Observations of Ingot Macrosegregation on Model Systems

D. J. HEBDITCH AND J. D. HUNT

The processes involved in the formation of macrosegregation in castings or ingots are discussed. A model ingot was used for studying the progress of macrosegregation as the growth front moved across the specimen. Pb-Sn and Sn-Zn alloys were chosen to illustrate the effect of the change in density of the interdendritic liquid during freezing. At slow growth rates, it was found that convective interdendritic flow was the dominant mechanism in all the castings.

IN this paper macrosegregation is used to describe the gradual change in composition from one part of the casting to another. This is in contrast to the microsegreation between dendrites and the local or channel type segregation, resulting from large pockets of liquid being formed[1-4] or left behind the growth interface.

Macrosegregation is considered to be the result of a number of separate processes:

1. The mixing[5] or flow of the diffusion layer ahead of the growth interface into the bulk liquid.
2. The precipitation of solid (or another liquid) phase in the bulk liquid and its subsequent deposition.
3. The flow of liquid in the semi-solid region resulting from a volume change on freezing.[6,7]
4. The convective flow of liquid in the semi-solid region resulting from liquid density changes within the freezing material.[1,4]

The first of these processes occurs when the diffusion layer ahead of the interface flows or is mixed into the bulk liquid. This mechanism is likely to be important when a material grows with a planar or almost planar interface. It will be less important in dendritic growth because of the much smaller diffusion layer ahead of the dendritic interface. Because flow or mixing is a slow process, appreciable macrosegregation only occurs when long freezing times are involved.

The second mechanism occurs when equiaxed crystals or non-metallic inclusions are preferentially deposited in one part of the ingot. Important factors in controlling the segregation will be the nucleation and growth of the new phases. Macrosegregation will however only occur when the new phase settles out, due to gravity or some other process. Again appreciable segregation will only be obtained when sufficient time is available during freezing.

Macrosegregation occurs by the third mechanism when fluid flows between the dendrites to take up the volume change on freezing. Appreciable segregation occurs when the growth conditions, the velocity and temperature gradients, are changing rapidly (no macrosegregation occurs during steady state growth). The rapidly changing growth conditions at the edge of small castings often causes inverse segregation (high solute at the edge of the casts). This is the only mechanism that becomes more important in rapidly solidified specimens.

The fourth process arises because the density of the liquid between the dendrites differs from that of the bulk liquid. This gives rise to convective fluid flow, and thus to macrosegregation. Macrosegregation occurs because a) liquid is moved, in a temperature gradient, from one part of the semi-solid to another, and b) channels develop which allow interdendritic liquid back into the bulk liquid, changing the bulk liquid composition. Because of the resistance to flow in the semi-solid region, macrosegregation by this mechanism is likely to be more pronounced when long freezing times are involved.

Theoretical models of the macrosegregation, assuming that the other mechanisms do not operate, have been proposed for some but not all of the processes. The Burton, Prim and Slichter treatment[5] can be used to describe macrosegregation in the first process when the bulk liquid is completely mixed. Kirkaldy and Youdelis,[6] and Flemings and Nereo[7] have analyzed the effect of volume change on freezing. Mehrabian *et al*[4] have attempted to analyze the more complex convective flow process, but their analysis is restricted to cases where liquid is not returned to the bulk.

In any casting or ingot, the final macrosegregation is the result of any or all of the four mechanisms. It is very difficult, given the completely solid casting, to identify the important mechanisms. The first three of the mechanisms are perhaps the classic explanations of macrosegregation, whilst the last (convective interdendritic fluid flow) is a more recent proposal.[1,4] One object of the present work was to establish that the fourth mechanism produced significant macrosegregation. Another was to study the progress of macrosegregation as it occurred in a particular casting so that the dominant mechanisms could be identified. It was hoped that the detailed knowledge of macrosegregation in a particular casting would lead to a better understanding of the conditions under which each mechanism was important in more general casting situations.

The progress of macrosegregation was studied using a quenching technique to determine the concentration distribution at a given stage of freezing. The shape

D. J. HEBDITCH, formerly Student, Department of Metallurgy, Oxford University, is now with the Marchwood Engineering Laboratory of the Central Electricity Generating Board, Totton. Hants. U.K. J. D. HUNT is University Lecturer, Department of Metallurgy, University of Oxford, Oxford, U.K.

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and position of the dendrite interface and the temperature distribution was also obtained. Concurrent experiments, described elsewhere,[9] were used to estimate the rate, and determine the direction of interdendritic fluid flow, using a radiotracer.

EXPERIMENTAL

Specimens were frozen directionally in a thin section mold. Since heat was extracted from only one edge, the thin section represented a slice of a much larger ingot. The mold is shown diagrammatically in Fig. 1. The dimensions of the ingot "slice" were 0.06 m high, 0.1 m long and 0.013 m thick. These were chosen small enough to allow an efficient quench but large enough to allow some convection, and to provide a reasonably long solidification time. The sides of the mold were made from stainless steel sheet painted with colloidal graphite. Growth was in a horizontal direction away from the graphite-painted copper cooling block on the left hand side of Fig. 1. To approximate the conditions in a larger ingot, the slice was held in a slot shaped furnace, maintained a degree or so above the liquidus temperature. Although enclosed within the furnace, the mold was well insulated from its surroundings by a $\frac{1}{2}$ in. thick Triton Kaowool ceramic fiber blanket. Separately controlled heaters prevented heat escaping at the top and bottom of the ingot slice. Removal of the lower heater allowed the slice to be pushed directly downwards into the quench bucket. The furnace set up ensured that as little heat as possible was conducted through the sides of the slice.

