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Primary dendrite spacing of directionally solidified

lead rich Pb-Sn binary alloys

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lead rich Pb-Sn binary alloys

by

Christopher Marvin Klaren

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ABSTRACT*

The primary dendrite spacing (d) of lead rich Pb-Sn alloys resulting from steady state directional solidification has been measured as a function of temperature gradient (G), alloy composition (C), and growth velocity (V). The relationship $d \propto G^{-1/3}$ was observed with three different alloy compositions and thermal gradients ranging from 11 to 358°C/cm. The effect of increasing solute content in the alloys was inconclusive, although dendrite spacing generally increased. Growth velocities were varied from 1 to 409 $\mu\text{m}/\text{sec}$ in the gradient range from 300 to 400°C/cm. At growth velocities less than 45 $\mu\text{m}/\text{sec}$ the dendrite spacings displayed no apparent dependence on the growth rates. This was attributed to the effects of convection and of the concept of a limiting maximum cell spacing as V approaches 0. At growth rates in excess of 45 $\mu\text{m}/\text{sec}$, a $d \propto V^{-1/2}$ relationship was exhibited.

The experimental data were analyzed in terms of several theoretical treatments of dendrite growth. The results indicated that perhaps a more detailed analysis of the problem is necessary in order to encompass the range of growth conditions encountered in this study.

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INTRODUCTION

Many alloys and commercially pure materials freeze with a cellular or dendritic growth front, the rate of movement and the direction of the front being determined by heat flow (Figures 1 and 2). Most of the detailed theoretical treatments of dendrite growth (5,13,18,25,26,40,43,44,45) have considered single dendrites growing into an originally isothermal medium. These treatments cannot be readily applied to an array of dendrites or cells growing in a temperature gradient.

One of the first theoretical analyses of the variables influencing the primary dendrite spacing was given by Brown and Adams (7) for ingot solidification. Their derivation resulted in the following equation:

$$d^2 = \frac{8D\Delta Ct}{m(1-k)C_0},$$

where d is the primary dendrite spacing, D the diffusion coefficient of solute in the liquid, ΔC the surface to center concentration difference in the ingot liquid zone, t the solidification time, k the equilibrium distribution coefficient, and C_0 the solute content. This agreed qualitatively with their experimental data from the arc deposition of aluminum base binary alloys as plots of d^2 vs. t yielded straight lines. Subsequently Rohatgi and Adams (30,31,32) showed the spacing to be a function of solidification rate, $\partial f_s / \partial t$, instead of solidification time. Reasonable agreement

Enlarged approximately 29%

Fig. 1. Dendritic microstructure of Pb-63.6 a/o Sn. Growth rate 20 $\mu\text{m}/\text{sec}$, temperature gradient 165°C/cm. Transverse section, 75X

Enlarged approximately 29%

Fig. 2. Cellular microstructure of Pb-53.8 a/o Sn. Growth rate 1 $\mu\text{m}/\text{sec}$, temperature gradient $350^\circ\text{C}/\text{cm}$. Transverse section, 75X

with $d \propto (\partial f_s / \partial t)^{-1/2}$ resulted from work on aluminum base binary alloys (30,32) and the freezing of aqueous solutions (31).

However, earlier work by Alexander and Rhines (1) with chill cast ingots of binary alloys resulted in $d \propto (\partial f_s / \partial t)^{-1}$, probably the result of non-steady state growth conditions.

Bolling and Fainstein-Pedraza (4) derived a relationship between the growth variables with a somewhat intuitive approach, resulting in the following equation:

$$d = \frac{8D}{V_0}, \quad (1)$$

where d and D are as defined previously, and V_0 is a velocity calculated from

$$V_0 = V + KG/\Delta H.$$

V is defined as the steady state growth velocity, G the temperature gradient in the liquid, K the thermal conductivity of the liquid, and ΔH the enthalpy of fusion. Equation 1 was shown to agree quite well with the available data for directional solidification (3,20,24) as logarithmic isoconcentrate plots of d vs. V_0^{-1} yielded slopes, S , well-within a factor of two of $8D$. The effect of solute other than through D was empirically correlated through a form of the well-known (41) solidification parameter $C_0(1-k)/k$. A form of this parameter, $C' = [C_0(1-k)/k]^{1/4}$ was found to normalize the quantity $S/8D$, unifying the results of the different investigations. However this concentration correction, as well as Equation 1, is

largely intuitive and empirical, and as such cannot be considered a rigorous treatment of the dendrite spacing problem.

Later work by Okamoto and Kishitake (27) with directionally solidified aluminum, tin, and zinc base binary alloys displayed primary dendrite and cell spacings which increased linearly with the square root of the inverse of cooling rate, $\partial T/\partial t$. This suggested relating the dendrite spacing to mass transport in the liquid phase. Making the following assumptions: (1) that secondary arms which grow in the same direction form plates; (2) solidification of the interdendritic liquid takes place by thickening of the plates; (3) there is no diffusion in the solid; and (4) that actual primary dendrite arm spacing is smaller than that expected for condition 2, Okamoto and Kishitake derived:

$$d = 2\epsilon \left[\frac{-m(1-k)DC_0}{\partial T/\partial t} \right]^{1/2}, \quad (2)$$

where m is the slope of the liquidus line on the phase diagram, and ϵ is a constant smaller than unity. Experimental work by Ibaraki et al. (17) and Okamoto and Kishitake (27,28) with binary alloys supported the relationship of $d \propto (\partial T/\partial t)^{-1/2}$. However, while the effect of solute content was found to agree with Equation 2 at low solute content, it deviated gradually from proportionality with increasing C_0 . It appears that the assumed conditions as well as neglecting the heat flow introduce factors which are not considered in their deriva-

tion.

Burden and Hunt (8) described reasonably satisfactorily the complex variation of tip temperature with velocity and temperature gradient of cellular and dendritic arrays. Hunt (15) attempted to extend the order of magnitude analysis of Burden and Hunt (9) to include cell and primary dendrite spacings. The object of his derivation was to provide a simple expression which would adequately describe the growth process near the actual growth conditions rather than to produce an accurate expression over a wide range of conditions.

