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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF APPLIED SCIENCE

in the Department of METALLURGY

We accept this thesis as conforming to the standard required from candidates for the degree of MASTER OF APPLIED SCIENCE

THE UNIVERSITY OF BRITISH COLUMBIA

August, 1970

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Date September 24, 1970

ABSTRACT

A qualitative investigation of interdendritic liquid flow was carried out on pre-cast Pb-20Sn ingots at temperatures where the casting was partially liquid. The liquid flow was found to be preferential in nature, and strongly dependent on surface tension effects.

Castings of Cu-8Ag and Al-30Ag were made in which the chill was removed during solidification to cause exudation of solute rich liquid. Macrosegregation was detected using radioactive tracer elements. The castings were characterized by a solute enriched exuded zone and a solute depleted region adjacent to the chill. Models based on the simple back-flow of residual liquid to feed exudation were developed to explain the composition profiles adjacent to the chill.

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ACKNOWLEDGEMENT

I am greatly indebted to my research director, Dr. F. Weinberg, for his excellent guidance and encouragement throughout this work. Assistance from other faculty members and fellow graduate students is also gratefully acknowledged.

I extend special thanks for generous assistance given by many members of the departmental technical staff; in particular Mr. J. Brezden for his unfailing aid during much of the experimental work.

I gratefully acknowledge financial assistance from the Defence Research Board [grant number 9535-51].

INTRODUCTION

Extensive theoretical calculations that quantitatively predict inverse segregation behaviour have been formulated by Scheil,¹ Kirkaldy and Youdelis,² and Flemings et al.³ The models used in these calculations are based on the assumption that inverse segregation is caused solely by the back-flow of interdendritic liquid to compensate for the volume shrinkage of dendrites on freezing and cooling. As a result, nearly all the experimental work in this field has been done on aluminum alloys because of their high volume changes on freezing and thermal expansion coefficients.

A typical inverse segregation experiment consists of directionally solidifying a melt from bottom to top and chemically determining the composition of thin slices cut from the ingot perpendicular to the solidification direction. Typical results for rapidly cooled castings in the Al-Cu system after Flemings³ and Adams⁴ are shown in Fig. 1.

The inverse segregation curve is generally explained in the following manner: As solidification begins, a semi-solid (mushy) zone is formed, and residual enriched liquid (resulting from normal segregation during freezing) feeds downwards to compensate for freezing shrinkage causing an enrichment in solute near the chill. As a result, the enriched liquid at the upper part of the mushy zone is



Figure 1. Typical inverse segregation profile for directionally solidified castings.

replaced by liquid of nominal composition, Co, causing a solute impoverishment in this region. As solidification progresses, this impoverished region is also fed by solute enriched liquid causing another impoverished zone to form above it. This process continues until the impoverished zone reaches the top of the ingot at which point feeding is no longer possible and the composition drops.

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Flemings et al,³ who present the most comprehensive analysis of macrosegregation in binary alloys, consider a volume element in the semi-solid zone containing both solid and liquid material, and examine the flow of fluid through this element. To predict microsegregation in the element, they use the classical non-equilibrium freezing equation:

$$C_s = kCo(1-g)^{k-1}$$

where C_s = solid composition at the solid-liquid interface g = fraction of solid material Co = initial average composition within the volume element considered.

k = partition ratio

This equation, which assumes no diffusion in the solid and no macrosegregation, was derived for one-dimensional solidification.

The other important assumptions made in the Flemings analysis are:

- (a) Negligible undercooling before nucleation.
- (b) No net flow of solute from the volume element by diffusion.
- (c) Diffusion in the liquid within the volume element is complete.
- (d) The partition ratio, k, applies at the interface and is constant throughout solidification.

In short, a number of assumptions are made concerning the flow of interdendritic liquid to derive theoretical solute distribution profiles which are subsequently compared to experimental profiles. The initial aim of this project was to directly study the flow-rate of interdendritic liquid in Pb-Sn alloys using radioactive tracers. The particular experiment designed for this investigation was unsuccessful, however, but yielded qualitative results which led to the study of exudations in the Cu-Ag and Al-Ag systems. This thesis, consequently, is divided into two parts.

In Part I, Pb-Sn ingots are heated into the semi-solid range and interdendritic liquid is displaced by eutectic liquid using gravity as the driving force. The only similar work known to the author was done by Piwonka and Flemings⁵ who used molten lead to displace the interdendritic fluid of an Al-4.5% Cu alloy. The flow observed was homogeneously distributed between dendrites and was compared to flow through porous beds. This can be expected when one realizes the extremely low solubility of aluminum in molten lead (0.1 wt. pct. Al at 600°C). The purpose of the present work, therefore, was to study a more realistic situation, where one might expect the partial dissolution of dendrites and subsequent widening of interdendritic channels.

In Part II, melts of Cu-Ag alloy and Al-Ag alloy are partially solidified from one end, and the chill is moved a short distance away from the casting causing reheating and exudation at the chill-face of the ingot. To the author's knowledge, this type of experiment has not been previously studied in any detail.

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PART I - INTERDENDRITIC FLOW IN LEAD-TIN

- 1. Introduction
- 1-1. Original Intent

The original objective was to measure the rate of flow of interdendritic liquid using radioactive tracer elements and tracer detection devices. The material chosen for this study was to have a broad semi-solid region with respect to both composition and temperature. The initial idea is shown pictorially in Fig. 2. The ingot



Figure 2. Apparatus for measuring the flow-rate of interdendritic liquid using tracers.

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was to be held at constant temperature in the semi-solid region and the tracer containing eutectic would flow downwards through interdendritic channels. Liquid falling through the ingot would be caught on an aluminum screen and immediately removed. A geiger counter would monitor the activity of the descending material and the count rate would be adjusted to give the flow-rate of interdendritic liquid. This specific experiment, unfortunately, was not successful, as will be seen later, and studies of interdendritic flow were confined to autoradiography, metallography, and drop experiments.

1-2. Choice of Materials

A Pb-20 wt.pct. Sn alloy was chosen for the following reasons:

(a) The low melting point of the system (327°C for pure lead) made furnace construction and handling relatively easy.

(b) At the composition selected, a broad semi-solid zone exists with respect to both tin concentration and temperature. The phase diagram⁶ is shown in Fig. 3.

(c) Radioactive T1²⁰⁴(T1^{*}) was available as a tracer element. Large concentrations of T1^{*} are completely soluble in lead and the physical properties of T1^{*} are virtually identical to those for pure lead. Being a beta emitter, T1^{*} is ideal for autoradiography because photographic film is much more sensitive to low energy radiation as opposed to, for example, higher energy gamma radiation. Good contrast and resolution are also possible since lead has a large capture crosssection for beta radiation.

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Figure 3. Phase diagram of the Pb-Sn system.

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During the experimental work, other advantages of Pb-20 Sn were discovered:

(d) The softness of the alloy made machining and polishing of specimens relatively simple.

(e) Eutectic formations made dendrites easily distinguishable for metallographic studies.

(f) The high coefficient of absorption of lead with respect to tin for electrons and X-rays made high resolution electron backscatter images possible on the electron microprobe.

2. Experimental

2-1. Alloy Preparation

The alloy was prepared using high purity Cominco Pb (99.999%) and high purity Vulcan Sn (99.999%). Starting ingots were made by melting the constituents in a graphite crucible, stirring, and casting into graphite moulds. Final cylindrical ingots having various dendritic structures were prepared by the following techniques:

(a) The ingot was made by furnace cooling the melt from 350°Cin a graphite crucible, producing an equiaxed dendritic structure (E).

(b) A starting ingot was placed inside the graphite mould of the apparatus shown in Fig. 4. The mould was heated and the melt was held at 310.0 ± 0.2 °C for 35 minutes to insure homogeniety. The bottom end of the ingot was chilled by spraying cold tap water from a constant head (18") against the copper plug. Ingots 2.2" long and 0.88" in diameter were made using this technique under an argon atmosphere to prevent oxidation. This produced a dendritic columnar



Figure 4. Apparatus for making columnar Pb-20Sn ingots.

structure with a small primary dendrite arm spacing (SC).

(c) This process is the same as (b) except that the chill is done using air at a constant flow-rate, producing a dendritic columnar structure of larger spacing (LC).

