MUSHY ZONE CHARACTERISTICS AND MACROSEGREGATION DURING DIRECTIONAL SOLIDIFICATION

S. N. Ojha* and S.N. Tewari**

* Department of Metallurgical Engineering, Banaras Hindu University, Varanasi-221005, India
**Department of Chemical Engineering, Cleveland State University, Cleveland-44115, USA

e-mail: shojha@bhu.ac.in

(Received 1 April 2004 ; in revised form 21 June 2004)

ABSTRACT

Directional solidification of an alloy containing Pb-5.8 wt% Sb has been carried out over growth rates varying from 1 to 10 µm s⁻¹ in a positive temperature gradient of 140 K cm⁻¹. The microstructural examination indicated cellular to dendritic transition at a growth rate of 1.5 µm s⁻¹. An analysis of composition revealed a large macrosegregation of Sb along the longitudinal section of the directionally solidified alloys. The degree of macrosegregation was observed to increase with a decrease in the growth rate during solidification of the alloy. The microstructural analysis indicated a progressive increase in volume fraction of the solid phase, variation in shape factor of cells/dendrites and decrease in the hydraulic radius as a function of distance from the solid-liquid interface in the mushy zone. These factors control the permeability of the mushy zone and resultant macrosegregation of the alloy. The macrosegregation behaviour of the alloy is discussed in light of thermo-solutal convection in the mushy zone as well as in the melt ahead of the solid-liquid interface during directional solidification.

1. INTRODUCTION

Solidification constitutes a major part of many materials processing techniques. The microstructure of a cast alloy is greatly influenced by macrosegregation of alloying elements during freezing of the melt. The macrosegregation occurs in a casting due to thermo-solutal convection in the melt. In addition, sedimentation of dendrite debris and solidification shrinkage of the alloy further aid to the degree of convection in the melt. The solute rejection during solidification and its effect on microstructural evolution in a cast alloy are qualitatively well understood. However, a quantitative correlation of this effect with the process parameters of solidification have been established only recently as a result of a series of elegant experiments. Due to the complex shape and uncontrolled growth conditions of phases in a casting, it is difficult to generate data of scientific importance to provide an insight into the occurrence of macrosegregation. As a result, directional solidification experiments have been carried out in the past to study the solute redistribution pattern generated during solidification of alloys. In such experiments growth rate and temperature gradients are independently varied during upward or downward solidification of the melt in a positive temperature gradient.

The solute build up in the interdendritic or intercellular regions and also in the melt ahead of the solid-liquid interface causes thermo-solutal convection. This effect substantially induces the macrosegregation of alloying elements in the solid phase. The convection of the melt causes longitudinal macrosegregation and formation of freckles in the cast alloy in case the density of the solute element is less than that of the solvent. Alternatively, when the solutes ahead of the interface have a density higher than that of the solvent metal then the macrosegregation would occur in the transverse direction and causes stippling of dendrites. In both
the cases the primary dendrite arm spacing have been reported to be lower than that predicted from theoretical models. Consequently the concentration gradient existing in the liquid adjacent to the mushy zone and within the mushy zone is affected. Such convection has been shown to be responsible for composition variation of the alloy observed in a casting and also during directional solidification.

There is no systematic investigation on the configuration of the mushy zone and its influence on the degree of macrosegregation. These effects are reported in the present investigation.

2. EXPERIMENTAL PROCEDURE

2.1 Directional Solidification

The Pb-Sb alloy was made from 5’N purity constituent metals. The melting was carried out in a graphite crucible in an induction furnace. The melting chamber was evacuated to a pressure of $10^{-3}$ torr followed by back filling with Ar gas. The melt was subsequently sucked into quartz tubes with one end immersed in the melt and the other end connected to a vacuum pump. Control of differential pressures on the surface of the melt in the crucible and within the quartz tube assembly initiated the melt flow into the quartz tubes and facilitated preparation of samples of 0.65 cm diameter and about 30 cm in length, used in the directional solidification experiments. The as-cast alloy was charged in another quartz tube with 0.70 cm internal diameter and 70 cm length. One end of the quartz tube was connected to a vacuum pump and argon gas cylinder assembly whereas the other end was sealed after inserting two flexible ceramic coated Chromel-Alumel thermocouples through a fine capillary silica tube. The hot junctions of the thermocouples were positioned 3.0 cm apart at predetermined locations in the quartz tube to monitor the temperature profile during translation of the tube. The other ends were connected to a temperature recorder and a data acquisition system.