The analysis was based on the assumption that a dendrite or cell tip may be approximated by a smooth steady state shape even when dendrite arms have been formed. This assumption, widely used in dendrite growth analysis (5,13,18,25,40,43), is based on the premise that the dendrite tip is sufficiently far enough ahead of the crystallizing secondary arms so that heat evolution and solute rejection from the secondaries have no effect on the growth conditions which exist at the dendrite tip. Thus the diffusion equations for heat and solute flow at the dendrite solid-liquid interface are simplified considerably.

Hunt then established the necessary equations and boundary conditions for solute and heat flow, as well as relating temperature, composition, and curvature on the solid-liquid interface of the growing dendrite. Solution of these equa-

tions followed the procedure of earlier work (9) with necessary modifications for relating dendrite spacings to the growth conditions. The major modifications were: (1) latent heat evolution from the solidifying dendrite is ignored in the analysis, a good approximation at low growth velocities; (2) each cell and dendrite is assumed to have radial symmetry, and as such to be grouped in hexagonal arrays; (3) the dendrites and cells are assumed to grow at the minimum undercooling for a given velocity (maximum growth rate at a given temperature). Condition 3 has been shown to agree reasonably well in eutectic growth (23,39). The equation resulting from the analysis is as follows:

$$d^4 = \frac{-64\theta D[m(1-k)C+kGDV^{-1}]}{VG^2} \quad (3)$$

where C is the composition of the liquid in atom fraction solute and θ is the curvature undercooling constant (9). The constant θ is given by:

$$\theta = \frac{V_{\sigma}^{\alpha}}{(\bar{S}_A^{\alpha} - \bar{S}_A^L)(1 - C^{\alpha}) + (\bar{S}_B^{\alpha} - \bar{S}_B^L)C^{\alpha}},$$

where V^{α} is the molar volume of α , $\bar{S}$ are partial molar entropies, the subscript A or B referring to components A and B and the superscript α or L referring to solid α and liquid L. σ is the surface energy and C^{α} is the B atom fraction composition of the α phase. (For dilute alloys θ may usually be approximated by $\theta = \sigma/\Delta S$ where ΔS is the entropy of melting

per unit of the solid material.)

At the critical condition when constitutional undercooling is just present on a planar interface, the bracket $[m(1-k)C+kGDV^{-1}]$ is equal to zero (15). When the critical condition is exceeded by increasing V or C or decreasing G , $m(1-k)C$ rapidly becomes the dominant term, giving for most of the growth range:

$$d^4 = \frac{-64\theta Dm(1-k)C}{VG^2} \quad (4)$$

Thus, Equation 4 predicts slopes of 1/4 from logarithmic plots of d vs. $1/VG^2$ and d vs. $m(k-1)C/VG^2$. This was found to agree fairly well with measurements of cell (19,29,33,42) and dendrite (3,12,36) spacings. However, calculating spacings from Equation 4 for Sn and Al base alloys only resulted in an order of magnitude agreement. This lack of agreement was attributed (15) to the simplifications made in the analysis, together with uncertainties in the surface energies and entropies of melting.

In addition to the numerous studies of dendrite spacings previously mentioned, other investigations of dendrite spacings have been made. A study by Dann et al. (11) dealt with the Al-Cu hypoeutectic alloy system. Solute contents varied from about 2 to 25 w/o Cu with temperature gradients ranging from 10 to 300 °C/cm. Jin and Purdy (22) worked with Fe-8 w/o Ni alloys and found that as G was increased, d decreased. Investigations of secondary arm spacings have also been made,

either in conjunction with work on primary spacings (11,24, 27,28,48) or as the focal point of basic research (2,14). Results different from primary spacings were obtained, as correlations between secondary arm spacings with the cube root of solidification time were observed (27). Another study (11) found coarsening time in the liquidus-solidus temperature interval to be the most important factor in secondary arm spacings.

The effects of fluid flow induced by solute density changes during solidification have been studied and found to affect the dendrite spacings and morphologies in $\text{NH}_4\text{Cl-H}_2\text{O}$ castings (10). Fluid flow was varied by changing the direction of growth of the interface from upwards to downwards. In the former case the less dense rejected solute aided mixing with the bulk liquid while in the latter case the solute filled the interdendritic regions during solidification. The effect of fluid flow in this system was quite large, as an order of magnitude difference in dendrite spacing was observed between the two growth modes (10).

While a great deal of work has been completed on dendrite spacings, only a small amount has been carried out at temperature gradients above 250°C/cm (11), velocities below $49\text{ }\mu\text{m/sec}$ (3,20), and solute content variations of more than 10% (11). Thus it was decided that the objective of the present research would be to determine the effects on dendrite spacings due to

the following conditions: (1) high temperature gradients; (2) a wide range of growth velocities; (3) a relatively large range of composition variation; and (4) the effect of varying temperature gradients at constant velocity and composition.

The Pb-Sn binary alloy system was selected for its low melting temperatures and ease of metallographic preparation. The Pb-Sn equilibrium phase diagram (12) is a simple eutectic. The solidus and liquidus lines are fairly straight, thus assuring that m and k are reasonably constant over the composition range studied. Body centered tetragonal Sn dendrites have been observed to grow in sheets parallel to the $(1\bar{1}0)$ plane (47), which could possibly complicate the analysis of dendrite spacings. Thus, lead rich Pb-Sn alloys were used to yield face centered cubic Pb dendrites which more closely resembles the "classical" morphology considered in dendrite growth analysis.

EXPERIMENTAL APPARATUS AND PROCEDURES

All experiments with thermal gradients greater than $99^{\circ}\text{C}/\text{cm}$ were carried out in the vertical solidification apparatus schematically illustrated in Figures 3 and 4. Temperature gradients less than $99^{\circ}\text{C}/\text{cm}$ were obtained with constant temperature oil chambers interchanged with various components of Figure 4 (46). The alloys were solidified in graphite coated 6 mm I.D./8 mm O.D. fused quartz tubing 60 cm long. A hollow brass bottom plug assembly was fitted 5.3 cm up into the bottom of the tubing. This rested on the lower support rod, and an O-ring and clamping plate were used to make a vacuum seal at the bottom junction. At the top the upper support for the tubing was connected to the vacuum system and clamped to the tubing with another O-ring seal. A nylon plug with a hole through the center was threaded into the upper support and was tightened down to the tubing to prevent any vertical motion during a run. At the bottom a water tight seal was formed between the tubing and the cooling cylinder as pictured in Figure 4. This seal must be well-lubricated since it is movable and any sticking would cause variations in the rate of movement of the solid-liquid interface. Resting on the clamping plate holding down the O-ring seal were a hollow lava spacer and a stainless steel jacket which contained the thermocouple that regulated the furnace temperature.