After casting the SC and LC ingots, 0.4" was machined off both ends to remove macrosegregation effects (i.e. the solute enriched zone near the chill and the depleted zone at the top of the ingot). Desired lengths were cut from the remaining casting, and the ends were machined smooth.

2-2. Tracer Prepartion

To investigate the effect of adding T1^{*} to the Pb-20Sn alloy, ingots were cast containing 1000 ppm. of T1^{*} as received from Chalk River. One ingot was quenched from the melt in water and the other was furnace cooled. The ingots were sectioned longitudinally and autoradiographed using Kodak Contrast Process Ortho Film. In both cases the film was blackened evenly, indicating that any segregation of T1^{*} could not be resolved using this technique.

A eutectic Pb-Sn alloy containing 1700 ppm. of T1^{*} was made for use in subsequent experiments and will be referred to as "Master Alloy". Being of eutectic composition, this alloy melts all at once at the lowest temperature at which liquid can exist in the Pb-Sn system. The importance of this will become obvious later.

2-3. Apparatus

Prepared specimens were placed in the furnace shown in Fig. 5.



Figure 5. Furnace for heating Pb-20Sn ingots.

The most important part of the furnace was a copper cylinder to provide temperature homogeniety. The inside of the cylinder had a diameter of 0.88" and was tapered such that the diameter of the bottom end was 0.020" greater than that of the top end. Specimens were pushed into the cylinder using a 0.75" diameter brass rod with a flat polished end. The result was a snug fit between the outside of the ingot and the inside of the copper cylinder, preventing any molten material from flowing down along this interface. Both inside and outside surfaces of the cylinder were coated with an adherent graphite layer using a colloidal graphite wash. This prevented any dissolution of copper by the lead or the tin. The graphite layer could be thickened somewhat to provide a snug fit for slightly undersized ingots.

In some cases a thin wafer of Master Alloy was placed on top of the ingot. To accommodate this wafer a small depression 0.1" deep and 0.73" in diameter was machined into the top of the ingot.

Two iron-constantan thermocouples were inserted in the copper block, as shown in Fig. 5; one for a Honeywell temperature controller, and the other for a Honeywell Electronik 194 temperature recorder. An ice bath was used as a cold junction for both thermocouples. The temperature control system using two heating elements is shown schematically in Fig. 6. The control circuit prevented a temperature drop at the open end of the furnace, while the main circuit controlled the overall temperature.

The complete copper cylinder assembly was supported by a brass tube and could be lowered into a water bath below the furnace for

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Figure 6. The temperature control circuit for heating Pb-20Sn ingots.

quenching. A long pyrex tube was inserted down the supporting tube to introduce an argon atmosphere and prevent oxidation of the upper surface of the ingot.

A long copper tray lined with a wire mesh and filled with water was used to catch drops of molten metal below the furnace. After a drop fell into the tray, the tray was shifted so that the next drop fell on a separate area and could subsequently be weighed separately. The time of falling was recorded on the temperature chart by briefly shorting the thermocouple.

2-4. Metallography and Autoradiography

Specimens were milled to the desired surface in the ingot with a 0.50" diameter milling tool at high speed. The milled surface was sufficiently smooth to proceed directly to a 5 micron alumina polishing lap, followed by a 0.05 micron alumina lap. The etching action of the water used in polishing was sufficient to obtain good resolution of dendritic structures. A diamond lap was found unsatisfactory for polishing Pb-20Sn specimens. Mounted specimens were also difficult to polish because the alloy was cut away faster than the epoxy mounting material. Metallographs were made with unfiltered lighting using a Reichert microscope and Polaroid Type 55 Positive/Negative film.

Radioactive specimens were prepared and polished as above. To autoradiograph, the polished surface was placed against a sheet of Kodak Contrast Process Ortho film for periods of time varying from 24 to 98 hours until the best resolution was obtained. In all the autoradiographs shown, tracer is present in the dark regions.

2-5. Electron Microprobe Analysis

Composition analysis of metallographic specimens was done using a JEOL Model JXA-3A Electron Probe X-ray Microanalyzer. Details of electron backscatter and absorption corrections are given in Appendix A.

3. Results

3-1. Temperature Distribution within the Pb-20Sn Ingot

A Pb-20Sn ingot 0.75" in length was cast with thermocouples in the locations shown in Fig. 7. Thermocouple #8 was placed up through the bottom



Figure 7. Locations of thermocouples to determine the temperature distribution inside a Pb-20Sn ingot.

of the furnace and just touched the surface of the ingot. The system was held at 200°C and the control circuit was adjusted to give the most homogeneous temperature distribution. This setting was used for all subsequent experiments. The temperature difference between thermocouples #1 and #2 was not detectable to within 0.1°C. The temperature recorded by the thermocouple inside the copper cylinder, therefore, was considered representative of the temperature of the ingot. The maximum temperature difference between any two thermocouples (#1 and #8) was 0.2°C.

3-2. Experiments on Type E Ingots

Type E ingots of Pb-20Sn alloy, 0.7" in length, were held at the eutectic temperature (183°C) for 5 minutes and then heated slowly at a rate of 0.5°C per minute. The undersurface of the ingot was observed using a mirror. Small bubbles of molten metal were visible at 209°C and these increased in size as heating continued. Finally these bubbles coalesced into one large bubble which hung from the bottom of the ingot. This bubble continued increasing in size and finally dropped into the water quench at 248°C.

A similar experiment was conducted with a thin wafer (0.1" thick) of Master Alloy covering the top of the specimen. The furnace was held at 248°C for 40 minutes. The first drop of molten metal fell when 248°C was first reached and all subsequent drops fell within the first 13 minutes. Nine droplets, each having approximately the same volume and weight, fell in all. The last droplet was quite radioactive indicating that some liquid from the top of the ingot had flowed through

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to the bottom. The total weight of the droplets was 9.7% of the total weight of the original ingot. According to the phase diagram (Fig. 3), the ingot was about 30% liquid.

The system was quenched and the remaining ingot, which had shrunken slightly in both length and diameter, was sectioned longitudinally. (The time for the ingot to become completely solid during quenching was 10 seconds.) The micrographs and autoradiographs are shown in Fig. 8. The Master Alloy was the first material to melt and it flowed downward replacing the interdendritic liquid in the casting. From Fig. 8, one observes that the flow was concentrated towards the center of the ingot, but was interdendritic in nature. The same phenomena was observed in repeated experiments using the same equiaxed structure.

3-3. Experiments on Type SC Ingots

A series of experiments were conducted on type SC ingots 0.4" in length. The ingots had a regular columnar structure and an average primary dendrite spacing of about 400 microns. The thermal conditions of the experiment are listed in Table 1. In all cases identical heating

Table 1.

Experiment No.	Holding Temperature	Holding Time at Temperature before Quenching	Other Conditions
A	220°C	0	
В	235°C	0	
С	245°C	2.3 min.	
D	_245°C	2.3 min.	Wire mesh posi- tioned at the bottom face of the ingot.

Thermal Conditions for Experiments on Type SC Ingots



Figure 8. Micrographs (a) and autoradiographs (b) of a longitudinal section of a type E ingot in which interdendritic flow has occurred.

rates of 6°C per minute were used in heating to temperature. For experiment D, a 24 mesh brass screen having a hole diameter of 0.03" was placed against the bottom face of the ingot. The mesh was coated with colloidal graphite to prevent wetting by molten Pb-Sn alloy.

After quenching, the ingots were sectioned and autoradiographed as shown in Fig. 9. The fineness of the dendrite structure, unfortunately, prevented good resolution. One observes, however, that the flow of interdendritic liquid was not homogeneously distributed over the entire cross-section of the ingot, but was preferential in nature.

Comparing the autoradiographs of tests C and D (Fig. 9), one sees that the presence of the wire screen greatly inhibited the flow of liquid. The grid, in effect, broke the large bubble, which normally hangs below the ingot as in Fig. 13, up into smaller bubbles. This indicates that surface tension effects at the surface of the ingot play an important role in restricting liquid flow.

The pressure, P, due to surface tension, T, on a droplet of radius r is given by:

$$P\alpha \frac{T}{r}$$

Referring to Fig. 10, as r decreases (due to the presence of a screen), the pressure restricting the flow of liquid increases.