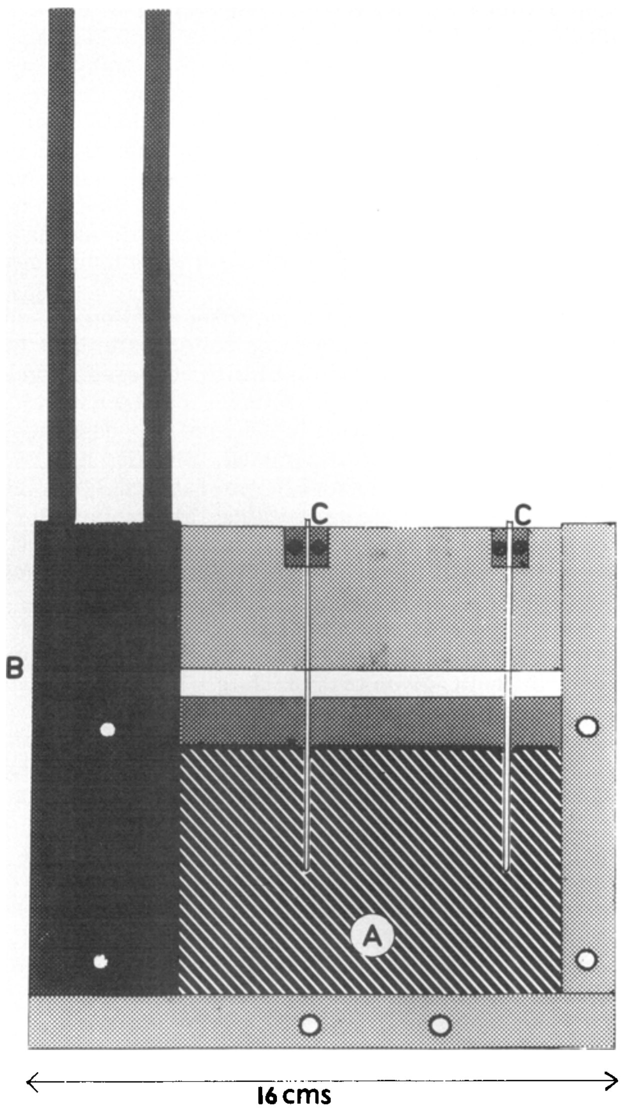

Fig. 1—Unidirectional solidification apparatus. A. alloy specimen. B. chill block. C. thermocouples.

Carefully homogenized liquid alloy was poured into the heated mold. The specimens were then left for 1 to 2 h, by which time the temperature of the melt had become constant ($\pm\frac{1}{2}$°C per h) within 1 or 2 degrees of the liquidus temperature.

Air or water was passed through the cooling block to freeze the samples directionally. The air flow rate, and thus the growth rate, was standardized by measuring the pressure drop across a constriction.

A number of thermocouples, 2 to 8, were used to measure temperature. The position of the dendrite interface could be determined by the drop in temperature as the interface passed a thermocouple. This enabled rough growth rates to be estimated and allowed quenching to be performed at various stages of growth.

After freezing, a thickness of 2 mm was removed from the sides of the ingots, followed by grinding, polishing and etching to show the macrostructure. A grid was drawn on the specimen, and the grid points were drilled to obtain samples for concentration analysis by flame absorption spectrophotometry. For the first series of experiments, the drill size was much larger than interdendritic spacings so that average compositions were obtained. The concentration values are considered to be accurate to ±2 pct of the concentration values.

Alloys of Sn-5 wt pct Zn, Sn-5 wt pct Pb and Pb-48 wt pct Sn were investigated. The purity of the Sn was 3N5, Zn was 4N and the Pb was 3N7. The compositions were chosen to give a reasonably wide freezing range. The alloys were chosen because the density variation of liquid in contact with solid differs in each alloy. In Sn-5 wt pct Pb, there is a large increase in density with decrease in temperature along the liquidus line[8] (*i.e.*, liquid in equilibrium with solid). In the Pb-48 wt pct Sn alloy there is a large decrease in liquid density with decreasing temperature along the liquidus line.[8] Whereas in the Sn-5 wt pct Zn alloy, the density variation was expected to be very small. In fact when measured, it was found to decrease slightly with decreasing temperature.[9]

An increasing liquid density with decreasing temperature along the liquidus line should cause liquid between the dendrites to tend to move downwards, whereas liquid should move upwards in the other case.

COARSE GRID RESULTS

Preliminary experiments were carried out to show that the growth front was vertical in specimens where the freezing temperature was invariant (*i.e.*, heat flow unidirectional). A Pb-Sn eutectic sample was partially grown then quenched. Fig. 2 shows the planar quenched interface, both on a horizontal and vertical section.