The furnace was 20 cm in height and contained non-

Fig. 3. Overall schematic view of experimental apparatus

Fig. 4. Sectional view of the alloy and surrounding equipment

inductively wound nichrome wire heating elements. The furnace and transite spacer were an integral unit resting on the top plate of the water chamber. By varying the furnace temperature and the thickness of the lava spacer surrounding the tubing, the solid-liquid interface could be adjusted to be planar at any given temperature gradient. The temperature gradient was measured by a thermocouple which extended down into the melt through the tubing upper support. The thermocouple was made from 4 mil chromel and alumel wires insulated from a 20 mil O.D./14 mil I.D. stainless steel sheath with powdered magnesia. The bead was formed by welding the end of the sheath to the chromel and alumel wires. Reaction with the lead-tin alloy during the experiments was prevented by coating the sheath with a thin layer of graphite.

The experiments were carried out at five compositions ranging from Pb-10 w/o Sn to Pb-50 w/o Sn in 10 w/o Sn increments. Master alloys were initially cast from 99.999% pure tin and lead, the purity as quoted by the suppliers. A total of not less than 350 g of the starting materials were weighed to within .05% of the desired composition. After placing the charge in a clean Pyrex crucible the crucible was transferred to a vacuum chamber. The chamber was then evacuated and back-filled with helium before final evacuation. During the melting of the charge the pressure in the chamber was 5×10^{-3} torr or less and remained constant. The charge was melted by a

resistance furnace at about 410°C and when the melting was complete a tantalum stirring rod with an attached paddle was lowered into the melt and oscillated to insure complete mixing. The melt was then left undisturbed for approximately five minutes and then restirred immediately before casting. In the casting operation a bundle of 5 mm I.D./7 mm O.D. internally graphite coated Pyrex tubes 60 cm long with one end sealed were lowered to the bottom of the melt and the system was quickly backfilled with helium thus forcing the molten alloy up into the tubes. The alloy rapidly solidified in the Pyrex tubes and the furnace was then removed allowing the system to cool. The master alloys cast in the 5 mm I.D. Pyrex tubes were then used as the starting point for all subsequent work.

After breaking the alloy out of the tubes and cleaning in methyl alcohol a 20 cm length was cut from the 60 cm long rods and placed in the previously described apparatus. The system was then evacuated to less than 25×10^{-3} torr, after which the cooling water was allowed to flow and the furnace raised to the desired temperature. After the alloy melted, the system was backfilled with argon and the furnace/carriage assembly was raised 1.3 cm at about 200 $\mu\text{m}/\text{sec}$. The system was then allowed to set idle for 40 minutes while the stainless steel jacket achieved a uniform temperature distribution.

Two solidification passes were made during each run, the

first to measure the temperature gradient of the liquid above the advancing dendritic array and the second to obtain the dendritic microstructure for spacing measurements. The first pass was initiated at a predetermined growth velocity of 1 to 409 $\mu\text{m}/\text{sec}$. After measuring the velocity with a dial gauge and electric timer and allowing sufficient time for the solid liquid interface to reach a condition of steady state heat flow, the stainless steel sheathed thermocouple was lowered into the melt to a position above the advancing interface and locked into place. The moving interface was allowed to solidify around the thermocouple tip and was halted soon after the eutectic front at the base of the dendrites passed the welded junction. The carriage was then lowered manually, remelting the alloy. Under an atmosphere of flowing argon the thermocouple was removed from the melt. A 12 cm section of identical composition alloy cut from the cast 60 cm rod was lowered into the melt to provide more metal for the final solidification pass. The carriage assembly was again raised 1.3 cm and allowed to equilibrate for 10 minutes. The assembly was then started on its second upwards solidification pass at the same predetermined growth velocity. After a suitable length of rod was solidified the run was terminated by quickly raising the cooling jacket-furnace combination manually, effectively "quenching" the remaining liquid. This created an interface which was clearly evident upon macroetching and

which proved useful in correlating the solidification rate data with the solidified specimen.

The temperature gradient calculations were quite simple to make. The output of the thermocouple was recorded on a strip chart as a function of time. The output recorded in this manner was essentially a straight line at temperatures greater than the liquidus temperature of the alloy under consideration. Using a straight edge the slope of the line in millivolts per second at the liquidus temperature could be determined. When correlated with the known temperature dependence of EMF for chromel-alumel thermocouples and the solidification rate data the thermal gradient in degrees Celsius per centimeter could be calculated.

Preparation of the samples for examination began by carefully breaking the glass from the solidified specimen and etching the entire specimen in a room temperature etch consisting of 67 v/o glycerol, 16 v/o glacial acetic acid, and 17 v/o nitric acid for approximately one minute. This revealed the start and quench interfaces. Two samples for examination were obtained by sectioning the specimen with a jewelers saw. One sample was 2.5 cm long with the quench interface positioned within .75 cm of the center of the section. The other sample was 2 cm long and positioned directly below the quench interface sample on the rod. The end closest to the quench interface was polished on a 600 grit silicon

carbide wheel with the aid of a small fixture to obtain a surface normal to the growth direction. Both samples were then mounted in self-setting acrylic resin, the quench interface sample positioned longitudinally along the bottom of its mount, and the second sample placed on its polished end such that the growth axis was normal to the flat bottom of the mount. The quench interface sample was then sectioned longitudinally by carefully grinding 2-3 mm deep with 180 grit and polishing through 600 grit silicon carbide. The transversely mounted sample was polished with 600 grit, keeping the plane of the polish perpendicular to the growth direction. Both samples were then cleaned in methyl alcohol in an ultrasonic cleaning machine and electropolished for 1-2 minutes at 30 volts in a 6 v/o perchloric acid methanol bath maintained at -60°C by a flow of liquid nitrogen regulated by a thermocouple in the bath itself.