The directional solidification set-up used in the present investigation is shown in Fig. 1. The experimental set up basically employed a 50 kW induction heater, an Inconel furnace with 1.2 cm inner diameter and 20 cm length and a stepper motor controlled pulling device. A copper chill with water circulation and a spray nozzle assembly were mounted concentric to the bottom end of the furnace. The quartz tube containing the as-cast alloy was centered through the furnace and chill block-spray assembly. The bottom end of the tube was connected to the pulling device. The quartz tube was repeatedly evacuated and back filled with Ar gas prior to melting the alloy. The melting of the alloy produced about an 18 cm liquid column in the quartz tub which was consistently maintained in all experiments. The required thermal profile in the furnace was established first by a series of experiments wherein the melt temperature and rate of pulling of the quartz tube were independently varied. A typical thermal profile generated in the samples during directional solidification is shown in Fig. 2. The temperature gradient in the melt ahead the solid liquid interface was observed to be 140 K/cm at both the thermocouple locations. In all subsequent experiments the same temperature gradient was ensured in the melt when the growth rate was varied from 1 to 10 µm/s. The melt ahead of the interface was quenched by water spray towards the end of directional solidification.

2.2 Materials Characterization

Samples for microstructural observation were prepared, in both the longitudinal and transverse
directions, following standard metallographic procedure and examined in an optical microscope. With the knowledge of the growth regime for the cellular dendritic solidification, four additional samples were directionally solidified for the macrosegregation study. Compositional analysis of Sb (CS) of two millimeter thick slices, machined along the length of the directionally solidified samples, was carried out by a wet chemical method using atomic absorption spectroscopy. The distance from the tip of the mushy zone at the onset of directional solidification to its tip at the time of quenching, as observed from the longitudinal microstructure, was taken as the total solidification distance. The ratio of the distance solidified as measured from the tip of the mushy zone at the onset of solidification to the total length of the melt column was taken as the fraction solid ($f_S$).

Selected samples were subjected to serial sectioning in the transverse direction in a Lica Microtom equipment attached to a diamond cutter. An optical microscope was used to view the microstructure of the sample section on line. A step height of 1µm was used in serial sectioning near the tip of cells and dendrites whereas distances far from the tips, the step height was varied from 20 to 200 µm. The sectioning was carried out upto the length of the mushy zone in the sample. The microstructure of the surfaces at each step of sectioning was viewed on a video screen and these were saved in a computer connected to a on line a video printer. The images were further processed in a sigma scan software to study the variation in solid fraction, shape factor of cells and dendrites and hydraulic radius of the mushy zone as a function of distance from the solidification interface. The results provided the configuration of the mushy zone consisting of solid and liquid phases during solidification processing of the alloys.

3. RESULTS

3.1 Microstructural Features

The microstructure of directionally solidified alloys generated at three different growth rates is shown in Fig. 3(a-c). At low growth rate, the microstructure exhibits a cellular solidification structure which changes to dendritic at higher growth rate. The cellular to dendritic transition in this alloy is observed at a growth rate of 1.5 µms$^{-1}$. The cells and dendrites are aligned in the growth direction. The eutectic isotherm in the longitudinal section of the microstructure was clearly delineated due to its different contrast with that of the quenched interdendritic liquid. The serial sectioning of the alloy showing fully cellular and dendritic microstructure was investigated in the transverse direction. The microstructures at three different distances from the tip of the dendrite are shown in Fig. 4(a-c). It is interesting to note that dendrite tips are not located at the same plane from the quenched solid-liquid interface. In addition, the volume fraction of the quenched liquid is very high close to the dendrite tip. At a distance of 50µm from the dendrite tip, the volume fraction of the quenched liquid has significantly decreased. This feature is more pronounced in the microstructure obtained further away from the dendrite tip at a distance of 400 µm. The variation in liquid phase along the length of the mushy zone is considered to have a strong influence on the degree of macrosegregation during solidification of the alloy.

3.2 Compositional Profile

The variation in solid composition along the longitudinal direction of the directionally solidified alloy is shown in Fig. 5. In the above figure, CS/CO is the ratio of the composition of the solid corresponding to a given fraction of solidification ($f_S$) of the alloy to the overall composition of the liquid. It is important to note that as the solid fraction
Fig. 3: Microstructure of directionally solidified Pb-5.8 Sb alloy showing (a) cellular solidification structure at growth rate of 0.8 μms⁻¹ (b) cell to dendrite transition at growth rate of 1.5 μms⁻¹ and (c) dendritic structure at growth rate of 3.0 μms⁻¹.

indicates that the alloy with a cellular solidification structure shows a large degree of macrosegregation compared to the alloy with a dendritic solidification structure.

of the alloy increases, the ratio CS/CO increases for all the growth rate conditions and finally approaches unity. However, the variation in CS/CO is more significant at lower growth rates, e.g., 1 and 1.5 μms⁻¹. As the growth rate of this alloy increases to 10 μms⁻¹, the ratio CS/CO becomes unity at an early stage of solidification. Subsequent solidification results in a uniform composition of the solid along the length of directionally solidified alloy. The result indicates that the alloy with a cellular solidification structure shows a large degree of macrosegregation compared to the alloy with a dendritic solidification structure.

