

The effect of an electric field on the solidification of off-eutectic tin-lead composite alloys

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The influence of an electric field upon the directional solidification of hypoeutectic and hypereutectic Sn-Pb composite alloys was studied. Equations were derived to account for the effect of electrotransport of solute in the liquid upon the solid composite composition. Experimental results support the theoretical predictions. Mixing in the liquid is more strongly influenced by unstable solute gradients than by current induced convection. Electrotransport shows limited promise as a method for control of the volume fraction fibre phase in the preparation of aligned composites by directional solidification.

1. Introduction

Directional solidification offers a potentially useful technique for producing aligned composite materials. Since the physical properties of composites are dependent upon the volume fraction fibre phase, it is very desirable to be able to control this volume fraction in the directional solidification technique. To achieve such control it is necessary to be able to produce aligned eutectic-like microstructures at off-eutectic compositions. Recent studies [1, 2] have shown that this is possible if one keeps the temperature gradient-to-growth rate ratio, G/R , sufficiently high. Control of the volume fraction fibre phase then becomes a matter of control of the composition of the composite.

To prepare off-eutectic composites of constant composition one desires that the composite solidify with the same composition as the original liquid composition. Recent studies [3, 4] have shown that this condition is obtained in steady state experiments only if thermotransport and liquid convection are negligible. Since high values of G/R are required for off-eutectic composite growth, thermotransport will be an inherent problem in some systems [3]. Also, it is not possible to eliminate convection at both hypoeutectic and hypereutectic compositions in the same system, because solute convection will virtually always be present on one side or other of the eutectic composition. For example, in

the Sn-Pb system convection is inherent in Pb rich off-eutectic growth because Pb is heavier than Sn, but convection may be eliminated for Sn rich off-eutectic growth [1].

One possible technique for controlling the composition in a system subject to thermotransport and convection is the application of an electric field across the solid-liquid interface. Studies on single phase growth [5] have shown that the electrotransport produced in the liquid allowed one to control the solid composition in such systems. The present work was undertaken to determine if an applied electric field would allow control of the composite composition in Sn-Pb alloys without destroying their aligned composite morphology.

2. Theory

Electrotransport causes a relative movement of the components of a binary alloy which is measured by a differential mobility, U_{12} , defined as,

$$v_1 - v_2 = U_{12}E \quad (1)$$

where $v_1 - v_2$ is the velocity difference of the two components of the alloy produced by the electric field, E . In off-eutectic solidification with an electric current the mass flux in the liquid relative to the solid-liquid interface will, in the general case, contain four terms which account for diffusion, electrotransport, thermotransport and the motion of the interface. Proceeding as in

[3], the mass flux of component 1 in the liquid relative to an interface moving in the positive z -direction at rate R is given as,

$$J_1 = x_1 \rho_s R - \rho_l D_{12} \left[\frac{dx_1}{dz} + x_1 \frac{D'}{D_{12}} G - x_1 x_2 \frac{U_{12}}{D_{12}} E \right] \quad (2)$$

where ρ_s, ρ_l = densities of the solid at the interface and of the liquid, respectively, D_{12} = mutual diffusion coefficient, D' = thermo-transport coefficient [3], G = temperature gradient normal to the interface, x_1, x_2 = mass fraction of components of the alloy. To obtain a tractable equation for a mathematical solution it is necessary to consider $x_2 U_{12}$ as a constant, U , independent of composition over the range of interest. We assume a stagnant film model which requires no convective transport within a film thickness, δ , of the interface and sufficient convection beyond distance δ to produce constant liquid composition. The differential equation obtained by substituting Equation 2 into the continuity equation is solved for this boundary condition assuming a quasi-steady state, as was done successfully by Burton *et al* [6]. From this solution one obtains a relation between the bulk liquid composition and the solid composite composition, and from a mass balance using this relation the composite composition is determined as a function of the fraction solidified, g . The analysis is described in detail in [7] and it is exactly similar to the analysis described in detail in [3], and the result is given as,

$$C_s = (1 + A)(C_o - B)(1 - g)^A + B \quad (3)$$

$$A = (1 + \eta e^{p\delta}) / (e^{p\delta} - 1)$$

$$B = (1 + \eta)C_E / (1 + \eta e^{p\delta})$$

where C_s, C_o, C_E = volume concentrations of the solid composite, the original alloy and the eutectic, respectively, $\eta = (D'G - UE)/R$, $p = (D'G - UE + R)/D_{12}$.