The longitudinally sectioned quench interface sample was examined at relatively low magnification to determine the morphology of the quenched dendritic and eutectic growth fronts. If the quenched eutectic interface was planar and perpendicular to the growth axis (Figure 5), a condition of directional heat flow through the solidifying sample was assumed. However, if the quenched interface was curved, either concave upwards or concave downwards, this was taken to be indicative of heat loss or heat gain through the walls

Fig. 5. Longitudinal sections of quenched interfaces

- (a) Pb-53.8 a/o Sn, growth rate $10\text{ }\mu\text{m/sec}$,
temperature gradient 351°C/cm , 38X
- (b) Pb-63.6 a/o Sn, growth rate $10\text{ }\mu\text{m/sec}$,
temperature gradient 355°C/cm , 38X

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(a)

(b)

Brother Jonathan
Bond
and Co's 100% PAC

of the quartz tubing near the growing interface. This implied that the steady state solid-liquid interface was not within the upper or lower surfaces of the lava spacer, a condition which was remedied by changing the furnace temperature and/or the thickness of the lava spacer. Runs which yielded non-planar interfaces suggested that heat flow was non-directional and were not included in the dendrite spacing data.

Dendrite spacings have been measured in various ways by previous investigators. The most obvious method is to measure the primary dendrite spacings of a large number of dendrites on a transverse section micrograph and calculate the average (27,48). Another method of direct measurement consists of measuring the separation between primary dendrite stalks on a longitudinal section of the sample (3). More sophisticated methods have employed a mean linear or random intercept concept (11,48). The average spacing is determined by counting the number of primary arms intersecting random lines of fixed length on a transverse section micrograph. Later refinements of this method included drawing a circle of constant radius around the center of each dendrite and an intercept was counted when a circle, rather than an array of secondary arms associated with a primary arm, crossed a random line (11). Another procedure counted the number of dendrite centers intersecting a line of fixed length along a direction of closest primary dendrite packing (24).

The method of determining the average dendrite spacing in the present work consisted of counting the number of dendrites within a fixed area on a micrograph. It was felt that this method would be more representative of the true average primary dendrite spacing than would any of the above mentioned procedures. To facilitate the implementation of this method, the dendrites were assumed to grow in hexagonal arrays as shown in Figure 6. With the aid of Figure 7 an expression for average dendrite spacing can be derived. If A is an area on the transverse section of a sample containing n number of dendrites, then $a = A/n$ is the area associated with each individual dendrite diffusion field. Letting d represent the average primary dendrite spacing and referring to Figure 7,

$$h = d/2$$

and

$$b = \frac{h}{\tan 60^\circ} = \frac{d}{2\sqrt{3}}$$

Calculating the hexagonal area associated with each primary dendrite and equating to A/n yields

$$\frac{A}{n} = a = 12\left(\frac{1}{2}bh\right) = \frac{\sqrt{3}}{2} d^2.$$

Solving for d,

$$d = \left(\frac{2}{\sqrt{3}} \frac{A}{n}\right)^{1/2}.$$

Letting A be the area of a circle of radius r/M , where r is the radius of a circle scribed on a micrograph of magnification M,

Fig. 6. Assumed ideal hexagonal array

Fig. 7. Geometric considerations of derivation of Equation 5

$$d = \frac{r}{M} \left(\frac{2\pi}{n\sqrt{3}} \right)^{1/2}.$$

If $r = 3$ cm,

$$d = \frac{5.714}{M\sqrt{n}} \text{ cm.} \quad (5)$$

Two micrographs were obtained from regions away from the edges of the transversely sectioned sample from each experimental run and were scribed with a 3 cm radius circle. The average dendrite spacing was then calculated with Equation 5 after counting the number of dendrites within the scribed area.

RESULTS AND DISCUSSION

Experimental results were obtained from runs exhibiting dendritic microstructures similar to Figures 1 and 8, and in one case the cellular structure of Figure 2. The dendrite spacings as calculated with Equation 5 were found to agree quite well with the average of individual measurements between centers of nearest neighbor dendrites of the first few experiments. Hence Equation 5 was assumed to calculate the dendrite spacings with reasonable accuracy.

The Pb-Sn solidification data is presented in Table 1. The error limits of d , V , and G are representative of the estimated maximum systematic error due to the limits of precision encountered in the various measurement processes. The equations determining d , V , and G were differentiated with respect to the measured experimental parameters to yield total differentials. Estimated values of the various measurement uncertainties were then used with the total differentials to calculate the error limits. Thus the calculated limits are indicative of the estimated precision resulting from the measurement processes and not of random errors introduced from unidentified sources.

The theoretical dependence of d on G is found in Equation 4 to be $d \propto G^{-1/2}$. Equation 2 related the cooling rate $\partial T / \partial t$ to dendrite spacing. Recognizing that $G = \partial T / \partial x$ and the isotherm velocity $V = \partial x / \partial t$, it is obvious that $\partial T / \partial t$

Enlarged approximately 29%

Fig. 8. Dendritic structure of Pb-63.6 at/o Sn. Growth rate 20 $\mu\text{m}/\text{sec}$, temperature gradient 109°C/cm. Transverse section, 75X

Table 1. Summary of Pb-Sn data on the effect of solidification rate (V), thermal gradient (G) and alloy composition (C) on the measured dendrite spacing (d)