- X 3
- Figure 9. Autoradiographs of longitudinal sections of type SC ingots showing liquid flow patterns.



Figure 10. Schematic representation showing the effect of bubble size on liquid flow.

3-4. Determination of the Liquid Flow-rate

A type SC ingot 0.4" in length with a 0.1" thick wafer of Master Alloy on top was heated at 6°C per minute to 245°C and held there until liquid droplets of metal stopped falling. Droplets were collected in the movable tray underneath the furnace and the time of falling was recorded. By weighing each droplet, the flow-rate was determined as follows. In the interval of time during which a drop starts to form until it falls, a linear build-up rate of material in grams per minute is assumed. The first droplet is assumed to start forming at the first liquid temperature (183°C) and stop forming when it falls. The weight of the first droplet is divided by this time interval to give the average rate of formation. The rate of build-up of subsequent droplets is determined by using the time interval between the falling of the droplet in question and the preceding one. The results for 3 such experiments are shown in Fig. 11. The important feature to notice is that most of the flow occurred catastrophically during a short interval of time.

In work done by Piwonka and Flemings,⁵ the flow-rate of molten lead through a semi-solid Al-4.5Cu alloy was compared to fluid flow through porous beds using Darcy's Law:

$$Q = \frac{K\Delta P}{uL}$$

where Q = flow rate per unit area.

 ΔP = pressure drop across an ingot of length L.

 μ = viscosity of the liquid.

K = permeability of the bed.

The permeability was found to vary with the square of the fraction of liquid, f_L , present in the ingot. Using their permeability versus fraction liquid data, assuming the liquid is of eutectic composition, and estimating the liquid fraction from the Pb-Sn phase diagram, the flow-rates obtained in this work (Fig. 11) were compared to Darcy's Law. The pessure drop, ΔP , was calculated from:

 $\Delta P = \rho g L$



Figure 11. The liquid flow-rate in type SC ingots heated to 245°C.

where ρ = density of the eutectic
g = gravitational field strength
L = ingot length

Two flow-rates were considered: the initial rate at low temperature (0.3 gm/min.) and that during catastrophic flow (2.5 gm/min.). The results are listed in Table 2. During catastrophic flow one observes that the flow was at least one order of magnitude greater than what is predicted by flow through porous beds.

Table 2

Comparison of Flow-rates with Darcy's Law

•		
Temperature (°C)	203	223
Liquid fraction, f _L	0.03	0.14
Permeability, K (cm ²)	3×10^{-11}	10^{-10}
Liquid viscosity, 7 μ (poise)	0.025	0.023
Liquid density, 8 ρ (gm/cm 3)	8.41	8.42
Ingot length, L (cm)	1.0	1.0
Pressure drop, AP (dynes/cm ²)	8.25×10^3	8.25 x 10^3
Calculated flow-rate (cm/sec)	1.0×10^{-5}	3.6×10^{-5}
Experimental flow-rate (cm/sec)	1.5×10^{-4}	1.3×10^{-3}

3-5. The Effect of Diffusion and Convection

The experiment consisted of determining the rate of penetration of Master Alloy into a partially melted casting with no flow out of the bottom of the ingot. As shown in Fig. 9, the dendritic structure of type SC ingots was too fine for good resolution in the autoradiographs.

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For further study, therefore, type LC ingots with larger dendrite spacings were used. The average primary dendrite arm spacing was 1400 microns.

The bottoms of the ingots were blocked off with a graphite plug. A wafer of Master Alloy was placed on top of the ingot and the system was held at 250°C for various periods of time. Heating between the first liquid temperature (183°C) and 250°C required 11 minutes. The penetration of tracer material was measured from autoradiographs as in Fig. 12. Using a value of $D = 10^{-5}$ cm²/sec in the approximate



X 8

Figure 12. Autoradiograph of a longitudinal section of a type LC ingot to show diffusion effects. Holding time: 20 minutes at 250°C.

expression: $x^2 = 2Dt$, where x is the diffusion distance and t is the time, penetration distances were calculated and compared with measurements as listed in Table 3.
Table 3

Theoretical and Experimental Penetration Distances

of Master Alloy

Temperature conditions	Penetration of tracer			
	observed x	calculated x		
5 min. at 250°C	0.1 cm	0.14 cm		
20 min. at 250°C	0.2 cm	0.19 cm		

The observed and calculated values of the penetration are essentially the same. This demonstrates that negligible fluid flow existed in the interdendritic liquid for the thermal conditions used in the experiments.

3-6. Experiments on Type LC Ingots

Experiments were done with two equally sized ingots, each 0.4" long, placed one on top of the other. The upper ingot was Master Alloy and the lower one was a type LC ingot. The furnace was heated at 6°C per minute and the system was quenched at various temperatures. The following observations were made:

(a) The first small bubbles of liquid metal became visible at : the undersurface of the ingot at 190°C.

(b) At 198°C, molten droplets began falling at a rate too fast to count using the sliding tray. A view of the bottom of the ingot after the first droplet has fallen is shown in Fig. 13.

(c) All the eutectic, which originally sat above the lower



Figure 13. Bottom view of a type LC ingot after the first droplet has fallen.



Figure 14. Longitudinal section of a type LC ingot quenched at 196°C.

ingot, passed through the ingot leaving it structurally intact.

Figures 14 and 15(a) show longitudinal sections of ingots quenched at 196°C and 209°C. In the first case, flow of interdendritic liquid has barely begun, but one can see thin continuous interdendritic pipes which extend the full length of the Pb-20Sn ingot. In the second case, flow has been completed and one observes widening of a few channels. Inside these channels are what could be interpreted as dendrite sections broken or melted off the side of the channel. If this was, in fact, true, these dendrite sections would not contain T1^{*} and would appear white in an autoradiograph. The autoradiograph of the channels, Fig. 15(b), shows an enrichment of tracer in the dendritic sections, indicating that the dendrites inside the pipes did not come from the casting, but were associated with freezing during the quenching process.

The preferential "flow-pipes" are clearly shown in a section of the ingot perpendicular to the columnar axis in Fig. 16. The plane shown is 0.1" from the original bottom end. The autoradiograph in Fig. 16(b) shows several large pipes and the outline of a dendritic structure in two large regions. This indicates that some of the flow was interdendritic in nature without substantial widening of pipes.

3-7. Electron Microprobe Results.

The purpose of this study was to determine compositional changes inside a flow-pipe. The microprobe was used to analyze composition at cross-sections taken from the top and bottom of an LC ingot through which complete flow of eutectic had occurred. Random counts were taken

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Figure 15. Longitudinal section of a type LC ingot quenched at 209°C: micrograph (a) and autoradiograph (b).



Figure 16. Cross-section of a type LC ingot quenched at 209°C: micrograph (a) and autoradiograph (b). in various regions of the ingot as depicted in Fig. 17(a), and averaged to give the results shown in Table 4. 20 random counts were taken for each region. An electron backscatter photograph of the ingot showing the two-phase dendritic structure and the two-phase eutectic structure is shown in Fig. 17(b).

Table 4

Region of ingot	Composition (wt.%)			
	Top of ingot	Bottom of ingot		
Pb rich phase in a flow-pipe (α ₁)	83.5% Pb	91.9% Pb		
Sn rich phase in a flow-pipe (β ₁)	84.8% Sn	93.2% Sn		
Pb rich phase of a dendrite (α_3)	90.0% Pb	89.7% Pb		
Sn rich phase of the interdentritic eutectic (β_2)	80.5% Sn	80.9% Sn		

Compositions of a Type LC Ingot

The measured tin compositions are not believed to be very accurate because of the high absorbitivity of lead. Consider, therefore, the composition of the α_1 phase in a flow-pipe. On quenching, nucleation of dendrites in the channel occurred first, followed by the sudden freezing of eutectic. Homogeneous freezing is assumed to occur since the dendrites have an equal size and distribution throughout the channel. Referring to Fig. 18, one starts with eutectic composition above the ingot. At the top of the ingot, enrichment of the eutectic

1 в,[©] α, ^a3 0 β₂ FLOW-PIPE MATRIX

(a)



Figure 17. Regions analyzed for composition (a) and an electron backscatter image (b) of a cross-section of a type LC ingot.