Examples of the macrostructure formed in the Pb-48 wt pct Sn, the Sn-5 wt pct Zn and the Sn-5 wt pct Pb partially grown casts are shown in Figs. 3, 5 and 7 respectively. The dendrite interface is clearly visible in each, together with the eutectic interface in Fig. 5. There is some evidence for channel type segregation in Figs. 3 and 7. From the concentration analyses, percentage macrosegregations corresponding to different stages of growth for slowly grown specimens (average growth rate 6×10^{-3} to 2×10^{-2} cm/sec) are shown in Figs. 4(*a*), (*b*), (*c*); 6(*a*), (*b*), (*c*); and 8(*a*), (*b*), (*c*). The percentage macrosegregation value shows the percentage deviation in composition, positive or negative, from the mean composition of the cast as obtained from all analyses of that cast. Further specimens were examined and these showed the same general trend. One specimen of each alloy was quenched, after stirring, before growth had started, and showed no significant segregation. The percentage macrosegregations of rapidly grown specimens, one of each alloy type, are

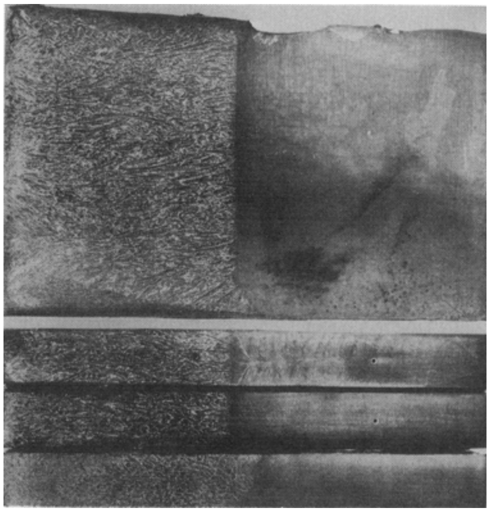

Fig. 2—Macroscopically planar interface in a partially grown Pb-Sn eutectic cast; horizontal and vertical sections.

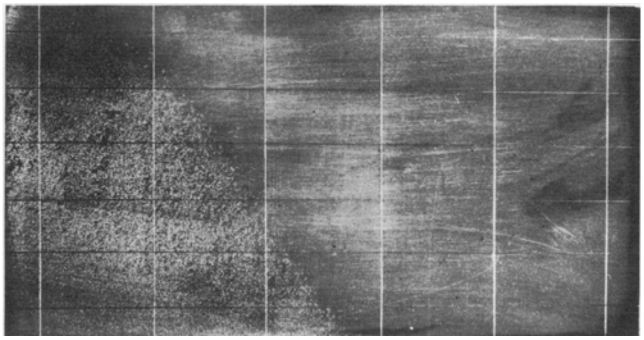

Fig. 3—Typical macrostructure in a partially grown Pb-48 wt pct Sn cast. Growth was from left to right, the growth front on quenching is clearly visible.