Run No.	d (μm)	V ($\mu\text{m}/\text{sec}$)	G ($^{\circ}\text{C}/\text{cm}$)	C (a/o Sn)
81	45.2 $\pm$.7	202.8 $\pm$.1	317 $\pm$ 23	63.6
97	51.1 $\pm$.6	100.8 $\pm$.2	355 $\pm$ 27	63.6
82	91.6 $\pm$.5	45.5 $\pm$.1	321 $\pm$ 13	63.6
98	98.8 $\pm$.5	20.3 $\pm$.1	325 $\pm$ 25	63.6
83	103.6 $\pm$.1	9.96 $\pm$.01	355 $\pm$ 26	63.6
106	121.2 $\pm$.5	20.4 $\pm$.04	165 $\pm$ 6.5	63.6
107	133.4 $\pm$.9	20.3 $\pm$.03	128 $\pm$ 5.0	63.6
108	130.6 $\pm$ 1.2	20.4 $\pm$.04	109 $\pm$ 4.3	63.6
109	190.1 $\pm$ 1.5	20.3 $\pm$.04	54.0 $\pm$ 2.4	63.6
110	201.0 $\pm$.2	20.2 $\pm$.04	30.7 $\pm$ 1.3	63.6
111	263.1 $\pm$.1	20.2 $\pm$.04	11.0 $\pm$ 0.8	63.6
120	31.5 $\pm$.4	409.0 $\pm$.2	390 $\pm$ 31	53.8
90	42.5 $\pm$.1	201.6 $\pm$.1	346 $\pm$ 25	53.8
99	53.2 $\pm$.3	100.8 $\pm$.2	374 $\pm$ 15	53.8
92	79.4 $\pm$.7	44.6 $\pm$.1	322 $\pm$ 13	53.8
100	89.2 $\pm$.6	20.3 $\pm$.04	349 $\pm$ 13	53.8
91	92.8 $\pm$.5	10.1 $\pm$.01	351 $\pm$ 26	53.8
121	88.6 $\pm$.8	4.46 $\pm$.02	356 $\pm$ 15	53.8
122 ^a	80.7 $\pm$.4	1.02 $\pm$.01	352 $\pm$ 28	53.8
112	109.7 $\pm$.7	20.3 $\pm$.04	185 $\pm$ 3.9	53.8
115	130.7 $\pm$.3	20.1 $\pm$.04	104 $\pm$ 2.2	53.8
116	159.3 $\pm$ 1.1	20.3 $\pm$.03	54.5 $\pm$ 2.1	53.8
119	215.5 $\pm$ 1.3	20.2 $\pm$.04	25.8 $\pm$ 1.2	53.8
85	39.7 $\pm$.03	204.0 $\pm$.1	372 $\pm$ 14	42.8
102	53.2 $\pm$.3	100.8 $\pm$.2	379 $\pm$ 15	42.8
86	80.8 $\pm$.1	45.0 $\pm$.1	346 $\pm$ 14	42.8
101	82.5 $\pm$.2	20.2 $\pm$.04	358 $\pm$ 14	42.8
84	88.3 $\pm$.6	9.96 $\pm$.01	352 $\pm$ 14	42.8
113	105.6 $\pm$.3	20.3 $\pm$.04	170 $\pm$ 13	42.8
114	126.9 $\pm$.3	20.3 $\pm$.04	101 $\pm$ 3.9	42.8
117	159.3 $\pm$.5	20.4 $\pm$.04	54.7 $\pm$ 2.1	42.8
118	183.3 $\pm$ 1.5	20.2 $\pm$.04	30.1 $\pm$ 2.2	42.8

^aCellular rather than dendritic structure was observed.

Table 1. (Continued)

Run No.	d (μm)	V ($\mu\text{m}/\text{sec}$)	G ($^{\circ}\text{C}/\text{cm}$)	C (a/o Sn)
95	38.3 $\pm$.4	205.3 $\pm$.1	363 $\pm$ 26	30.4
104	56.3 $\pm$ 1.0	101.4 $\pm$.2	380 $\pm$ 15	30.4
93	84.5 $\pm$ 1.5	44.6 $\pm$.1	346 $\pm$ 14	30.4
103	85.0 $\pm$ 1.6	20.3 $\pm$.04	369 $\pm$ 14	30.4
94	87.0 $\pm$.3	10.1 $\pm$.01	352 $\pm$ 14	30.4
88	32.1 $\pm$ 1.2	204.0 $\pm$.1	392 $\pm$ 29	16.2
87	69.6 $\pm$ 1.5	45.3 $\pm$.1	371 $\pm$ 28	16.2
89	77.6 $\pm$ 2.0	9.96 $\pm$.01	365 $\pm$ 27	16.2

is equivalent to GV. As Okamoto and Kishitake (27) derived $d \propto (\partial T / \partial t)^{-1/2}$, their calculated dependence of dendrite spacing on thermal gradient agrees with that of Hunt (15) of Equation 4.

The effect of temperature gradient on dendrite spacings was determined by varying the gradient over a large range at growth velocities of 20 $\mu\text{m}/\text{sec}$. The results of this procedure is graphically portrayed in Figure 9 where d versus G is plotted on logarithmic axes. The average least squares fit slope of -0.322 with a standard deviation of 0.017 indicates a $d \propto G^{-1/3}$ relationship. This relationship is well-supported by the results of calculations in Table 2 made from existing data in the literature. Agreement with Dann et al. (11) is excellent, and while Kotler et al. (24) and Young and Kirkwood (48) do not agree exactly, their values are well within one standard deviation of the expected -1/3. The large deviation

Table 2. Calculated values of least squares analysis of d versus $\log G$ obtained from literature data

Source	Alloy system	Mean slope	Std. deviation	Mean corr. coeff.
Dann <u>et al.</u> (11)	Al-Cu	-0.332	0.009	-0.963
Kotler <u>et al.</u> (24)	Pb-Sb	-0.304	0.130	-0.869
Young and Kirkwood (48)	Al-Cu	-0.409	0.158	-0.875

Fig. 9. Effect of temperature gradient on dendrite spacings. Growth velocity $20 \mu\text{m}/\text{sec}$

observed in Young and Kirkwood's data could be due to the small range of gradients encountered in their study, 0.5-13 °C/cm, allowing random errors to noticeably affect any observed empirical relationship. Considering the amount of evidence, it appears that $d \propto G^{-1/3}$, rather than $G^{-1/2}$ as predicted by the theoretical analyses (15,27).

The effect of alloy composition on dendrite spacings at constant velocity is displayed in Figure 10. The data plotted is from the high thermal gradient runs, minimizing the effect of varying gradients. As shown in Figure 10 the effect of alloy composition on dendrite spacing is not conclusive, as evidenced by the negative slope of the 100 $\mu\text{m}/\text{sec}$ curve. However, the average effect of increasing solute content seems to be that of increasing dendrite spacing. There appears to be no rational explanation why the effect of composition should be different at 100 $\mu\text{m}/\text{sec}$ than it is for the other velocities. Even when spacings are normalized with respect to temperature gradient and $dG^{1/3}$ is plotted against C, the trends are similar as $dG^{1/3}$ decreases as C increases at 100 $\mu\text{m}/\text{sec}$ and increases with increasing C at 10, 20, 45, and 200 $\mu\text{m}/\text{sec}$. The effect of concentration as observed in the literature is also inconclusive. Although most (3,24,27,28,32) report a positive dependence of d on C, a study of Fe-C alloys by Ibaraki et al. (17) yielded no effect of carbon content on primary austenite dendrite spacings. Dann et al. (11) ob-

Fig. 10. Effect of alloy composition on dendrite spacings

served that dendrite spacing reached a maximum with alloy composition equal to the solubility limit of Cu in Al and then decreased as solute content increased. In view of the different relationships observed in the present work as well as in the literature, it would seem that the general effect of increasing solute concentration is to increase dendrite spacings, although evidence to the contrary does exist.