Equation 3 predicts the variation of the composite composition along the length of the solidified rod. Analysis of the equation shows that for any given values of initial concentration, C_o , thermo-transport velocity, $D'G$, interface rate, R , and boundary layer thickness, δ , one may cause the composite concentration to either increase or decrease along the length of the rod by simply changing the applied electric field, E ; and by adjusting E to give $B = C_o$, one may obtain a constant composition along the length of the composite. Hence, by applying an electric

field, one should be able to grow constant composition composites even in systems inherently subject to convection and thermo-transport. The solid composition, C_s , must lie in the two phase region of the phase diagram in order to have composite growth. Consequently, Equation 3 is only valid for the following values of initial concentration, C_o ,

$$C_E e^{-p\delta} + \frac{C_\alpha(1 - e^{-p\delta})}{1 + \eta} < C_o < C_E e^{-p\delta} + \frac{C_\beta(1 - e^{-p\delta})}{1 + \eta} \quad (4)$$

where C_α, C_β are the volume concentrations for the α and β phases at the ends of the eutectic tie-line on the phase diagram.

3. Experimental

Lead and tin of 99.999 % purity were weighed to within 0.02 wt % of nominal composition, and alloyed under vacuum at 400°C before quench-casting into a 5 mm i.d. Pyrex tube under pressure. The sample tube, shown in Figs. 1 and 2, was quartz with a bottom section 2 mm i.d. fused to a 6 mm i.d. top section. The lower

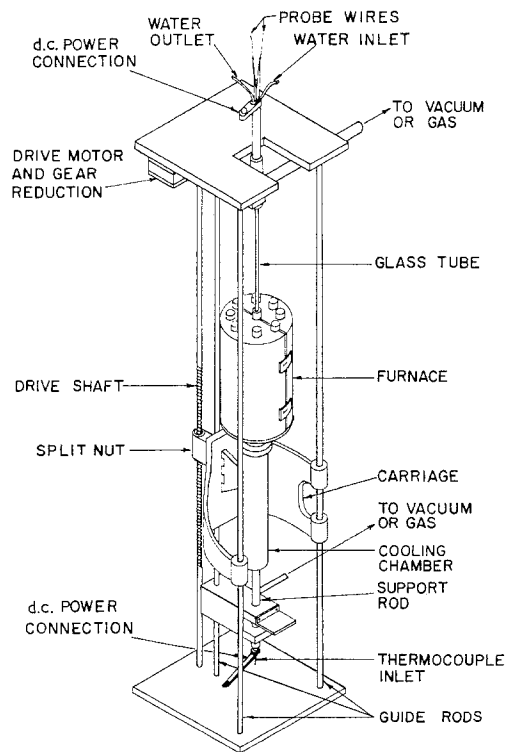


Figure 1 Experimental apparatus for the controlled solidification of alloys in an electric field.

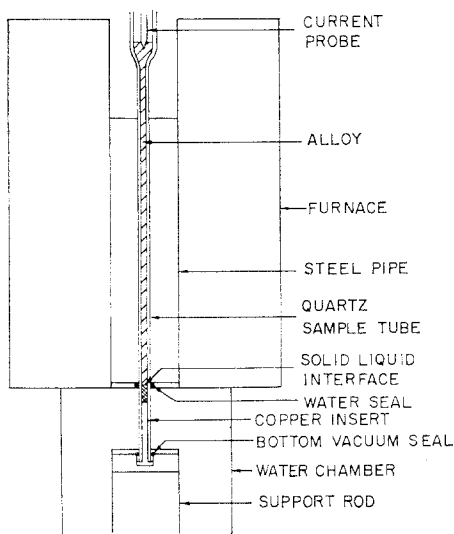


Figure 2 Sectional view through the sample and surroundings.

section was 15 cm long, the top 20 cm. A copper insert covered with graphite slurry extended 5 cm up into the lower tube. Each run required 3.5 g of alloy to fill the bottom section and extend about 6 mm into the top section. The steel pipe surrounding the sample tube was packed with graphite wool to eliminate temperature fluctuations owing to air currents inside the furnace.