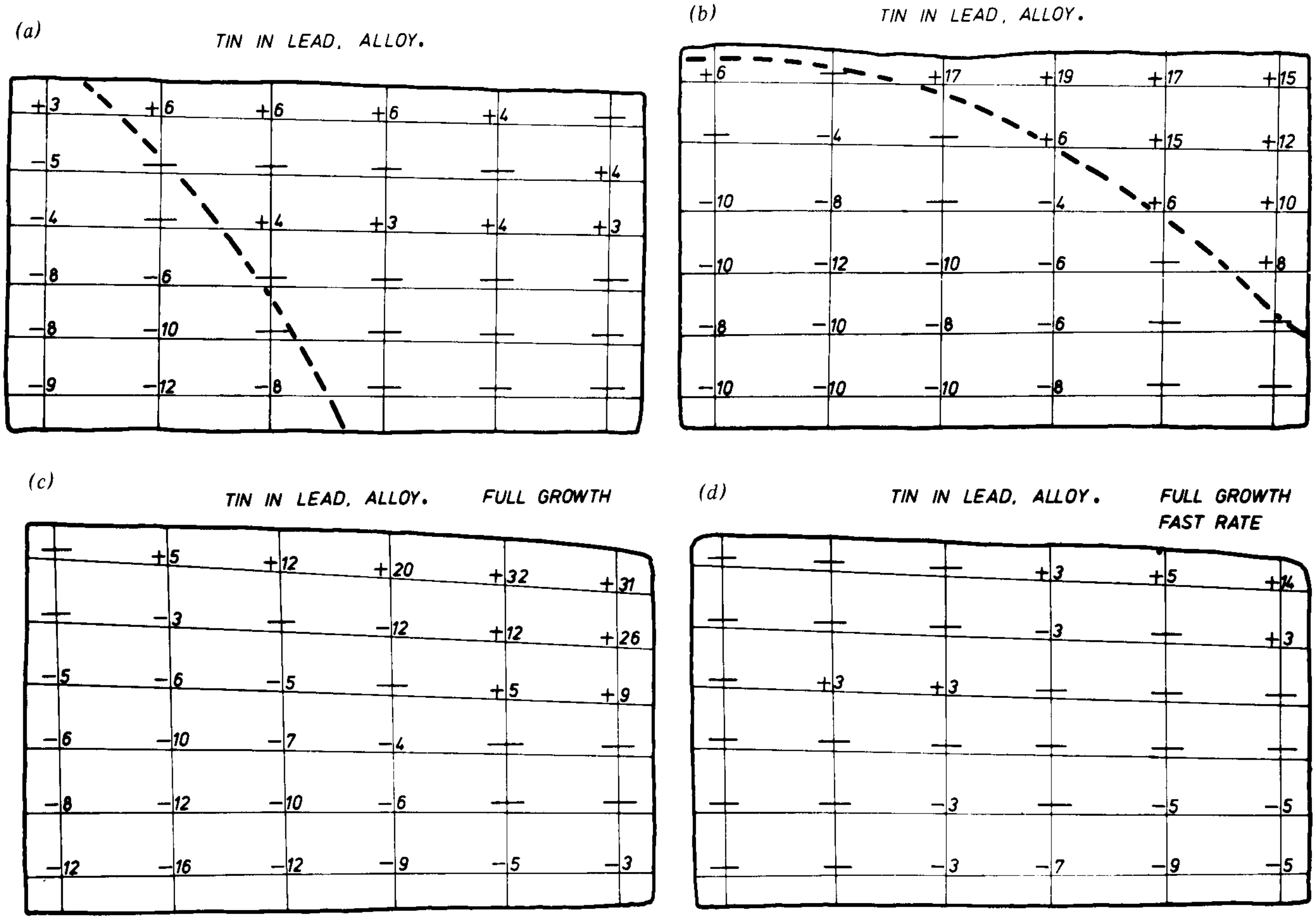

Fig. 4—Percentage macrosegregation diagrams for Pb-48 wt pct Sn casts. Dendrite interface shown by dashed line. Specimens (*c*) and (*d*) were fully grown; (*a*), (*b*) and (*c*) were slowly grown, and (*d*) was a rapidly grown specimen. Growth was from left to right.

shown in Figs. 4(*d*), 6(*d*) and 8(*d*) (average growth velocity 1×10^{-1} cm/sec).

It was found that in the Sn-5 wt pct Pb alloys, a thin Sn rich layer was present at the top of the specimens. Since the layer is lighter than the bulk liquid it remains on the top. The layer was present in specimens which were held at a high temperature for a typical time, and were quenched but not grown. The layer was not present in specimens which were stirred then quenched. Showing that the layer was not the result of quenching or growth, it is suggested that the layer is due to preferential oxidation. The layer will not be considered further.

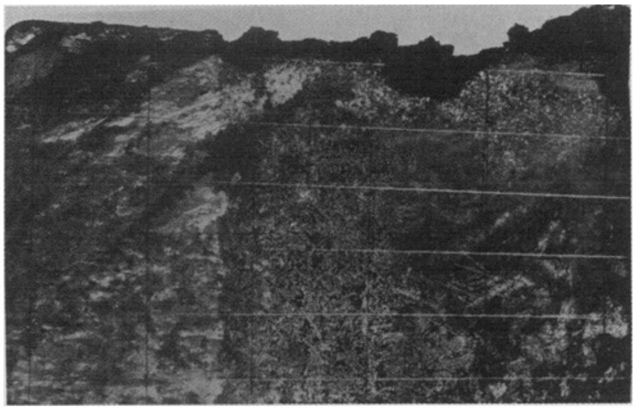

Fig. 5—Typical macrostructure in a partially grown Sn-5 wt pct Zn cast. Growth was from left to right. Equiaxed crystals ahead of the growth front, both eutectic and dendritic interfaces are visible.

The important experimental observations are summarized below:

1. The dendrite interface is very far from planar even though the isotherms were shown to be vertical (see Fig. 2 and also the eutectic interface of Fig. 5). In the case of the Pb-48 wt pct Sn and, to a lesser extent, Sn-5 wt pct Zn, the interface is retarded at the top, whereas the dendrite interface is retarded at the bottom of the Sn-5 wt pct Pb casts.

2. The bulk liquid composition becomes enriched with solute as freezing progresses. This occurs to a lesser extent with Sn-5 wt pct Zn casts.

3. The bulk liquid does not remain homogeneous. The denser liquid tends to stay at the bottom showing that mixing is not complete.

4. Vertical segregation develops in the semi-solid region at a very early stage. This occurs before the bulk liquid composition has appreciably changed. Negative segregation occurs in the semi-solid region at the bottom of the Pb-48 wt pct Sn and, to a lesser extent, the Sn-5 wt pct Zn, but at the top of the Sn-5 wt pct Pb.

5. The final segregation pattern consists of a low solute region at the bottom near the chill, and a high solute region at the top away from the chill for Pb-48