The effect of growth velocity on primary dendrite spacings was investigated in the high temperature gradient regime of 317-392°C/cm with five different alloy compositions. Figure 11 is a master plot of the d versus V data on logarithmic axes. Temperature gradients are fairly constant over the growth range studied, so that normalized dendrite spacings, $dG^{1/3}$, yield curves of the same shape. As shown in Figure 11, velocity appears to have its greatest effect at growth rates greater than 45 $\mu\text{m}/\text{sec}$. Below 45 $\mu\text{m}/\text{sec}$ the dendrite spacings seemingly become velocity independent. This change in slope of the d versus V curve can be attributed to at least two possible mechanisms: convection and finite cell spacing as velocity approaches zero.

During the growth of lead dendrites in Pb-Sn binary alloys, a tin rich solute is rejected from the freezing dendrites. This rejected solute is less dense than the surrounding bulk liquid and tends to rise upwards, away from the solidifying dendrites. However, if the growth rate of the

Fig. 11. Effect of growth velocity on dendrite spacings

dendrites is greater than the rate at which the less dense solute rises into the bulk liquid, the solute will flow into the interdendritic regions. Under diffusion controlled growth conditions it is suggested that the spacing coarsens until there is no longer an appreciable overlap in the radial diffusion field. In the present experimental work, interdendritic fluid flow occurs. In the case of growth velocity much greater than $45 \mu\text{m}/\text{sec}$, the lighter tin rich solute is trapped within the interdendritic regions of the dendrite array (Figure 12a). This aids the radial transport of material and leads to a larger spacing. When growth is much slower than $45 \mu\text{m}/\text{sec}$, the net flow at the dendrite tips will be in the opposite direction as before, as the solute will rise faster than the approaching tips and into the bulk liquid (Figure 12b). This aids solute rejection and the need for lateral segregation, reducing the dendrite spacing. At intermediate growth rates, neither condition will predominate, resulting in a compromised effect on primary spacing.

The validity of the convection mechanism was determined by measurement of the degree of macrosegregation which occurred along the length of the solidified samples. As noted by Verhoeven (46), convection is required for macrosegregation to occur during steady state solidification. Three Pb-53.8 a/o Sn samples solidified at 5, 20, and $200 \mu\text{m}/\text{sec}$ were sectioned at various positions along their lengths

Fig. 12. Schematic diagram showing solute flow between lead dendrites growing at velocities (a) much greater than $45 \mu\text{m}/\text{sec}$, (b) much less than $45 \mu\text{m}/\text{sec}$

with a lathe and chemically analyzed to determine the weight percent lead. All three samples exhibited a lead rich initial transient at the start of solidification. The 20 and 200 $\mu\text{m}/\text{sec}$ samples were within -0.8 w/o Pb of the starting alloy composition along the remaining length of rod, indicating very little macrosegregation. However, the 5 $\mu\text{m}/\text{sec}$ sample exhibited +3.0 w/o Pb in the directionally solidified region and -3.6 w/o Pb in the quenched liquid, thus suggesting quite thorough mixing of the rejected solute with the bulk liquid. It appears that a change in fluid flow characteristics could account for the change in slopes of the d versus V curves. The order of magnitude difference observed by Burden and Hunt (10) would be more than sufficient to raise the low velocity end of the curve to a position where the logarithmic plot would become a straight line.

The second proposed mechanism involves the process of a planar solid-liquid interface breaking up into a cellular structure at the onset of constitutional supercooling. If the slopes of the high velocity regime in Figure 11 are extrapolated to the limit as V approaches zero, d becomes infinitely large. However, at the point of planar to cellular transition, the cell structure has a finite spacing, which is approached in the low velocity regime. Thus at high temperature gradients, dendrite and cell spacings could be a function of the form $d = f(V) + d_0$, where f is some function of

velocity and d_0 is the maximum cell or dendrite spacing for a particular temperature gradient. The change in the slopes of the curves of Figure 11 could then be partially attributed to d approaching d_0 as V is decreased. This is analogous to the situation observed by Burden and Hunt (8) in their investigation of dendrite tip undercooling. They observed with Al-2 w/o Cu alloys that tip undercooling was largely influenced by temperature gradient and growth velocity at velocities less than 50 $\mu\text{m}/\text{sec}$. In the high growth rate regime undercoolings became gradient independent and were found to be a sole function of velocity. Thus if d_0 is a function of temperature gradient and alloy composition, similarities are found to exist between the dendrite tip undercooling study and the present study.

Experimental support for this second mechanism of changing d versus V slope is found in other work with silver rich Ag-Pb alloys (Appendix). As lead rich solute is rejected from the solidifying dendrites, convection should not occur. However, the normalized dendrite spacing $dG^{1/3}$ versus V curves display a change in slope at 45 $\mu\text{m}/\text{sec}$ for five different alloy compositions. Jin's (20) study of dendrite spacing in Fe-Ni alloys also yielded data which showed a similar break in the d versus V curve at about 20 $\mu\text{m}/\text{sec}$. As this phenomenon is observed in systems in which convection should not be a variable, the concept of a limiting dendrite or cell spac-

ing appears plausible. However, other investigations (3,11, 24,48) did not indicate a break in the curves, probably the result of growth rates not less than 38 $\mu\text{m}/\text{sec}$. Thus the effect of low velocities could not have been determined from these studies.