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Figure 18. Phase diagram showing the effect of dissolution on the composition inside a flow-pipe.

in lead by dissolution at the walls of the pipe produces an off eutectic composition, A. The first solid of this material forms at B. With continued cooling, solid B approaches F, and liquid A approaches C until eutectic nucleates and the remaining liquid freezes. At the bottom of the pipe, increased dissolution causes a greater enrichment of the eutectic D. As before, D approaches C and E approaches G. The lead concentration, G, at the bottom of the pipe is, therefore, greater than the lead concentration, F, at the top of the pipe. This enrichment of eutectic was observed experimentally as shown in Table 4 (α_1 phase).

4. Discussion

(a) The rate of interdendritic liquid flow in a single pipe could not be measured with the experimental apparatus used because of the preferred nature of the fluid flow. Had the flow been homogeneously distributed, one could have calculated the interdendritic flow-rate by dividing the total flow-rate by the number of interdendritic channels.

(b) The use of a geiger counter to measure the flow-rate was impractical because of the formation of large liquid droplets at the underside of the ingots. Determining a flow-rate by counting the activity of Tl^{*} in these droplets would introduce complicated geometrical factors concerning the size and shape of these droplets since lead is a good beta radiation absorber.

(c) Flow on a more extensive scale, producing massive exudation of liquid metal, was, therefore, studied. The model for such flow is shown schematically in Fig. 19. With eutectic liquid above the ingot,



Figure 19. Interdendritic fluid flow model for Pb-20Sn.

flow occurs as follows: As flow starts, it is more or less evenly distributed between dendrites over the entire cross-section of the ingot. Because no two interdendritic channels are exactly alike, flow is more rapid in some channels than in others. The more rapid flow in these channels causes faster dissolution of the channel walls and hence more rapid widening. These pipes, as a result, pass more fluid causing further widening. Given a certain cross-section of ingot, therefore, flow becomes more and more localized with time. Localization of exudations is observed in continuous cast aluminum ingots, and is believed to occur when the ingot breaks away from the mould wall due to shrinkage. (d) Surface tension effects at the surface of the ingot can affect the flow of interdendritic liquid.

(e) No correlation was found between liquid flow-rates in Pb-20Sn and those predicted by porous bed theory. The experimental flow-rates were considerably higher than those predicted by Darcy's Law, presumably because of the dissolution and widening of interdendritic channels causing increased flow.

PART II - BACK-FLOW IN COPPER-SILVER AND

ALUMINUM-SILVER

1. Introduction

1-1. Objective

The results of Part I demonstrated that flow through interdendritic channels in the model system examined was not homogeneous. As a result, further attempts to analyze the rate of back-flow using classical inverse segregation concepts were abandoned. A new type of experiment was developed instead, to study the more massive back-flow phenomenon responsible for exudation at the chill-face of a casting. Forced exudation was produced in melts of binary alloy systems by partially solidifying a melt from one end, and removing the chill. Tracer elements were used for composition analysis.

1-2. Choice of Materials

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Binary systems having a broad semi-solid range as in the Pb-Sn system were chosen. Most of the experimental work was done on Cu-8 wt. pct. Ag alloy and later experiments on Al-30 wt. pct. Ag. The phase diagrams⁶ are shown in Fig. 20. Silver was chosen as a solute constituent so that radioactive Ag^{110} (Ag^{*}) could be used as a tracer element. This tracer was used to calculate solute concentrations and was chosen for the following reasons:



Figure 20(a). Phase diagram of Cu-Ag



Figure 20(b). Phase diagram of Al-Ag.

(a) The properties of Ag^{*} are virtually identical to those of pure silver. The tracer, therefore, is assumed to segregate in exactly the same manner as the silver.

(b) Ag^{*} is a strong γ emitter. High energy radiation is required to minimize geometry effects when counting the activity of radioactive specimens.

(c) Ag^{*} has a reasonably long half-life (249 days) which eliminates the necessity of correcting for decay effects during the counting operation.

(d) In the Pb-Ag^{*} system, Weinberg⁹ found a linear dependence between the activity of the alloy and the composition.

2. Experimental

2-1. Apparatus and Casting Procedure

The equipment, as shown in Fig. 21, consisted of an upper graphite crucible for holding a molten charge, and a lower graphite mould with a water-cooled copper chill at the bottom end. The chill consisted of a movable copper pedestal. A Lepel induction furnace provided power.

Molten charges were held in the upper crucible for 1 hour with occasional stirring by an alumina paddle to insure homogeniety of the melt. The temperature of the melt was monitored by a chromel-alumel thermocouple. Temperature corrections were made by manually adjusting the power setting on the induction furnace. During this operation, the copper pedestal was in a lowered position, removed from the graphite mould.



Figure 21. Apparatus for casting Cu-Ag and Al-Ag ingots.

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Immediately before casting, the induction furnace was switched off and the pedestal was raised into position. This last minute raising of the pedestal prevented the graphite mould, whose temperature was comparable to that of the melt, from cooling substantially before casting. A vycor sleeve around the top of the chill helped to hinder such cooling.

To cast, the alumina plug was pulled causing the molten charge to pour into the lower mould against the chill After pouring, the chill could be pulled away at any desired time. A chromel-alumel thermocouple contained in a 0.13" diameter silica tube was located on the longitudinal axis of the casting 0.3" from the chill. Using room temperature as a cold junction, this thermocouple monitored the cooling rate on a Honeywell chart recorder. The ingots made using this method were cylindrical in shape: 1.0" in diameter and 3.2" long.

In all cases, the casting temperature for Cu-8Ag was 1250°C and for Al-30Ag was 800°c.

2-2. Alloy Preparation

Cu-8Ag alloy was prepared by adding the constituents to the upper crucible and holding at 1250°C. High purity Koch-Light Cu (99.99%) and Johnson-Matthe-Mallory Ag (99.95%) were used to make a 370 gm molten charge. In some cases, 50 ppm. of Ag^{*}, as received from Chalk River, were added to the melt. The alloy was prepared at a pressure of about 10 microns of mercury; the vacuum being supplied by a Welch Duo-Seal vacuum pump. This prevented oxidation of the alloy and the graphite

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components of the apparatus.

Al-30Ag alloy was prepared from high purity Alcan Al (99.99%) and the same silver as above, to make a 140 gm molten charge. For composition analysis, 35 ppm. of Ag^{*} were added. This alloy was prepared under an argon atmosphere at 800° C.

2-3. Composition Analysis

To analyze for composition, thin cross-sectional slices 0.005" thick were removed from ingots containing Ag^{*} perpendicular to the solidification direction (i.e. parallel to the chill-face) on a lathe. The activities of the turnings from these sections were measured with a Hamner scintillation counter. Counts were taken over a 20 sec. time interval. Ten such counts were made on each batch of turnings. These were averaged and normalized to the weight of the sample, giving counts/ 20 sec./gm.

Loose batches of turnings gave the same counts as compacted batches. Geometry effects were, therefore, neglected. From statistics, the counting error involved is approximately equal to the square root of the counts. Since most of the counts obtained were in the 12,000 counts/20 sec. range, the counting error is about 1%.

The measured activity was assumed to be directly proportional to the silver concentration. Experimental results by Weinberg⁹ show a direct linear correspondence between the activity and the silver concentration in Pb-Ag alloys. The above assumption is reasonable, therefore, because aluminum and copper both have much lower capture cross-sections for γ radiation than lead.

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Activities were plotted versus distance along the ingot. A mean activity line was then drawn to equalize areas under the curve, above and below this line. This activity corresponded to the average composition, Co, of the ingot. The actual composition profile was established by multiplying the activity ratios, taken with respect to the mean activity, by Co.

2-4. Metallography and Autoradiography of Cu-8Ag.

The final stages of polishing were done on 6 micron and 1 micron diamond laps. Polished specimens were etched with a dilute solution of HCl and FeCl₃. Best results were obtained with unounted specimens and metallographic photographs were taken as in Part I.

Autoradiography was done as in Part I.