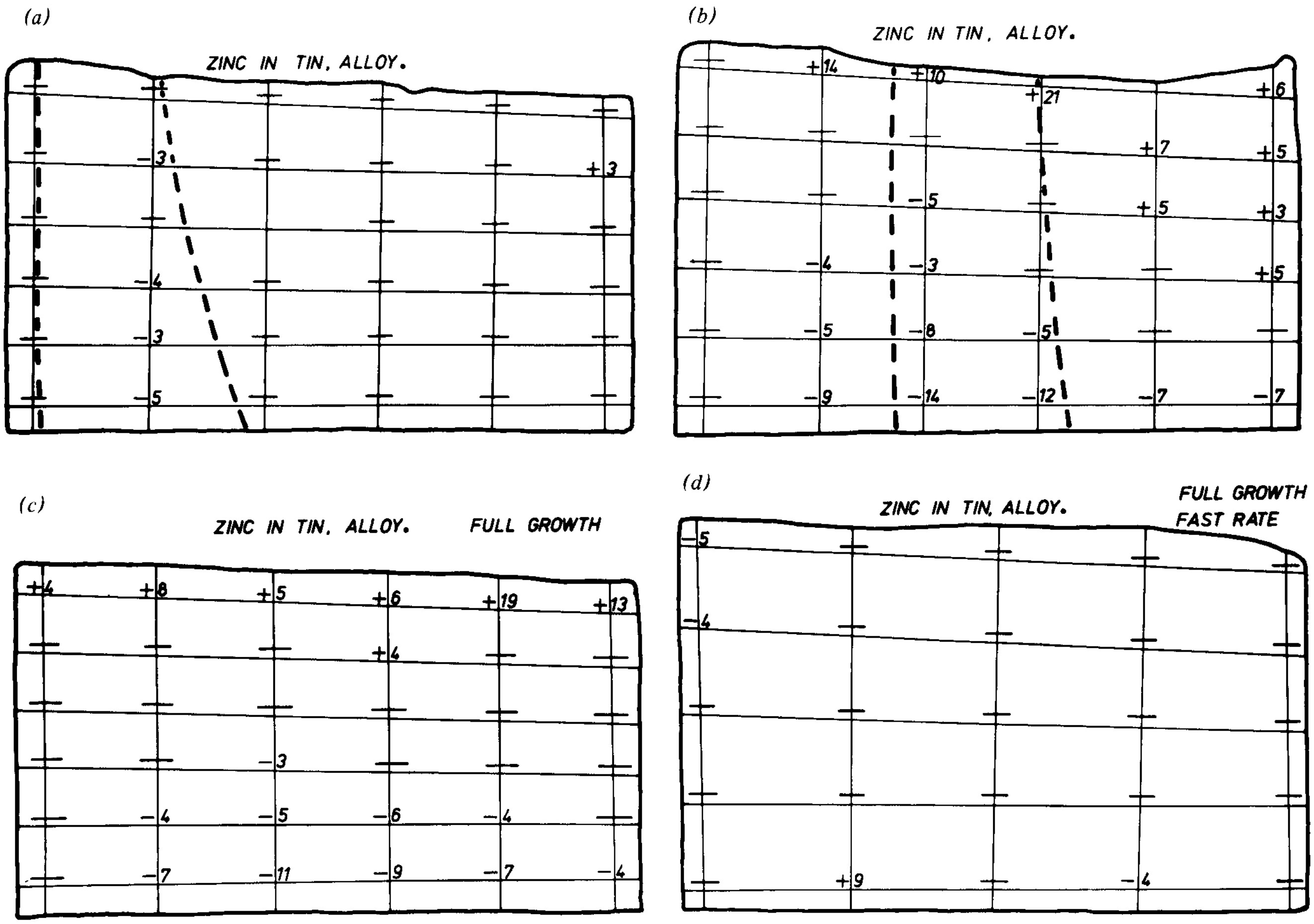

Fig. 6—Percentage macrosegregation diagrams for Sn-5 wt pct Zn casts. Dendritic and eutectic interfaces shown by dashed lines. Specimens (*c*) and (*d*) were fully grown; (*a*), (*b*) and (*c*) were slowly grown, and (*d*) was a rapidly grown specimen. Growth was from left to right.

wt pct Sn and, to a lesser extent for Sn-5 wt pct Zn, but the reverse is true for Sn-5 wt pct Pb.

6. The form of macrosegregation in the rapidly grown casts, see Figs. 4(*d*), 6(*d*) and 8(*d*), is similar to that in the slowly grown casts, see Figs. 4(*c*), 6(*c*) and 8(*c*). However the magnitude of the segregation is much less in the fast grown casts.

In these experiments there is no evidence for macrosegregation resulting from volume change on freezing or from equiaxed zone formation. The macrosegregation can be explained in terms of convective interdendritic fluid flow. Considering for the moment, the Sn-5 wt pct Pb alloy, at the start of freezing the Pb rich liquid between the dendrites is heavier than the bulk liquid and so tends to move downwards. Vertical motion is only possible if liquid moves towards the chill at the top and away from the chill at the bottom. See diagram of flow in Fig. 9. Liquid moving towards the chill means that solute, rejected by the freezing solid, is removed more easily so that more solid is deposited, leading to negative segregation.[1,4]

Liquid moving away from the chill, so becoming hotter, leads to instability in the flow, and the eventual formation of channel type segregates.[1-4] When non-equilibrium liquid emerges from the dendrite interface at the bottom, it changes the bulk liquid composition. However the liquid from the channels is denser than that of the bulk, so that it tends to remain at the bottom. The presence of Pb rich liquid at the bottom of the bulk explains why the dendrite interface is retarded at the bottom. The final segregation pattern is the combined result of flow in the semi-solid region, and growth of the semi-solid into an inhomogeneous bulk liquid. Less segregation occurs in the more rapidly frozen specimens because there is less time for fluid transport.

Exactly equivalent arguments are used for the Pb-48 wt pct Sn and the Sn-5 wt pct Zn alloys, except that in these cases the interdendritic liquid tends to move upwards, so that vertical segregation occurs in the opposite direction. Solute rich liquid emerges at the top of the specimen so the dendrite interface lags in

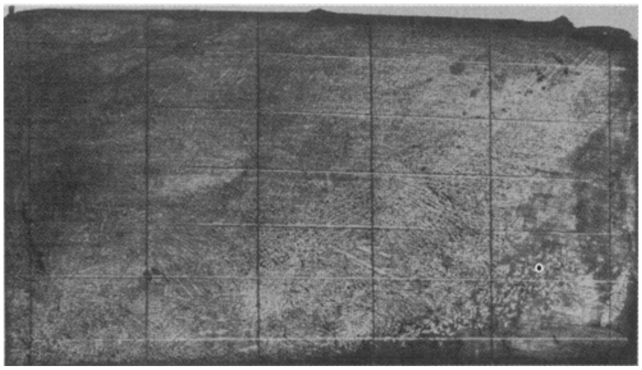

Fig. 7—Typical macrostructure in a partially grown Sn-5 wt pct Pb cast. Growth was from left to right. The dendritic interface is clearly visible.