While the change of slope at 45 $\mu\text{m}/\text{sec}$ in Figure 11 confuses the analysis of the spacing data, the slope at velocities greater than 45 $\mu\text{m}/\text{sec}$ is found to be fairly constant. The mean of the high velocity slopes was calculated with a least squares fit analysis and found to be -0.479 with a standard deviation of 0.045. While this agrees with the relationship $d \propto V^{-1/2}$ predicted by Okamoto and Kishitake (27), it does not agree with the more rigorous derivation of Hunt (15) in which $d \propto V^{-1/4}$. The gradient normalized mean slope was found to vary only slightly as the mean slope was -0.466 with a standard deviation of 0.049. Data from the literature were calculated with a least squares fit $dG^{1/3}$ versus V analysis with the results tabulated in Table 3. These slopes are

Table 3. Calculated values of least squares analysis of $\log dG^{1/3}$ versus $\log V$ obtained from literature data

Source	Alloy system	Mean slope	Std. deviation	Mean corr. coeff.
Bell & Winegard (3)	Sn-Pb	-0.740	0.015	-0.979
Dann <u>et al.</u> (11)	Al-Cu	-0.365	---	-0.982
Kotler <u>et al.</u> (24)	Pb-Sb	-0.767	---	-0.949
Young and Kirkwood (48)	Al-Cu	-0.299	0.035	-0.873

found to have fairly good average correlation, thus indicating a wide range of spacing dependence on velocity. Thus only a qualitative agreement between the various studies can be found in that the effect of increasing growth velocity is to decrease dendrite spacing.

Testing of the various theoretical analyses is accomplished by plotting various combinations of the growth parameters C , V , and G against d and calculating the slope of the resultant least squares fit slope. Recalling that $\partial T/\partial t$ in the Okamoto and Kishitake (27) analysis is equivalent to VG , examination of Equation 2 shows that if d is plotted against C/VG on logarithmic axes a straight line of slope $1/2$ should result, making the fairly accurate assumption that the rest of the terms are constant (15). Except for the position of the data points of 1 and 4.5 $\mu\text{m}/\text{sec}$, a reasonably straight line is formed in Figure 13. However, a least squares calculation finds the value of the slope, neglecting the two low velocity data points, to be 0.265 with a correlation coefficient of 0.922, barely more than half of the expected slope of $1/2$. It seems that the simplified analysis ignored some very real aspects of dendrite growth, at least in the range of conditions encountered in this study.

The result of the Bolling and Fainstein-Pedraza analysis (4) for Pb-53.8 a/o Sn is presented in Figure 14, and is similar in shape to the curves for the other Pb-Sn alloys.

Fig. 13. Results of Okamoto and Kishitake analysis (27) of Pb-Sn dendrite spacings data

Fig. 14. Plot of Bolling and Fainstein-Pedraza analysis (4) of Pb-53.8 a/o Sn alloy

According to Equation 1, a logarithmic plot of d versus V_o^{-1} should yield a slope of unity. (A value of $K/\Delta H = 7.7 \times 10^{-4} \text{ cm}^2/\text{°C-sec}$ was employed in the calculation of V_o^{-1} (4).) As Figure 14 shows, one slope due to data points with $G < 300^\circ\text{C/cm}$ and another at $G > 300^\circ\text{C/cm}$ results. Although Equation 1 described fairly well the primary dendrite spacing dependence resulting from other studies over a limited range of growth conditions (4), it is inadequate for the wide range of conditions encountered in this work.

The relatively rigorous derivation of Hunt (15) would be expected to more accurately describe the effect of the growth conditions on dendrite spacing. Equation 4 predicts a slope of $1/4$ from Figure 15, a logarithmic plot of d versus C/VG^2 . It appears that the Hunt analysis at values of $C/VG^2 < 0.001$, the high velocity high gradient range, the slope is much closer to $1/4$ than are the points described by $C/VG^2 > 0.001$, the low gradient $20 \text{ } \mu\text{m/sec}$ growth range. This apparent better fit of the data in the high velocity growth regime is probably the result of the inclusion of a surface energy term in θ of Equation 4. At lower growth rates the surface energy of the crystallizing dendrites becomes less important in relation to other factors affecting dendrite growth, although there is no provision in Equation 4 for changing the velocity dependent effect of surface energy. Neglecting the data points of 1 and $4.5 \text{ } \mu\text{m/sec}$, a least squares calculation yielded an average

Fig. 15. Results of Hunt analysis (15) of Pb-Sn dendrite spacing data

slope of 0.191 with a correlation coefficient of 0.947. While the predicted dependence of dendrite spacings on the individual growth parameters in Equation 4 is not correct, Figure 15 indicates that the Hunt analysis is much closer to what is experimentally observed in the present study than were the other two treatments of the dendrite spacing problem. However a more accurate description of the observed individual growth dependences must be left to a more detailed theoretical study.

SUMMARY

The primary dendrite spacings of steady state directionally solidified lead rich Pb-Sn alloys have been observed as a function of the solidification parameters G , C , and V . The relationship of dendrite spacing (d) with the thermal gradient (G) was found to be $d \propto G^{-1/3}$. This concurred with other studies of Pb-Sb (24) and Al-Cu (11,48) alloys solidified at growth velocities (V) from 50 to 500 $\mu\text{m}/\text{sec}$. Thus in the growth ranges investigated, the gradient dependence appears to be invariant. The effect of the initial alloy composition (C) was found to be rather weak and to vary in this study, as well as in the literature. Generally, however, an increase in solute concentration resulted in an increase in dendrite spacing.

Logarithmic plots of d versus V displayed a significant change in slope at 45 $\mu\text{m}/\text{sec}$, the low velocity regime apparently independent of growth velocity. This was attributed to the occurrence of convection during steady state solidification as well as the concept of dendrite spacings approaching a limiting maximum value of cellular spacing. At high growth rates the constant slopes implied $d \propto V^{-1/2}$, qualitatively agreeing with the literature. However the observed dependence cannot be universally assumed, as calculated values of the exponent from data in the literature encompass values from -0.299 to -0.767.

The theoretical dendrite spacing analysis by Hunt (15) was found to describe more accurately the observed relationship between the combined growth parameters and the dendrite spacing than the analyses of Okamoto and Kishitake (27) and Bolling and Fainstein-Pedraza (4). However the predicted dependencies of each growth parameter were not observed in this study and must await a more complete treatment of the problem.

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I wish to dedicate this thesis to my wife Sharon, without whose patience and understanding my graduate career may have never been realized.