2-5. Electron Microprobe Analysis

Electron microprobe analysis was done on polished and slightly etched specimens using the same apparatus as in Part I. Details of the correction factors for Cu-Ag are given in Appendix B.

3. Results

3-1. General

A number of castings were done in which the chill was rmeoved at various times during solidification, causing liquid metal to flow down through the original chill face. Removing the chill did not arrest the overall cooling of the system. Cooling continued at a slower rate until the back-flow of liquid eventually stopped. A typical Cu-8Ag casting is shown in Fig. 22.



X 2

Figure 22. A typical Cu-8Ag casting in which the chill has been removed during solification.

Most of the experimental work was directed towards Cu-8Ag alloy since difficulties were encountered in obtaining consistent and reproductable results with A1-30Ag.

3-2. The Cu-8Ag System

3-2-a. Composition Profiles

The composition profiles and the accompanying cooling curves are shown in Figures 23 and 24 respectively. The profile labelled N represents a "normal casting" in which the chill was not removed. This profile shows classical inverse segregation with a slight increase in solute concentration near the chill and a depletion in solute at the top of the ingot.

In the cases where the chill has been pulled away (A, B, and C), one observes a solute rich region below the chill (the flow-through zone) and a solute depleted region just above the chill. All ingots exhibited a depletion in solute at the top of the ingot.

Details of the castings are listed in Table 5.

Table 5

Details of Cu-8Ag Castings

Casting	N	A	В	С
Time between pouring and removing the chill (sec.)	0	12	14	16
Estimated volume of the flow- through zone (in. ³)	-	0.23	0.094	0.023
Average composition of the flow- through zone (%Ag)	-	10.3	12.3	12.6
Minimum composition of the depleted zone adjacent to the chill (%Ag)	-	5.25	6.05	7.25

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Figure 23. Composition profiles of Cu-8Ag ingots.

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Figure 24. Cooling curves for Cu-8Ag castings.

The important features to notice are:

(a) As the time interval between pouring and the removal of the chill increases, the maximum reheat temperature at the thermocouple location decreases and less back-flow of liquid metal occurs.

(b) As the flow-through region increases in volume, the average solute concentration in this region decreases, while the maximum dip in concentration adjacent to the chill increases.

(c) In castings A and C, the bottom of the flow-through zone came in contact with the chill causing rapid freezing of the zone and the distribution of solute within this zone as shown in Fig. 23. The liquid to flow through the chill-face first was presumably the richest in solute and froze first.

(d) Back-flow in casting B occurred without a second chill contact being made. The flow-through zone cooled slower, producing the reverse segregation effect to that in (c).

(e) The rise in composition above Co, past the depleted zone adjacent to the chill, is believed to be a result of normal inverse segregation after back-flow has stopped.

3-2-b. Optical Examination

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A longitudinal section of a casting where the chill has been pulled causing considerable back-flow, as in casting A, is shown in Fig. 25. Notice the columnar structure which was characteristic of all the Cu-8Ag castings.

Above the original chill-face a region can be observed which etches lighter than the rest of the ingot. This region is solute

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X 2

Figure 25. Longitudinal section of a Cu-8Ag casting in which the chill has been removed during solidification.

dilute since the etchant used darkens solute rich regions which are not eutectic. There exists, however, no discontinuity of grain structure at the interface between this region and the rest of the ingot. A higher magnification photograph of the interface is shown in Fig. 26. Notice also the increase in eutectic above the boundary.

Coalescence of porosity is observed at the chill-face as shown in Fig. 27.

3-2-c. Autoradiography

Cross-sections taken at the chill-face and 0.05" above the chillface of casting A were autoradiographed. The films showed a uniform darkening, and, therefore, gave no indication of preferential flow of interdendritic liquid. One must note, however, that the γ radiation from Ag^{*} can penetrate copper to a considerable depth allowing only limited resolution using the autoradiograph technique.

Micrographs of the same cross-sections, as in Fig. 28, also show no signs of preferred flow. One assumes, therefore, that back-flow occurred in a homogeneous interdendritic fashion without the formation of large pipes as seen in Part I.

3-2-d. Electron Microprobe Results

A normal casting was sectioned parallel to the chill-face, 0.21" from the face, and examined by microprobe analysis. Line counts were taken through dendrite centers and eutectic regions at 1.25 micron steps, as shown in Fig. 29. Random line counts using 5 micron steps were also taken at other distances above the chill of a normal casting.



X 100

Figure 26. Longitudinal section through the interface between the depleted zone and the rest of the ingot.



X 7

Figure 27. Longitudinal section through the chill-face.



X 160

Figure 28. Cross-section at the chill-face of casting A.



Figure 29. Microsegregation 0.21" above the chill-face.

All the counts corresponding to a silver concentration less than Co were averaged. For each cross-section about 100 such counts were averaged to give a silver concentration, C_s , for use in a model to be discussed later. See Fig. 30.



Figure 30. Plot of C vs. distance from the chill.

3-3. The A1-30Ag System

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3-3-a. Composition Profiles

As with Cu-8Ag, a number of castings were made in which the chill was removed at various times after pouring. The composition profiles and the cooling curves are shown in Figures 31 and 32 respectively. Profiles N_1 and N_2 represent a normal casting, and D and E are castings where the chill has been removed.



Figure 31. Composition profiles of A1-30Ag ingots.

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Figure 32. Cooling curves for Al-30Ag castings.

In the cases where the chill has been removed, one observes a solute rich flow-through region below the chill, and a solute

depleted region just above the chill. Details are given in Table 6.

Table 6

Details of A1-30Ag Castings

Casting	N ₁	^N 2	D	E
Temp. at which the chill was removed (°C)	-	_	569	580
Estimated volume of flow- through zone (in. ³)	-	-	0.047	0.078
Minimum solute concentration of depleted zone adjacent to the chill (%Ag)	-	-	22.3	22.0
Average composition of flow- through zone (%Ag)	_ '·	-	30.8	32.5
Distance from chill of columnar to equiaxed transi- tion (in.)	2.8	0.6	1.0	0.7

3-3-b. Discussion

The composition profiles, unfortunately, were not reproducible, on the casting apparatus used. Normal castings $(N_1 \text{ and } N_2)$, for example, were in some cases completely columnar and in others almost completely equiaxed. Aluminum has a considerably higher specific heat and latent heat of fusion than copper. This property, combined with the lower pouring temperature, produced a drastically lower cooling rate for Al-30Ag than for Cu-8Ag. As a result, nucleation occurred ahead of the columnar dendritic interface at unpredictable distances from the chill, producing an equiaxed structure. Small amounts of impurities may have acted as nucleants to assist this transition from a columnar to an equiaxed structure.

3-4. The Length of the Semi-solid Zone

Normal castings were made with two chromel-alumel thermocouples in place; 0.4" and 2.0" from the chill. Each thermocouple was connected to a separate temperature recorder. The cooling curves are shown in Figures 33 and 34. Defining the mushyzone as lying between the liquidus and solidus temperature of the phase diagram for the particular composition of the ingot, and assuming a linear temperature gradient between the two thermocouples, the length of the mushy zone at various times from the beginning of solidification was estimated. These estimates at the instant the chill is pulled are given in Table 7.

Table 7

Estimated Lengths of the Semi-solid Zone

	· ·					
Casting		A,	В	С	D	E
Length of the zone (in.)	semi-solid	0.45	0.56	0.66	0.85	0.85

4. Discussion

4-1. General

The back-flow phenomena observed are complex and a simplified model is necessary. Measurements were made of the average solute concentrations



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Figure 33.
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Cooling curves to determine the length of the mushy zone in Cu-8Ag.


in Al-30Ag.

of thin sections cut parallel to the chill face. Before the chill was removed, the section was made up of solid and liquid of different and non-homogeneous compositions defined by the conditions for solidification in that section. In addition, liquid flow perpendicular to the section plane occurred due to volume changes on cooling and freezing which changed the average solute concentration of the liquid in the plane section.

When the chill was removed followed by reheating of the partially solid ingot, several things occurred:

(a) Liquid pipes were present or opened up, allowing vertical flow of liquid below the initial chill-face. This markedly changed the composition of the residual liquid in the section.

(b) The composition change of the plane section was a function of the composition of the liquid entering as well as that leaving.

(c) The remelting of dendrite arms changed the liquid composition.