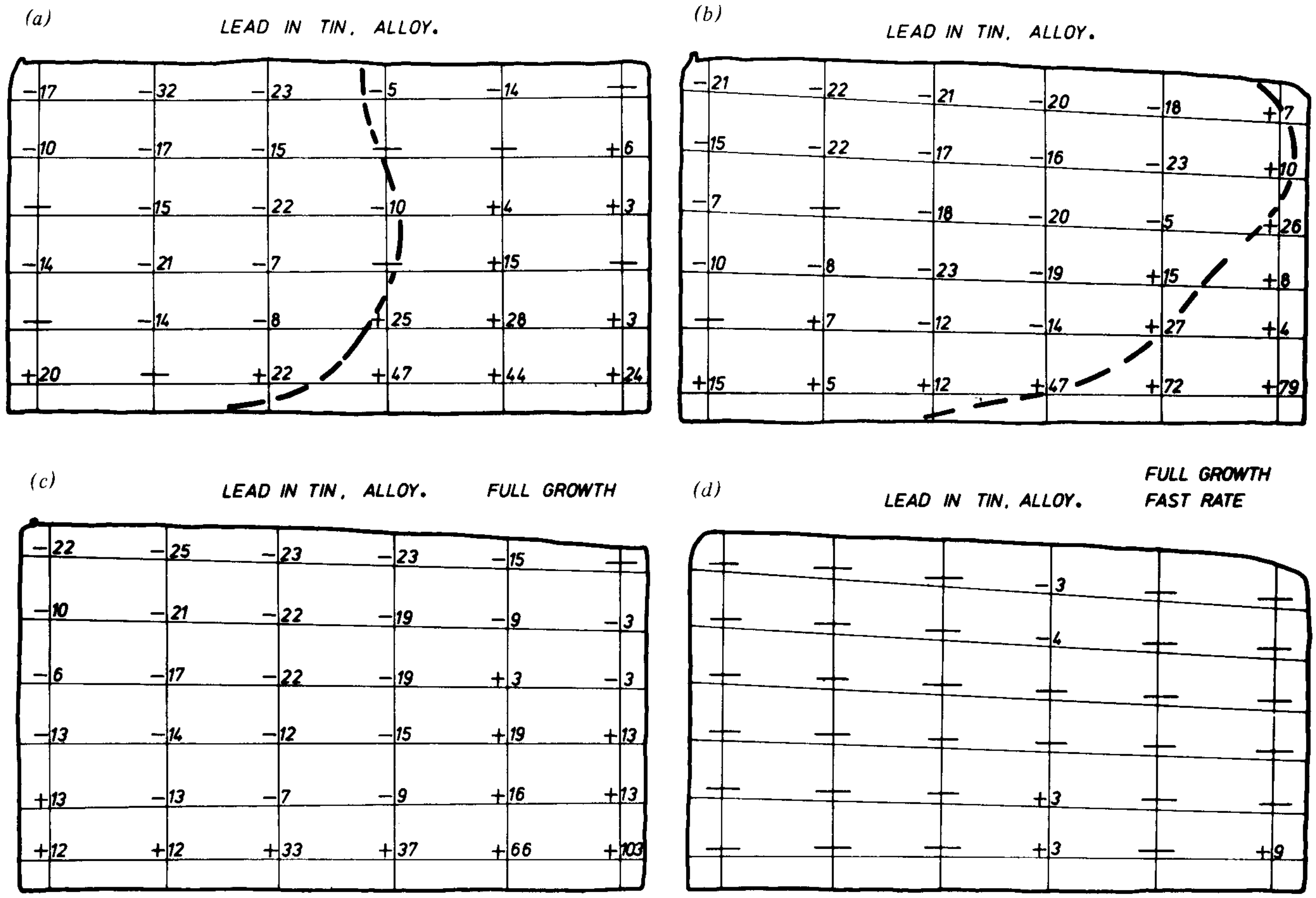

Fig. 8—Percentage macrosegregation diagrams for Sn-5 wt pct Pb casts. Dendrite interface shown by dashed line. Specimens (*c*) and (*d*) were fully grown; (*a*), (*b*) and (*c*) were slowly grown and (*d*) was a rapidly grown specimen. Growth was from left to right.

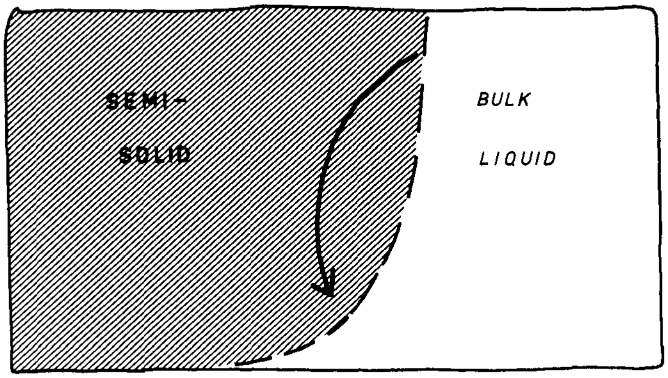

Fig. 9—Schematic diagram of convective flow through semi-solid region for a partially grown Sn-5 wt pct Pb cast.

this region. As expected the macrosegregation is much less in the Sn-5 wt pct Zn alloy because there is a much smaller change in liquid density with composition in this alloy. It is perhaps surprising that so much segregation occurs in the Sn-5 wt pct Zn alloy when the change in liquid density along the liquidus line is considered[9] (~ 0.01 g.cc^{-1}). Note that there is some evidence for a small amount of equiax zone formation at the bottom of the cast in Fig. 5. The composition analyses show a low value in this region.

