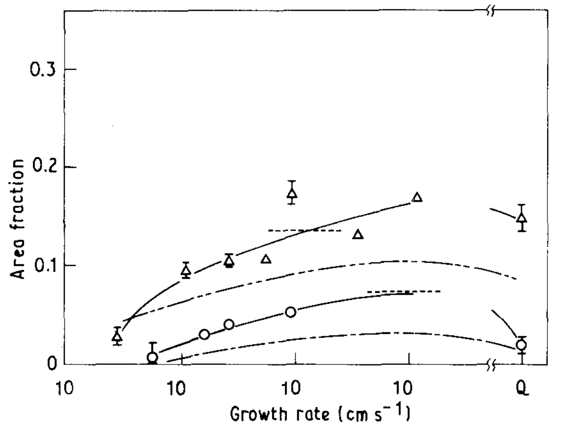

Figure 4 Dependence of Sb primary area fraction on growth rate. 28 wt % In: (○) experimental, (——) Equation 5. 26 wt % In: (△) experimental, (— - —) Equation 5. (---) Equilibrium values.

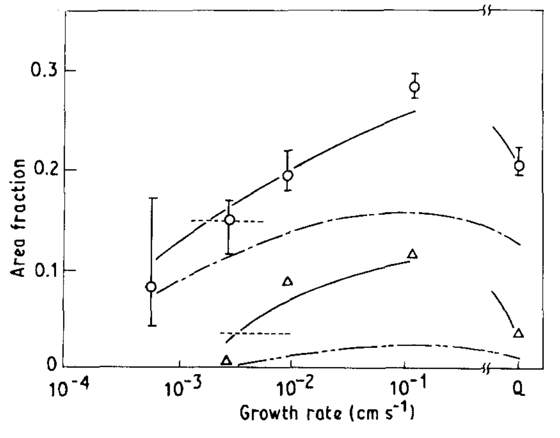

Figure 5 Dependence of InSb primary area fraction on growth rate. 33 wt % In: (○) experimental, (——) Equation 5. 31 wt % In: (△) experimental, (— - —) Equation 5. (---) Equilibrium values.

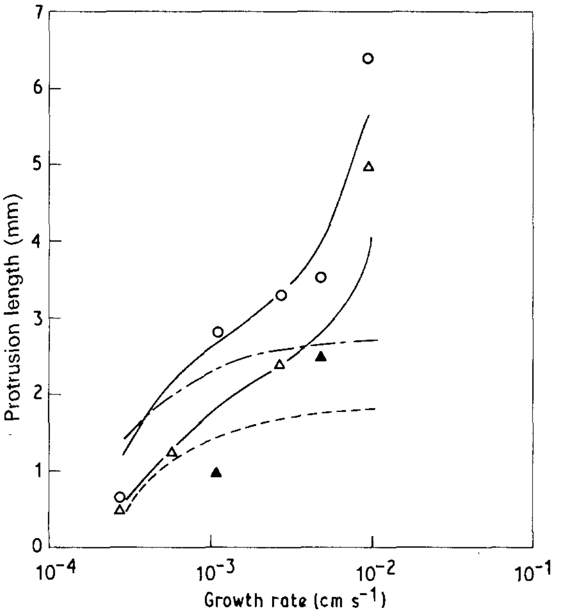

Figure 7 Dependence of primary dendrite protrusion length on the growth rate for Sb and InSb primary phases. (○) 26 wt % In (Sb primary); (▲) 33 wt % In (InSb primary); (△) 34 wt % In (InSb primary); (— - —) Equation 7, 26 wt % In; (— - —) Equation 7, 34 wt % In.

4. Discussion

Formation of primary phase in an alloy causes a change in the composition of the matrix eutectic, C_M, to maintain material balance. The equilibrium volume fraction of the primary phase can thus be taken as the volume fraction at a matrix composition of 30.5 wt % In (the eutectic composition, C_E) for the Sb–InSb system where the intersolubility of constituent phases is negligible [11]. This value is indicated by a broken line in Figs 4 and 5.

The weight fraction of primary phase, f_P, can be expressed, using a simple lever rule, as follows:

$$f_P = \frac{C_M - C_0}{C_M - C_S} \tag{1}$$

where C_S is the composition of primary phase at the actual eutectic temperature, T_E. The actual eutectic temperature for nf–nf (nf = non-faceted) eutectics depends on the growth rate according to the following equation [12]:

$$T_E = T_{E(e)} - AR^{1/2}$$

where $T_{E(e)}$ is the equilibrium eutectic temperature and R is the growth rate. Since C_S lies on the solidus metastable extension at T_E, C_S is given as

$$C_S = \frac{-Q - AR^{1/2}}{m_S} \tag{2}$$

where Q is the difference between $T_{E(e)}$ and melting temperature of the constituent component, and m_S is the solidus slope. With the assumption that the trace of the matrix eutectic composition constitutes a boundary line of the coupled region [5, 10], one may write C_M for nf–nf eutectics directly from Burden and Hunt's equation (Equation 6 in [13]) as follows:

$$C_M = C_E - \Delta C = C_E + \frac{1}{m_L} \times \left[\frac{GD}{R} + (B - A)R^{1/2}\right] \tag{3}$$

where G is temperature gradient, D diffusivity, m_L liquidus slope and B a constant in Burden and Hunt [14]. Using Equations 1 to 3, one can obtain a relationship between the growth rate and the weight fraction:

$$f_P = \left[(B - A)R^{1/2} + \frac{GD}{R} - Q - m_L C_0\right] \Big/ \left\{\left[(B - A)R^{1/2} + \frac{GD}{R} - Q\right] + k(AR^{1/2} + Q)\right\} \tag{4}$$

where C_0 is the alloy composition and k the distribution coefficient. A difficulty in solving the above equation is the lack of data concerning the constants A and B. However, since $k = 0$ for the Sb–InSb system [11], combining Equations 3 and 4 and rearranging gives

$$f_P = 1 + \frac{m_L C_0}{m_L \Delta C + Q} = 1 - \frac{C_0}{C_E - \Delta C} \tag{5}$$

While Equations 2 to 4 are for the nf–nf eutectics, Equation 5 can be applied to any type of eutectic if $k = 0$ is satisfied, since it gives only the constitutional relationship which can also be derived directly from Equation 1. Sb–InSb eutectics are known as f–f type (f = faceted).

f_P can be plotted as a function of growth rate from the experimentally determined ΔC of Fig. 1, as given in broken lines in Figs 4 and 5. It is to be noted that in these figures, the values calculated from Equation 5 represent the volume fraction, Φ_P, instead of the weight fraction (in the Sb–InSb system, $\Phi_{Sb} = 38.94 f_{Sb}/(11.7C_0 + 38.94)$, $\Phi_{InSb} = 38.94 f_{InSb}/(10.2C_0 + 33.99)$, where C_0 is the alloy composition given in weight fraction of In). ΔC, therefore, the boundary of the coupled region, can also be calculated by Equation 5 from f_P values evaluated from the measured area fraction. This result is plotted in Figs 8 and 9, together with curves redrawn from Fig. 1 for comparison. The plots calculated at different alloy compositions are seen to give a reasonable match with each other. However, some discrepancy exists between the calculated curves and those experimentally obtained. Such a discrepancy seems to be derived from the difference between the area fraction and the volume fraction. Usually the area fraction of a phase determined on any arbitrary section through the volume can represent its volume fraction for a system with randomly distributed phases [15]. However, this is not the case for the present investigation where the primary phases grown unidirectionally exhibit an oriented arrangement, though not complete, to a certain extent. If the phases under investigation are well aligned with complete order, which is only possible in unidirectional solidification with lower growth rates, the area fraction on the transverse section is essentially equal to the volume fraction. The fact that the calculated curves give a reasonably good fit with the experimental data in the range of lower growth rates supports this assumption.

As shown in Figs 4 and 5, f_P decreased remarkably in the quenched specimens. This result permits a prediction that ΔC will increase in the range of growth rates corresponding to quenching. Therefore it could be justified that the boundary line of the coupled region is drawn such that ΔC widens outward at those range of growth rate, although there is no transition in microstructural feature corresponding to the presence of primary phases.

The meaning of Equation 5 is that the shape of the coupled region may be approximately estimated from a quantitative measurement of the area fractions of the primary phases, if negligible intersolubility in the constituent phases can be assumed. This estimation is also possible through a measurement of protrusion length, as described below. The length of primary dendrite (x) protruding ahead of the eutectic interface can be given by

$$x = \frac{T_L - T_E}{G} = \frac{1}{G} \times \left[m_L C_0 + Q - \frac{GD}{R} + (A - B)R^{1/2}\right] \tag{6}$$

where T_L is the dendrite tip temperature of nf primary,

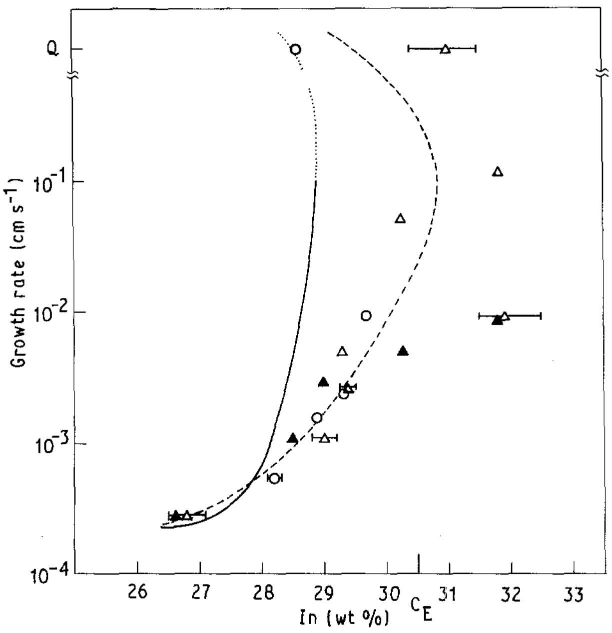

Figure 8 Comparison of the estimated boundary with that experimentally determined for the hypoeutectic side of the coupled region. From Equation 5: (△) 26 wt % In, (○) 28 wt % In. From Equation 7: (▲) 26 wt % In. (——) Redrawn from Fig. 1.