APPENDIX

An investigation of the primary dendrite spacings of silver rich Ag-Bi and Ag-Pb binary alloys was conducted prior to the Pb-Sn study. As shown in the equilibrium phase diagrams (12,38) in Figures A1 and A2, a considerable composition range exists over which silver dendrites can be grown. However the curvature of the solidus and liquidus lines preclude any direct comparison of dendrite spacings with the current theoretical analyses.

The previously described Pb-Sn experimental procedure was employed for the silver dendrite study, with the exception that a bundle of Vycor tubes was used in the casting operation, necessary due to the greater liquidus temperature of the alloys in this study. The samples resulting from directional solidification were similarly sectioned, but instead were polished with a Linde A polishing wheel. The Ag-Bi alloys were then etched with a 50 v/o nitric acid, 50 v/o water etchant, while Ag-Pb alloys were etched with 20 v/o glacial acetic acid, 30 v/o hydrogen peroxide, and 50 v/o methyl alcohol. The resulting dendritic microstructure revealed faceting Ag dendrites at high Bi and Pb concentrations, along with considerable formation of secondary dendrite arms at low solute concentrations (Figures A3 and A4). The latter condition was apparently the result of the large temperature range which existed between the liquidus and eutectic tempera-

Fig. A1. Ag-Bi equilibrium phase diagram

Fig. A2. Ag-Pb equilibrium phase diagram

Enlarged approximately 29%

Fig. A3. Faceted dendritic structure of Ag-71 a/o Bi. Growth rate 10.1 $\mu\text{m}/\text{sec}$, temperature gradient 267 $^{\circ}\text{C}/\text{cm}$. Transverse section, 50X

Enlarged approximately 29%

Fig. A4. Dendritic structure of Ag-30 a/o Ph. Growth rate $43.6 \mu\text{m}/\text{sec}$, temperature gradient $140^\circ\text{C}/\text{cm}$. Transverse section, 38X

tures at low concentrations.

The results of the primary silver dendrite spacings for the two alloy systems are found in Tables A1 and A2. Although limits of precision for d , V , and G are not tabulated, they are assumed to be of similar magnitude as those calculated for the Pb-Sn alloys, as the experimental procedures were identical in both studies.

The effect of growth velocities on the dendrite spacings displayed a variable dependence, as a change in slope of the isoconcentrate logarithmic plots of $dG^{1/3}$ versus V curves at $45 \mu\text{m/sec}$ was characteristic of both alloy systems (Figures A5 and A6). As convection should only occur during steady state solidification of Ag-Bi alloys, the concept of dendrite spacing approaching a limiting value of cell spacing at low growth rates is reinforced. Calculations of the average slopes of the $V > 40 \mu\text{m/sec}$ area of the plots yielded means of -0.460 and -0.514 with standard deviation of 0.142 and 0.076 for the Ag-Bi and Ag-Pb systems respectively. These values are indicative of a $d \propto V^{-1/2}$ relationship at constant composition and gradient, in excellent agreement with the Pb-Sn study.

As solute concentration was varied over the range of compositions investigated, the isovelocity $dG^{1/3}$ versus C curves of Figures A7 and A8 exhibited minimums at 44 to 57 a/o Bi and 44 a/o Pb. Referring to Figures A1 and A2, the

Table A1. Summary of Ag-Bi data on the effect of solidification rate (V), thermal gradient (G), and alloy composition (C) on the measured dendrite spacing (d)

Run No.	d (μm)	V ($\mu\text{m}/\text{sec}$)	G ($^{\circ}\text{C}/\text{cm}$)	C (a/o Bi)
45	75.6	202.8	332	85
46	148.	44.8	298	85
47	224.	10.1	295	85
54	70.7	201.6	327	71
56	119.	45.0	283	71
55	140.	10.1	267	71
48	61.4	202.8	314	57
49	114.	44.8	274	57
50	138.	10.0	258	57
51	50.7	201.6	292	44
52	148.	45.0	244	44
53	198.	9.96	215	44
57	105.	201.6	233	30
59	269.	45.5	198	30
58	334.	10.1	180	30
77	156.	201.6	191	20
79	282.	45.3	170	20
78	461.	10.1	162	20

Table A2. Summary of Ag-Pb data on the effect of solidification rate (V), thermal gradient (G), and alloy composition (C) on the measured dendrite spacing (d)

Run No.	d (μm)	V ($\mu\text{m}/\text{sec}$)	G ($^{\circ}\text{C}/\text{cm}$)	C (a/o Bi)
63	139.	202.8	355	85
60	261.	44.8	323	85
62	313.	10.1	334	85
65	78.1	202.8	293	71
66	172.	45.5	263	71
64	266.	10.2	271	71
68	78.1	202.8	237	57
67	170.	45.5	226	57
69	264.	10.1	201	57
75	74.7	201.6	198	44
74	189.	44.6	175	44
73	223.	10.1	165	44
72	93.2	202.8	208	30
70	257.	43.6	140	30
71	295.	10.1	134	30

Fig. A5. Effect of growth velocity on normalized Ag-Bi dendrite spacings

Fig. A6. Effect of growth velocity on normalized Ag-Pb dendrite spacings

Fig. A7. Effect of alloy composition on normalized Ag-Bi dendrite spacings

Fig. A8. Effect of alloy composition on normalized Ag-Pb dendrite spacings

concentrations of observed minimum spacings are seen to occur at points where the liquidus curve encounters a significant change of slope, increasing the equilibrium distribution coefficient (K) at a much faster rate. Perhaps the changing value of K is responsible for the minimum normalized spacing observed in the curves. However, the minimums are observed at compositions where the dendrite morphology degenerated to an extent that distinguishing a primary dendrite arm from a secondary arm became very difficult. Ag-Bi compositions of 85, 71, and 57 a/o Bi and Ag-Pb compositions of 85 and 30 a/o Pb produced definite dendritic structures. The remaining compositions were characterized by the degenerate morphology, and must be suspect in their values for absolute dendrite spacings. Therefore the minimums observed in the curves of Figures A7 and A8 could be a result of the difficulty encountered in the determination of dendrite spacings of the degenerate morphologies.

The effect of temperature gradient was not studied in the Ag-Bi and Ag-Pb systems as the liquidus temperatures of the silver alloys were sufficiently high to prevent the establishment of a large range of gradients in the directional solidification apparatus.