Two models (I and II) are proposed to explain the dip in concentration adjacent to the chill face; one for minor back-flow (I) and one for extensive back-flow (II). In both cases the inverse segregation effect is neglected. As seen from the experiments, compositional changes due to inverse segregation are small compared to the concentration differences caused by exudations. The simplest model is chosen first and then expanded to reach the best approximation to experimental data.

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4-2. Model I

4-2-a. First Approximations

Assume an ingot is cast, as in the experiments, and after a given interval of time a semi-solid (mushy) zone of length, L, is formed. (The mushy zone is defined as the zone lying between the liquidus and solidus of the alloy.) At this point, the chill is suddenly removed. Because of the hydrostatic pressure of the liquid above the semi-solid zone, the liquid inside the zone is pushed out and replaced by liquid of composition C_{o} , the average composition of the original melt. This back-flow occurs concurrently with the continued cooling of the ingot at a slower rate, and, hence, the flow stops after a period of time. During this period, remelting of dendrites at their tips and in interdendritic regions can occur. In this model it will be assumed that L remains constant while back-flow is occurring. This may not be unreasonable since the overall system is still cooling with the chill removed causing dendrites to grow; but at the same time heat transfer from the superheated liquid causes dendrites to melt. It is also assumed, therefore, that the position of the region of length L remains fixed with respect to the original chill-face during back-flow.

Consider a slice of thickness dy in the mushy zone perpendicular to the solidification direction. The distribution of solute in the solid portions of this slice is assumed to follow the Pfann equation:

$$C=C_{o}k(1-g)^{k-1}$$
 (1)

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where, g, the fraction solidified, is measured in the plane of the slice. This equation which was derived for one-dimensional solidification, is, therefore, being applied directly to a two-dimensional situation. The equation assumes complete mixing in the liquid during solidification and no diffusion in the solid. For rapid cooling rates, other researchers^{3,10} have found this equation to agree reasonably well with experimental microsegregation data for g values up to about 0.8. For higher values of g, the composition, C, goes to infinity and the equation becomes meaningless. The model proposed here, however, compensates for this effect, because as the composition approaches infinity, the amount of material having this composition approaches zero. This will become apparent in the mathematics to follow.

Some solid-liquid distribution is assumed in the region L, making the volume of solid per unit thickness of the casting some function of distance from the chill. For convenience, reference points and axes are denoted as in Fig. 35.



Figure 35. Schematic representation of Model I.

Consider the fraction solidified at some point y_1 in an element of width dy. Assuming a Pfann distribution of solute in the solid, the total solute, S, in this fraction is given by:

$$S = kC_{0}f_{0}^{g_{1}} (1-g)^{k-1}dg$$
(2)
= C_{0} - C_{0}(1-g_{1})^{k}

Therefore, the average composition, C_{SA} , in the solid at point y_1 is given by:

$$C_{SA} = \frac{C_{o} - C_{o}(1 - g_{1})^{k}}{g_{1}}$$
(3)

For simplicity, a linear solid-liquid distribution during solidification is now assumed. This model, shown in Fig. 36, makes the fraction solid



Figure 36. A linear solid-liquid distribution.

a linear function of distance along the ingot. The average composition of the solid in a cross-sectional slice at some point y now becomes:

$$C_{SA} = \frac{C_{o} - C_{o} (1 - \frac{y}{L})^{k}}{y/L}$$
(4)

and the average composition of the entire slice, $\boldsymbol{C}_{A}^{},$ is:

$$C_{A} = C_{SA}(y/L) + C_{L}(1 - y/L)$$
 (5)

where C_{L} = average composition of the liquid in the cross-sectional element.

Using this analysis, it is not necessary to know the structure of the ingot.

One now assumes that all the residual liquid is displaced by liquid of composition C_0 . Assuming no segregation in the y direction when this liquid eventually freezes, the composition of this new liquid when averaged in cross-section will be C_0 . The average composition, C_A , at some point y is given by:

$$C_{A} = C_{SA}(y/L) + C_{O}(1 - y/L)$$
 (6)

A family of these curves are plotted in Fig. 37 for various k values. Notice that these curves are independent of the absolute value of L.

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Figure 37. Plot of Equation 6 for various k values.

4-2-b. Selection of the Distribution Coefficient.

In determining a reasonable value for the distribution coefficient k, two sets of data are available:

(i) According to experiments done by Weinberg¹⁰ on Cu-8Ag using the same apparatus as in this work, the average k value 0.2" to 1.0" from the chill lies somewhere between 0.55 and 0.69 (see Fig. 38).



Figure 38. Solute distribution across primary dendrites at various distances, d, from the chill. The concave upwards curves were calculated using the Pfann equation and the k value shown.

(ii) If k = 0.6, the minimum composition at the dendrite centers, given by kC_0 , is 4.8% Ag for Cu-8Ag alloy. This is close to what is observed in the microprobe data, Fig. 29. Although k decreases considerably with increasing distance from the cill (Fig. 38), the region of interest in Cu-8Ag extends only 0.7" past the chill. In subsequent calculations, therefore, k is assumed constant at 0.6.

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4-2-c. Modifications

A more detailed analysis of back-flow is considered by calculating the composition of the interdendritic liquid just before the chill is pulled away. Let part of this liquid be displaced by liquid of composition C_0 . Assume that no mixing occurs between the C_0 liquid and the original interdenritic liquid during back-flow. This is a reasonable assumption for two reasons:¹¹

(i) The liquid of composition C which is probably the less dense of the two solute enriched liquids, rests above the interdendritic liquid.

(ii) The temperature gradient is such that hot liquid is above

Both these effects would hinder any free convection from occurring.

To determine the composition of the initial interdendritic liquid, let $C_A = C_o$ in Equation 5. (Neglecting inverse segregation effects, the average composition of a cross-sectional slice before the chill is removed must be C_o .)

Therefore:

$$C_{A} = C_{o} = C_{o} - C_{o}(1 - y/L)^{k} + C_{L}(1 - y/L)$$

$$C_{L} = \frac{C_{o}(1 - y/L)^{k}}{(1 - y/L)}$$
(7)

* The author could find no information regarding the density vs. composition of Cu-Ag alloys.

This gives the initial average composition, C_L , of the liquid in any given cross-sectional element of the mushy zone.

Let a given volume of interdendritic liquid be displaced by an equal volume of liquid having composition C_0 . Schematically this occurs as in Fig. 39.



Figure 39. Interdendritic liquid displacement.

For a linear solid-liquid distribution, the volumes of liquid displaced are shown in Fig. 40. Pipes at the bottom of the mushy zone are assumed small and neglected in the following calculations.



Figure 40. Displacement of liquid for a linear solid-liquid distribution.

When V_2 is removed, $(V_1 + V_3)$ fill up the volume $(V_2 + V_3)$. Therefore:

$$V_1 = \frac{1}{2} - \frac{1}{2} \left(1 - \frac{y_1}{L}\right)^2$$
(8)

$$V_2 = \frac{1}{2} \left(1 - \frac{y_2}{L} \right)^2$$
(9)

Equating (8) and (9) since $V_1 = V_2$, and g = y/L:

$$g_2 = 1 - \sqrt{1 - (1 - g_1)^2}$$
 (10)

The liquid which was once distributed between 0 and $\frac{y_2}{L}$ is now distributed between $\frac{y_1}{L}$ and 1.

Every cross-sectional liquid element of constant width, a, when moved down a given distance, b, increases in width by a constant amount, c, as shown in Fig. 41. This indicates that one can simply replot the





liquid composition function, f(y/L), formerly between 0 and $\frac{y_2}{L}$, on an expanded scale between $\frac{y_1}{L}$ and 1. One does this mathematically using an extension factor, μ . For details see Appendix C.

$$\mu = \frac{g_2}{1 - g_1}$$
(11)

The average liquid composition, $C_L^{}$, as defined by Equation 7 becomes:

$$C_{\rm L} = \frac{C_{\rm o} (1 - \mu g)^{\rm k}}{(1 - \mu g)}$$
(12)

if $\frac{y_1}{L}$ is used as a zero reference point for g.