Flow of non-equilibrium liquid into the bulk leads to density and composition stratification. The amount of stratification will depend on the alloy and the size of the mold. However, it seems probable that some stratification occurs even in much larger ingots because of the difficulty of mixing a gravitationally stable layer into the bulk with bulk convection currents.

Although the observations fit the expected results very well, a less convincing but similar line of reasoning could have been developed to explain the observations in terms of flow or mixing of the diffusion layer ahead of the dendrite front (mechanism 1). Evidence for the convective interdendritic fluid flow was obtained in concurrent experiments using a radioactive tracer technique.[9] These experiments showed that even for the Sn-5 wt pct Zn alloy, where the flow is expected to be small, appreciable interdendritic liquid flow occurred in the predicted direction.

To provide further evidence that convective interdendritic fluid flow produced the macrosegregation rather than the alternative mechanism, a second series of analyses were carried out.

FINE GRID RESULTS

The results of the previous section give some indication that macrosegregation is complete, or almost complete, some 1 to 2 cm behind the dendrite interface. In this series of experiments, an attempt was made to determine whether the process of macrosegregation took place at the dendrite tip interface or behind the interface. Some samples were grown as before. A fine grid of 0.25 cm squares (cf a rectangular grid of 1.8 cm × 1.0 cm in the previous analyses) was inscribed near the interface. Samples for analysis were obtained by drilling a 0.15 cm hole. Other specimens of Sn-5 wt pct Pb were grown vertically upwards in a mold similar to that shown in Fig. 1, except that the cooling block was at the bottom. No interdendritic flow should occur under these conditions since the rejected Pb rich liquid should stay between the dendrites. The possibility of interdendritic movement was reduced still further by including vertical glass tubing partitions in the mold.

The drill size in the experiments is very similar to the dendrite size so that scatter is obtained between individual analysis points. To minimize this difficulty the analyses were averaged in columns at equal distance from the growth front.

The macrostructure and the position of the grids are shown for Pb-48 wt pct Sn in Fig. 10, and Sn-5 wt pct Pb in Fig. 12. The average compositions are plotted as a function of distance in Figs. 11 and 13. In Fig. 13, average compositions are shown for both horizontal and vertical growth. On each plot for horizontal growth, there is a gradual decrease in composition into the semi-solid, which tends to flatten out after about 2 cm. This indicates that the macrosegregation is occurring behind the interface and not as a sharp discontinuity at the interface.

It is interesting to note that the concentration profile Fig. 13 for both the top and the bottom of the specimen shown in Fig. 12 are very similar. As was discussed previously, liquid moving at equilibrium towards the chill causes more solid to be deposited and thus a decrease in average composition. The movement of liquid away from the chill does not however lead to the opposite profile. The movement of liquid away from the cooler region, if the flow remained uniform, would lead to a uniform partial melting. In practice, the flow is unstable and channels form.[1-4] Melt-

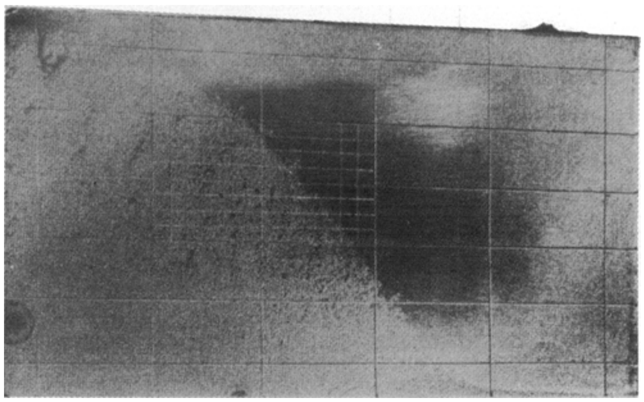

Fig. 10—Macrostructure with superimposed fine grid for a Pb-48 wt pct Sn cast. Growth was from left to right.

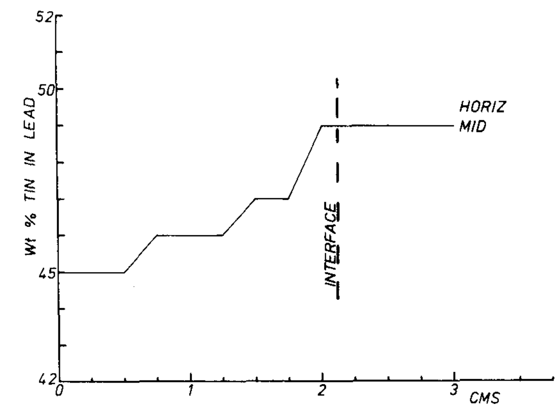

Fig. 11—Average composition versus distance plot for the fine grid shown in the horizontally grown Pb-48 wt pct Sn cast, Fig. 10.

ing occurs around the channels, however freezing continues elsewhere. The channels can drain solute from the surrounding material thus leading to more solid being deposited as for the previous case.