In preparation for a run, the system was first heated to 650°C. A tantalum rod was lowered into the small tube, thereby forcing the alloy up into the hottest portion of the furnace, and the system was outgassed under vacuum for $\frac{1}{2}$ h at 725°C. The tantalum rod was then removed and a small tungsten wire was put in, rotated, and slowly raised in order to remove any bubbles which had formed in the small tube. After an additional $\frac{1}{2}$ h outgassing at 725°C, any remaining bubbles were removed and the system was backfilled with $\frac{1}{3}$ atm methane, balance He, to a positive pressure of 1 lb gauge. The furnace and water jacket were raised 2.5 cm at a rate of over $50 \mu\text{m sec}^{-1}$, while the furnace temperature was reduced to 600°C. Then the furnace drive was shifted to the desired rate, and the current turned on. The run was continued until the upper water seal approached the neck of the sample tube, 10 cm above the start point. Then the current was turned off, which caused the interface to move up sharply, quenching the interface.

At the conclusion of each run the sample was

removed from the tube and electropolished [8] to reveal the start and stop interfaces. For chemical analysis 1 mm sections were machined from each 5 mm length. The remaining 4 mm sections were mounted in room temperature setting resin, ground through No. 600 silicon carbide grit, and electropolished. Without further treatment it was immediately obvious at a magnification of $\times 50$ whether a particular transverse section contained dendrites or not. Every second milled section was chemically analysed, as well as the top and bottom sections.

The solidification rate, between 2 and $6 \mu\text{m sec}^{-1}$, was measured by means of a timer and a dial gauge mounted near the centre-line of the water jacket. The current density was maintained at 1280 A cm^{-2} . For the measurement of temperature gradient an alloy of bismuth in tin was used [7]. A thermocouple was inserted from below to record the temperature profile during solidification. The tip of the thermocouple consisted of two 0.075 mm Chromel and Constantin wires coated with Pyrex, while the bead was covered with boron nitride. The bead was thus less than 0.5 mm across, electrically insulated from the melt but quite sensitive to sudden changes in temperature. By recording the output from the thermocouple on a strip chart recorder, the gradient was determined from the time-temperature trace [9] to be $648^\circ\text{C cm}^{-1}$. Experimental results indicated that the gradient in the tin-lead alloys was similar. Without the electric field the gradient was about $250^\circ\text{C cm}^{-1}$. A computer simulation of the experimental system indicated that a thermocouple of the size used here would not affect the measured temperature gradient significantly [7].

4. Results and discussion

A series of ten experiments was carried out at various compositions above and below C_E . A majority of these experiments contained dendrites at some point along their length so that the analysis leading to Equation 3 was not directly applicable. Data are presented for two runs not containing dendrites in Figs. 3 and 4. Fig. 5 presents data from a run which contained dendrites only in the first third of the solidified rod. These data are presented because the dendrites were quite short and occupied only a small volume fraction of the rod. Consequently, their presence would have only a weak influence on the solute profile. It was observed that the eutectic morphology was not affected by steady

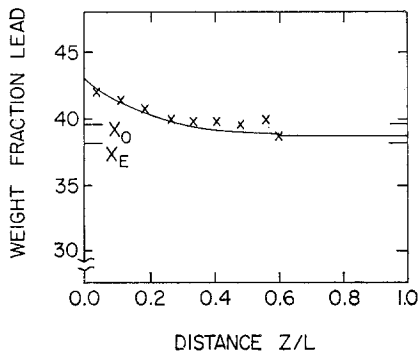


Figure 3 Comparison of observed and predicted composition profiles. The small break at $z/L = 0.6$ is the quench point. $x_0 = 39.55$ wt % Pb, $R = 3.94 \mu\text{m sec}^{-1}$, $\delta = 0.005$ cm, $E = -0.07$ V cm^{-1} .