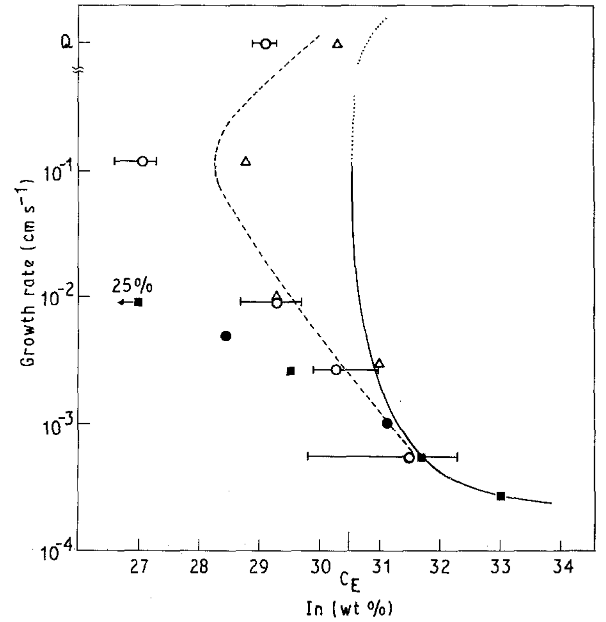

Figure 9 Comparison of the estimated boundary ,with that experimentally determined for the hypereutectic side of the coupled region. From Equation 5: (○) 33 wt % In, (△) 31 wt % In. From Equation 7: (●) 33 wt % In, (■) 34 wt % In. (——) Redrawn from Fig. 1.

as expressed in Burden and Hunt [14]. Combining Equation 6 and Equation 3 one can express x as a function of ΔC as follows:

$$x = \frac{1}{G}(m_L C_0 + Q + m_L \Delta C)$$

$$= \frac{1}{G m_L}(C_0 - C_E + \Delta C) \qquad (7)$$

As described previously in relation with Equation 5, Equation 7 can be applied to any type of phase, either nf or f.

From. the above equation it can easily be determined that x is only dependent on the degree to which the alloy composition deviates from the boundary of the coupled region if G is assumed constant. This is in agreement with the results: the length is longer for 34 wt % In than for 33 wt % In. The protrusion length can be calculated from Equation 7 using a value of 5.7 °C mm^{-1} for G and values of m_L obtained from the phase diagram, $m_{L(Sb)} = -6.56\,°C(wt\,\%)^{-1}$ and $m_{L(InSb)} = -1.51\,°C(wt\,\%)^{-1}$. The calculated values are compared with the experimental results in Fig. 7. A relatively larger x value at $9.8 \times 10^{-3}\,cm\,s^{-1}$ is attributed to the lower G at this high growth rate than at any other lower growth rates within the scatter of measured G. ΔC (that is, the boundary of the coupled region) can also be calculated from Equation 7. This value is indicated in Figs 8 and 9 as a dotted line. A somewhat larger misfit is shown between the calculated and the experimental boundaries, similar to the case of the area fraction. However, a relatively good match is maintained between the two kinds of plot, even though the calculated plots are obtained from two independent equations.

The protrusion of a primary dendrite arises from competitive growth between the eutectic and the primary dendrite: a phase with a higher interface temperature essentially protrudes ahead of another phase with a lower one, under conditions where a positive temperature gradient is established. Assuming that G is constant, the protrusion length is an estimate of the difference between the two interface temperatures. Thus in a symmetric coupled region with a waist zone the length should increase with increasing growth rate up to a maximum length, but decrease with a further increase of growth rate, finally to zero. At this zero point, the primary phase begins to disappear and a fully eutectic structure again appears. The same quantitative change as in the protrusion length occurs in the volume fraction with an increase of growth rate. The boundary of the coupled region estimated from the area fraction and protrusion length by Equations 5 and 7, respectively, gives moderate qualitative agreement with the experimentally obtained results, even though accurate matching was difficult in the present experiments.

5. Conclusions

A coupled region can be constructed with reasonable accuracy merely by systematic quantitative measurement of the area fraction or the protrusion length for the primary phases. Only specimens of two different compositions, one of hypo- and one of hyper-eutectic composition, will be required. The assumption was qualitatively demonstrated on the Sb–InSb system, known as an ideal eutectic system.

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