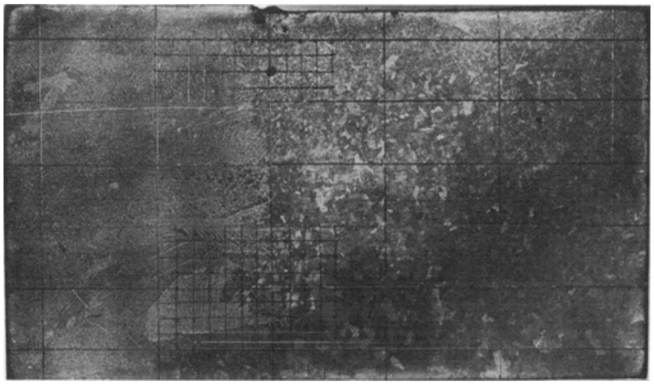

Fig. 12—Macrostructure with superimposed top and bottom, fine grids for the horizontally grown Sn-5 wt pct Pb cast. Growth was from left to right.

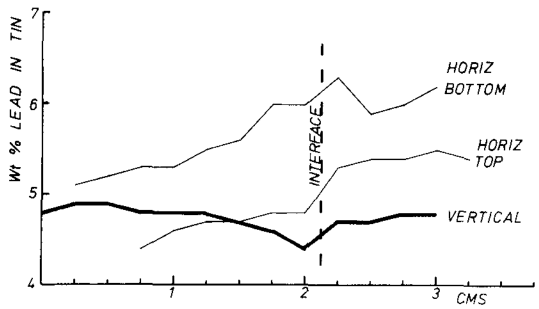

Fig. 13—Average composition versus distance plots for top and bottom fine grids for the horizontally grown Sn-5 wt pct Pb cast shown in Fig. 12. Also a similar plot for upward vertical growth in Sn-5 wt pct Pb casts.

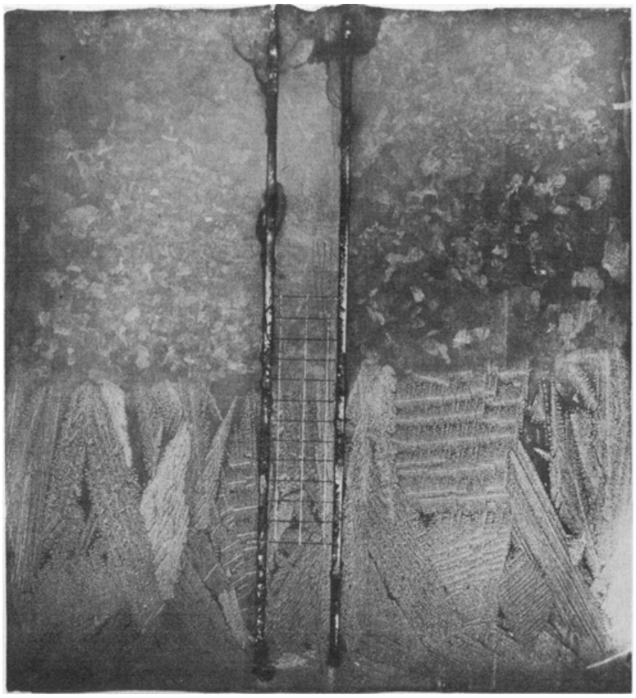

Fig. 14—Macrostructure with superimposed fine grid for vertically grown Sn-5 wt pct Pb cast. Growth was vertically upwards.

A number of other horizontally grown samples were analyzed. These confirmed the trend shown in Fig. 13. However there was some indication that the actual slope of the curves increased towards the end of the casting.

The macrostructure of a vertically grown Sn-5 wt pct Pb specimen is shown in Fig. 14. In contrast to the macrostructures of horizontally grown Sn-5 wt pct Pb specimens shown in Figs. 7 and 12, in Fig. 14, the interface is flat and parallel to the chill face. The average analyses of the vertically grown specimens are also shown in Fig. 13.

The resulting curve is very different for these specimens. Except for a small dip near the interface, there is practically no change in composition with distance. This clearly indicates that macrosegregation by interdendritic fluid flow is occurring in the horizontally grown specimens but not in those grown vertically upwards. The difference in slope between the curves of the horizontally and vertically grown specimens provides a measure of the rate of macrosegregation at a given distance behind the interface.

It is interesting to note that the absence of macrosegregation in the vertically grown specimens (observed from coarse grid analyses) confirms that volume contraction fluid flow is producing little macrosegregation in these specimens. Similarly the fine grid analyses show that the quenching is not producing a large quench artifact.

CONCLUSIONS

These experiments have shown that in these model castings the dominant mechanism was convective interdendritic fluid flow. The macrosegregation arose partly because of the motion of liquid within the semisolid region, but also because this motion led to a change in bulk liquid composition and its stratification into layers of different density.

The theoretical model[4] of convective interdendritic fluid flow does not allow any liquid to return to the bulk, and thus cannot be used to describe experiments such as these.

The present work together with less detailed work reported elsewhere give an indication of the conditions under which each of the macrosegregation mechanisms, listed in the introduction, would be dominant. The mixing or flow of the diffusion layer into the bulk liquid is expected to be dominant in slowly grown specimens growing with an almost planar interface. For dendritic growth this mechanism will become less important and convective interdendritic flow, for slowly grown castings, will become dominant. The fluid flow resulting from volume change on freezing will be dominant in specimens frozen rapidly, *i.e.*, those completely solid in seconds. The precipitation of solid in the bulk liquid will be important whenever it occurs provided there is time for the solid to settle out.

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