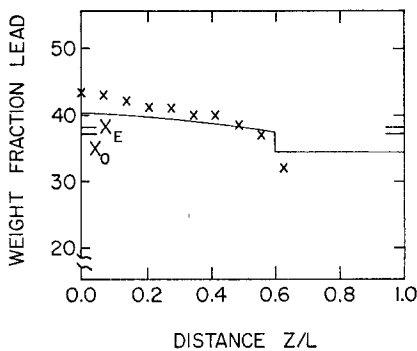


Figure 4 Comparison of observed and predicted composition profiles. $x_0 = 37.13$ wt % Pb, $R = 3.68 \mu\text{m sec}^{-1}$, $\delta = 1.0$ cm, $E = +0.07$ V cm^{-1} .

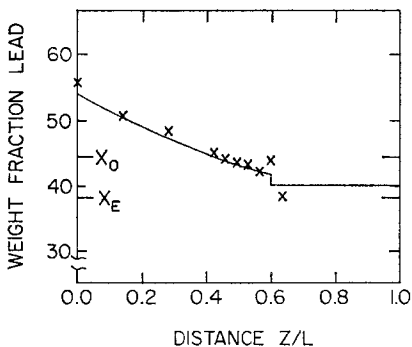


Figure 5 Comparison of observed and predicted composition profiles. $x_0 = 44.32$ wt % Pb, $R = 3.54 \mu\text{m sec}^{-1}$, $\delta = 0.012$, $E = -0.07$ V cm^{-1} .

state current densities up to the highest values studied, 2000 A cm^{-2} .

The theoretical analysis requires that the bulk liquid composition be constant but experimental evidence indicates that this was not the case. It was observed that the composition at the very bottom of the sample, which had been frozen quickly after outgassing and did not experience the electric field, contained much higher concentrations than could reasonably be expected. In one 40.0 wt % Pb alloy the concentration at the bottom was 68.4 wt % Pb. It was suspected that this concentration build-up might be due to thermotransport during outgassing since Pb migrates toward lower temperatures. Consequently, two runs were made to determine the concentration profile in the liquid. The first was set up in the normal way, but the furnace drive mechanism was not turned on and the electric field was run for 5.5 h, about two-thirds the normal run time, such that Pb was forced toward the bottom, which would enhance hydrodynamic stability of the liquid. The second run used neither drive nor electric field. The furnace was set at 725°C , the outgassing temperature, and left on for 18 h. In the first case the electrotransport produced an approximately exponential concentration curve with a decay length of about 2 cm. In the second case the composition profile produced by thermotransport did not drop to the "bulk" liquid value until 5 cm above the interface. These two results indicated that the assumption of uniform composition in the bulk liquid was seriously in question. Apparently, the convecting mixing, known to be produced by the electric current [10], was insufficient to produce a uniform concentration in the relatively small diameter tubes used here. In addition, thermotransport during the final $\frac{1}{2}$ h outgassing may have been sufficient to cause the initial liquid concentration to be non-uniform.

With the electrotransport flux of Pb upward (E negative) one would expect the Pb concentration in the bulk liquid to increase in the vertical direction, and with the flux of Pb downward (E positive) one expects the Pb concentration to decrease in the vertical direction. This effect could be expected to influence the experimental analysis in two important ways. First, with E negative an unstable density gradient is produced in the liquid, and experiments have shown that the solute convection so produced is significantly larger than the convection induced by the electrotransport current alone [11]. Consequently, while one expects a δ of the order