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Equating back to the original zero reference:

$$C_{L} = C_{o} \text{ between 0 and } \frac{y_{1}}{L}$$

$$C_{L} = \frac{C_{o} [1 - \mu(g - g_{1})]^{k}}{1 - \mu(g - g_{1})} \text{ between } \frac{y_{1}}{L} \text{ and } 1$$
(13)

1

Using Equation 5, the total average composition, therefore, is given by:

$$C_{A} = C_{o} - C_{o}(1 - g)^{k} + C_{o}(1 - g) \text{ between 0 and } \frac{y_{1}}{L}$$
(14a)
$$C_{A} = C_{o} - C_{o}(1 - g)^{k} + C_{o}(1 - g) \frac{[1 - \mu(g - g_{1})]^{k}}{1 - \mu(g - g_{1})} \text{ between } \frac{y_{1}}{L} \text{ and } 1$$
(14b)

where g = y/L

Equations 14a and 14b are plotted in Fig. 42 for k = 0.6 and various values of g_1 .



Figure 42. Plot of Equations 14a and 14b.

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Integrating Equation 7 between $\frac{y_2}{L}$ and 1, and dividing by the liquid volume in this region, gives the average composition of the liquid, \bar{C}_{L} , which has flowed through the chill-face.

$$\bar{C}_{L} = \frac{C_{o}}{1/2(1 - g_{2})^{2}} \int_{g_{2}}^{1} (1 - g)^{k} dg$$

$$\bar{C}_{L} = \frac{2C_{o}(1 - g_{2})^{k-1}}{k+1}$$
(15)

In the special case where all the original interdendritic liquid has been completely displaced, $g_2 = 0$.

Therefore:
$$\bar{C}_{L} = \frac{2C_{o}}{k+1}$$
 (16)

Solving Equation 15 for various values of g_1 and for $C_0 = 8\%$ Ag, one obtained Table 8.

Tε	ŧЪ	1.	е	8
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The Variation of \bar{c}_L with respect to g_1

:

$$(k = 0.6; C_0 = 8)$$

		0	
	ε _l	Ē	
•	0.05	15.96	
	0.10	13.94	
	0.20	12.27	
	1.00	10.00	

The important point to note here is that the less material that has flowed back, the higher the average composition of the flow-through zone. This effect was observed experimentally.

4-2-d. Effect of Remelting

In considering the remelting of dendrites, one assumes that a substantial amount of interdendritic liquid has been displaced. Solute dilute material is dissolved from the surface of the dendrites and swept downwards as shown schematically in Fig. 43.



Figure 43. The remelting of dendrites.

The length of the mushy zone, L, is assumed constant during dissolution and the solid-liquid distribution is assumed to remain linear after dissolution (Fig. 43b). The effect of pipes forming at the base of the mushy zone is neglected.

The dissolution of dendrite material causes the solute concentration of the displacing liquid to drop. As a first approximation, this dilution is assumed to be linear with respect to y/L. Referring to Fig. 43a, therefore, the composition of the liquid at the base of the semi-solid zone, C_a , is less than C_o . Incorporating this effect into Equation 6, the average composition, C_A , is given by:

$$C_{A} = C_{o} - C_{o}(1 - g)^{k} + [C_{o} + (C_{a} - C_{o})g](1 - g)$$
 (17)

An interesting feature of this equation is its use as a first approximation to Equation 14 if $C_a > C_o$. Equation 17 is plotted in Fig. 44 for various values of $(C_a - C_o)$. Notice the shift in minima from left



Figure 44. Plot of Equation 17.

to right as the remelting situation is approached. Such a shift was observed experimentally for Cu-8Ag.

4-3. Model II

This model considers the case where considerable back-flow has occurred after all the initial interdendritic liquid has been washed away. Considerable widening of interdendritic channels is believed to occur in the region which is almost completely solid at the base of the mushy zone. Schematically this is shown in Figure 45.



Figure 45. Schematic representation of Model II.

One must remember that the Pfann equation for solute distribution is not valid in the lower region of the semi-solid zine. A simplified distribution is, therefore, adopted and related to a linear solidliquid distribution as in Fig. 46.





 C_s represents the average of all compositions below C_o , and C_e is the eutectic composition. The fraction of eutectic in a normal casting is given by n.

Assume all the original interdendritic liquid and all the eutectic in the region n has been displaced by liquid of composition C_0 . The average composition, C_A , taken in cross-section at some point y/L becomes:

$$C_{A} = C_{S}g + C_{O}(1 - g)$$
 for $0 < y/L < (1 - n)$ (18)
 $C_{A} = C_{O}$ for $(1 - n) < y/L < 1$

To evaluate n, an estimate of C is required. By equating areas under the solute distribution curve (Fig. 46a):

$$(C_{p} - C_{0})n = (C_{0} - C_{s})(1 - n)$$
 (19)

4-4. Comparison of Models with Experiment.

4-4-a. General

A direct quantitative comparison is made between the two models proposed and castings A, B, and C. Castings D and E were not considered because of the unreproducibility of the results. In these castings other more complex solidification variables must have existed which were not considered in the models.

The location of the base of the mushy zone at the instant the chill is removed is not accurately known. From the micrograph in Fig. 27, it is assumed to be at the termination of the initial fine-grained chill structure: 0.075" from the chill. This corresponds approximately to the point where the composition profiles (Fig. 23) first cross the C₀ line. The distance between this point and the point where the second intersection occurs is assumed to be the length of the mushy zone, L.

The initial volume of interdendritic liquid is assumed to be 1/2 the volume of the semi-solid zone. Details are given in Table 9.

Table !

Casting	Length of mushy zone from composi- tion profiles(in.)	Length of mushy zone from cooling curves (in.)	Volume of liquid in the mushy zone (in. ³)	Volume of flow-through zone (in. ³)
A	0.25	0.45	0.10	0.23
В	0.55	0.56	0.22	0.094
С	0.50	0.66	0.20	0.023

Additional Details of Cu-8Ag Castings

4-4-b. Casting A

The volume of liquid which has flowed back is about twice the volume of liquid in the mushy zone. This indicates that all the original interdendritic liquid has been washed out causing remelting of dendrites and the widening of interdendritic channels. Because the velocity of liquid is highest at the base of the dendrites, most widening and remelting is assumed to occur at this location. In this region the Pfann equation is not valid and Model II is considered. As a first approximation, one assumes that all the solute rich material has been displaced by liquid of composition C_o and no remelting of solute dilute material has occurred.

From the microprobe data (Figure 29 and 30), $C_s = 5.4\%$ Ag and $C_e = 70\%$ Ag. Substituting into Equation 19, n = 0.04. This value of n is used in plotting Equation 18 as in Fig. 47. In this case, the equation describes only half of the composition profile. The remaining profile is not described by the model, and is merely considered as a transient between the minimum composition and the solute-enriched flow-through region. The important information given by the model is

the minimum composition of the solute depleted zone.

4-4-c. Casting B

In this case, 0.4 volume fraction of the original interdendritic liquid has been displaced. This means that all the greatly solute enriched liquid has been washed away. From equation 15, the average composition of the flow-through zone is 12.0% Ag; comparing favourably with the experimental value of 12.3% Ag. One cannot attach too much significance to this since the Pfann equation is not valid for liquid highly enriched in solute. Note, however, that the effect of the Pfann distribution approaching infinity is compensated for as the volume of material having such a distribution approaches zero in Model I.

It is arbitrarily assumed that the composition of the new liquid in the mushy zone has been altered by the remelting of dendrites such that a linear composition gradient of $(C_a - C_o) = -2\%$ Ag exists in the liquid. (Refer to Fig. 43). This assumption must be made since no data is available on the nature and magnitude of remelting. Using Equation 17, the theoretical curve is compared with experiment in Fig. 47.

4-4-d. Casting C

Comparing the volume of liquid in the mushy zone with that in the flow-through region, only a small amount of displacement of the original interdendritic liquid has occurred. Assume, therefore, that no remelting of dendrites occurred. Using the volume data in Table 9 and Equation 8, $g_1 = 0.05$. The theoretical solute distribution is calculated using Equation 14 and compared with experiment in Fig. 47.





4-5. A Parabolic Solid-Liquid Distribution

The comparison of the models with experiment show that all the theoretical composition curves are shifted to the left of the experimental ones. The effects of a parabolic distribution of solid in the mushy zone are, therefore, briefly considered. A comparison of linear and parabolic distributions is depicted in Fig. 48. Consider Equation 6 of Model I in a general case:





Figure 48. A comparison of models: Model I (a), Model II (b), and a parabolic solid-liquid distribution (c).

$$C_{A} = C_{o} - C_{o} [1 - f(y/L)]^{k} + C_{o} [1 - f(y/L)]$$
 (19)

where f(y/L) is a function of the solid -liquid distribution

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For a parabolic distribution:

$$\dot{g} = f(y/L) = 1 - (1 - y/L)^2$$
 (20)

and Equation 19 becomes:

$$C_{A} = C_{o} - C_{o}(1 - y/L)^{2k} + C_{o}(1 - y/L)^{2}$$
 (21)

Similarly for Equation 17 of Model II:

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$$C_{A} = C_{s} [1 - (1 - y/L)^{2}] + C_{o} (1 - y/L)^{2}$$
for $0 < y/L < (1 - \sqrt{n})$

$$C_{A} = C_{o}$$
for $(1 - \sqrt{N}) < y/L < 1$
(22)

Plotting (21) and (22), as in Fig. 49, one observes that the minima are shifted to the right.





From simple phase diagram considerations, a parabolic distribution may not be unreasonable. Considering the curvature of the solidus line of the phase diagram (Fig. 20a), a plot of the fraction liquid versus the temperature would have a "parabolic type" shape which could be correlated to the proposed parabolic solid-liquid distribution if one assumes the temperature gradient in the casting is linear with respect to distance from the chill.

GENERAL DISCUSSION AND CONCLUSIONS

- In Part I it was discovered that the flow of interdendritic liquid need not necessarily be distributed homogeneously between dendrites. A major force determining the movement of residual liquid arises from the surface energy of that liquid.
- 2. In experiments done by Adams⁴ and Fricke¹² on rapidly chilled directional Al-Cu castings, a solute depleted zone was observed about 0.1" from the chill. In such castings, Adams noticed a thin exuded layer at the chill-face, but made no correlation between this and the depleted zone. Fricke, on the other hand, observed small protuberances on the chill-face which he claims were associated with interdendritic voids within the casting. These voids would, therefore, cause the depleted zone.
- 3. In this work, a large coalescence of voids was observed right at the chill-face, with a reasonably homogeneous distribution of voids throughout the rest of the ingot. The depleted zone adjacent to the chill, therefore, was not attributed to the formation of voids, but was explained by the simple back-flow of residual liquid to feed exudations at the chill-face.
- 4. The formation of large flow-pipes as in the Pb-20Sn experiments was not observed in the Cu-8Ag castings. The back-flow was presumably reasonably homogeneous, therefore, and confined to the initial stage of the flow-rate curve (Fig. 11). In other words, back-flow did not have sufficient time to reach the catastrophic stage.

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SUGGESTED FUTURE WORK

- 1. For a given composition and structural make-up of a binary alloy, and given solidification conditions, it should be possible to calculate the distribution and size of flow-pipes per unit area of the casting taken perpendicular to the flow direction. Flemings et al¹³ have already attempted this in a recent paper.
- 2. In the type of experiment done in Part II, other variables to investigate are the casting temperature (the temperature gradient) and the head of liquid above the mushy zone when the chill is removed.
- 3. It would be useful to find a more specific correlation between the models proposed here and exudation phenomena observed in the continuous casting processes.

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APPENDIX A

Electron Microprobe Corrections for Pb-Sn

X-ray analysis was done at 35 KV on Pb-L α_1 and Sn-L α_1 radiations. Because of the large difference in atomic numbers, 82 for Pb and 50 for Sn, fluorescence corrections are not necessary.¹⁴ To correct for electron backscattering effects, Belk's atomic number correction¹⁵ was used:

$$K_{Ab} = \frac{C_A}{1 + (\frac{Z_A - \bar{Z}}{100})}$$
(23)

where K_{Ab} = apparent concentration of element A due to electron back-scatter.

 C_{A} = actual concentration of element A

 Z_A = atomic number of element A

 \overline{Z} = average atomic number for a given concentration, C_{Λ} .

For a binary system with 2 elements, A and B:

$$\overline{Z} = f_A C_A + (1 - f_A) C_B$$

where f_A = weight fraction of element A.

An absorption correction was then applied using Philibert's absorption factor, 16 F(χ):

$$\frac{1}{F(X)} = (1 + \frac{\chi}{\sigma}) [1 + h(1 + \frac{\chi}{\sigma})]$$
(24)

where
$$h = 1.2 \frac{\overline{A}}{\overline{z}^2}$$

 $\sigma \stackrel{\sim}{=} 1820(\frac{30}{v})^2$
 $\chi_A = \mu'_A \csc \alpha$
 $\mu'_A = f_A \mu_{AA} + f_B \mu_{BA}$
 $\sigma = \text{Lenard Coefficient}$
 $\alpha = \text{take-off angle}$
 $V = \text{accelerating voltage of the electron beam}$
 $\overline{A} = \text{average atomic weight}$
 $\mu_{AA} = \text{self absorption coefficient of element A for its own}$
 $\text{characteristic radiation}$
 $\mu_{BA} = \text{mass absorption coefficient of element B for characteristic}$

' radiation from element A.

The apparent concentration, $\boldsymbol{K}_{A}^{},$ for element A is given by:

$$K_{A} = \frac{I_{A}}{I_{100A}} = K_{Ab} \frac{F_{A}(\chi)}{F_{100A}(\chi)}$$
 (25)

where $I_A = X$ -ray intensity from some concentration of element A in B. $I_{100A} = X$ -ray intensity from pure element A

 $F_A(\chi)$ = absorption correction factor of some concentration of element A in B.

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 $F_{100A}(\chi)$ = absorption correction for pure element A.

Actual coefficients¹⁷ are:

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- h(Pb) = 0.037
- h(Sn) = 0.057

 $\alpha = 20^{\circ}$ $\sigma = 1,340$ $\mu_{PbSn} = 1528.9$ $\mu_{SnPb} = 123.2$ $\mu_{SnSn} = 437.4$ $\mu_{PbPb} = 116.6$

Ξ.

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The calibration curve (Equation 25) is plotted in Figure 50.

Some experimental microprobe data is plotted in Fig. 51 such that the corrected Pb and Sn compositions of a spot count are summed The actual sum, therefore, must be 100%. The scatter shows the quantity ative inaccuracy for the Pb-Sn system.



Figure 50. Microprobe corrections for Pb-Sn.



Figure 51. The summation of %Pb and %Sn for spot counts.

APPENDIX B

Electron Microprobe Corrections for Cu-Ag

X-ray analysis was done at 25 KV on $Ag-L\alpha_1$ and $Cu-K\alpha_1$ radiations. Fluorescence calculations were neglected because of the large difference in atomic numbers.¹⁴ 29 for Cu and 47 for Ag. The correction formulas used, therefore, were the same as those in Appendix A. Actual coefficients are¹⁷:

$$h(Ag) = 0.058$$

$$h(Cu) = 0.091$$

$$\alpha = 20^{\circ}$$

$$\sigma = 2,620$$

$$\mu_{CuAg} = 802.7$$

$$\mu_{AgCu} = 217.6$$

$$\mu_{CuCu} = 53.7$$

$$\mu_{AgAg} = 521.9$$

The calibration curve is plotted in Fig. 52. In this case the results were much more accurate than for Pb-Sn. Summations of Cu and Ag concentrations for spot counts were within 100 \pm 0.7%. For C_{Ag} < 8% the calibration is linear and the correction factor is simply 1.40.



Figure 52. Microprobe corrections for Cu-Ag.

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APPENDIX C

The Extension Factor

Consider a function, f(g), between 0 and g_2 :



This function is replotted between g_1 and 1 to form a new function, F(g), such that $f(g_2) = F(1)$ and $f(0) = F(g_1)$. Considering an arbitrary point, g_n :

$$F(g_n) = f[(g_n - g_1)(\frac{g_2}{1 - g_1})]$$

where $\frac{g_2}{1 - g_1} = \mu$, the extension factor.