of 2 cm for E positive based on the experiment described above, for E negative, the δ value would be expected to be considerably less than this. Second, the non-uniform liquid concentration would cause deviations from the above theoretical analysis which assumed a constant bulk liquid concentration. With E positive, one would expect the liquid concentration gradient to increase the interface composition relative to its value for the case of uniform liquid concentration and, hence, the experimental results should be higher than the theoretical prediction. While solutions of the form of Equation 3 have not been derived for the case of non-uniform liquid concentration, a solution for simple normal freezing in the presence of a quadratic liquid concentration profile has been obtained [7]. Results of this analysis show that for the case of a decreasing solute content away from the interface (as for E positive) the composition of the first half of the solidified rod would be higher than the normal freezing equation alone would predict. Consequently, it is expected that the non-uniform liquid concentration would cause the theoretical analysis to be low for the case of E positive and high for the case of E negative in the first half of the rod.

The experimental results were compared with the theoretical predictions of Equation 3 by making adjustments in δ as necessary. In all cases the following values of the constants were used, $U = -4.5 \times 10^{-4} \text{ cm}^2 (\text{V} - \text{sec})^{-1}$ [12], resistivity = $55 \mu\Omega - \text{cm}$ [13], $D = 1.0 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ [14], $D' = 2 \times 10^{-8} \text{ cm}^2 (\text{K} - \text{sec})^{-1}$ [3], where the values were taken for the eutectic composition and an estimated mean temperature in the boundary layer of 350°C . For those runs with the initial liquid concentration, C_0 , greater than C_E and the flux of lead upward (E negative), a δ of between 0.05 and 0.001 cm fits the data best, as illustrated in Figs. 3 and 5. For those runs with C_0 less than C_E and flux of lead downward (E positive), a $\delta = 1 \text{ cm}$ or larger gave the best fit, as illustrated in Fig. 4. Equation 3 becomes insensitive to δ for values larger than 1 cm. Experiments with $C_0 > C_E$ and E positive as well as experiments with $C_0 < C_E$ and E negative did not yield flat interfaces under the present experimental conditions at rates of 2 to $3 \mu\text{m sec}^{-1}$.

The much smaller δ values for the case of E negative indicate stronger liquid convection than for E positive, as was expected owing to the unstable density gradient produced by the

upward motion of the heavier Pb atoms when E is negative. This result confirms other work in a Hg system [11] which found that the convection produced by the electrotransport current alone is less than the solute convection which results when the heavier atoms are caused to migrate upward. The theoretical curves are lower than the data for E positive, see Fig. 4, which is the correct direction of the deviation predicted by the analysis of the effect of a non-uniform liquid concentration. For E negative, the small δ value indicates quite effective liquid mixing so that one expects a fairly uniform liquid composition. Consequently, one would expect the theoretical analysis to apply directly, and in this case the predicted curve does fit the data reasonably well, see Figs. 3 and 5.

It was originally held by Mollard and Flemings [1] that one of the necessary conditions for aligned composite growth at off-eutectic compositions is the absence of liquid convection. Later work [4] put forth arguments that off-eutectic aligned composites could be grown in the presence of convection. The data of Figs. 3 and 5, as well as other data in this study, present direct experimental evidence that aligned composites can be grown in the presence of convection.

5. Conclusions

The final solute profile in at least some directionally solidified composites can be significantly altered by electrotransport without destroying the morphology of the aligned composite and, therefore, electrotransport can provide control over the volume fraction fibre phase. It should be possible to obtain a uniform off-eutectic composition even in systems which are inherently subject to solute induced convective mixing in the liquid. However, quite large current densities are required to achieve significant control so that one is restricted to small sample diameters in order to increase the surface to volume ratio for more efficient dissipation of the Joule heat produced by the large current densities.

The equations derived for off-eutectic solidification with electrotransport were able to predict the composition profiles reasonably well. In small tubes on the order of 2 mm with current densities on the order of 1000 A cm^{-2} the liquid composition may be decidedly non-uniform. Stirring forces owing to large electric current densities are of significantly smaller

magnitude than those owing to solute induced density instabilities.

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