3.3 Mushy Zone Characteristics:
The mushy zone is constituted of cells and dendrites depending on the growth rate exercised during
directional solidification. The serial sectioning experiments facilitated measurement of the solid fraction from the tip of cells/dendrites to the other end of the mushy zone closer to the eutectic isotherm. The variation in solid fraction is shown in Fig. (6). It is worthwhile to point out that the alloy solidified at a growth rate of 1 $\mu$ms$^{-1}$ exhibits cellular morphology whereas those solidified at a growth rate of 3 $\mu$ms$^{-1}$ have a dendritic morphology. The cellular to dendritic transition is observed in alloy at a growth rate of 1.5$\mu$ms$^{-1}$. It is also interesting to observe that the solid fraction is consistently higher for cellular structure compared to that of dendritic structure along the complete length of the mushy zone. Furthermore, the solid fraction rapidly increases with distance in the mushy zone closer to the tip of the cells whereas there is a gradual increase in solid fraction of dendrites. Similar behavior is observed for the sample exhibiting a cellular to dendritic transition. A variation in the shape factor of cells and dendrites in the mushy zone from the solidification interface is shown in Fig. 7. A shape
Fig. 5: Macrosegregation of directionally solidified alloys as a function of growth rate.

Fig. 6: Variation in solid fraction from tip of cells and dendrites in the mushy zone.

Fig. 7: Variation in shape factor of cells and dendrites in the mushy zone region.

Fig. 8: Variation in hydraulic radius of the mushy zone from the solidification interface.

The shape factor of one corresponds to the perfect round shape. The above figure shows that neither cells nor dendrites appear to have a round shape. However, the dendrites show the highest shape factor near the tip compared to that of the cells. The shape factor for both cells and dendrites considerably decreases at after a distance of 200 µm from the tip. In these regions the shape factor of cells is observed to be higher than that of dendrites. The solid fraction and shape factor together provides configuration of the mushy zone and resultant channel for the fluid flow during directional solidification. The variation in hydraulic radius in the mushy zone is shown in Fig. 8. The hydraulic radius is observed to be high closer to the tip of cells and dendrites.
However, it considerably decreases only at a distance of less than 50 µm from the tip of cells or dendrites. It is worthwhile to note that hydraulic radius for dendritic structure is significantly lower that that of cellular solidification structure up to nearly 200 µm from the tip of dendrites. Further away from the tip the hydraulic radius for both cells and dendrites becomes considerably lower. The hydraulic radius has finally a great influence on the fluid flow and convection in the mushy zone.

4. DISCUSSION

The solid-liquid interface during directional solidification is either planar, cellular or dendritic. The existence of a planar interface is commonly encountered in most of the crystal growth techniques. However, the planar interface condition is rarely observed in casting processes. The reasons for the break down of planar interface is understood in the light of constitutional supercooling of the melt ahead of the solid-liquid interface\(^\text{11}\). The growth rate regime employed in the present investigation exhibits cellular and dendritic morphology of the primary phase. A growth rate of 1.0 µms\(^{-1}\) results in cellular solidification structure of this alloy which changes to dendritic at higher growth rate. The cellular to dendritic transition is observed at 1.5 µms\(^{-1}\) as shown in Fig. 3. The pattern of macrosegregation considerably depends on the solidification morphology which depends on the growth rate used during solidification. This effect is evident from the variation in solute profile in cellular and dendritic solidification regime of the alloy (Fig. 5).

Earlier models\(^\text{10}\) developed to describe macrosegregation assume a planar interface and basically consider diffusion as the mode of solute transport. However, the assumption of mixing in liquid by diffusion only is very unlikely to be realized. The convection occurs in the bulk liquid and also in the mushy zone during directional solidification. A density gradient is caused by differences in temperature and also by compositional variations due to rejection of solutes. The planar front solidification is simpler to model compared to that involving cellular or dendritic interfaces. Even the former becomes more complicated when convection occurs in the bulk liquid phase.

Furthermore, a planar interface system is more clearly delineated compared to a cellular-dendritic interface. In the later case, there is existence of a semi-solid mushy zone as a third region. This zone is characterized by the variation in solid fraction and shape of the cells or dendrites along the complete length of the mushy zone i.e from the tip of the dendrites to the eutectic isotherm. These factors significantly influence the permeability of the mushy zone and resultant convection of the melt within the mushy zone. The nature of mushy zone and its interactions with the bulk liquid have led to the development of several models of macrosegregation\(^\text{13,14}\). However, many simplifications have been made in the shape of cells or dendrites. The specific contribution of the mushy zone and the bulk melt ahead the interface on the degree of convection is not clearly understood. There is a lack of experimental data to understand the characteristics of the mushy zone itself.

The results of the present investigation clearly indicates that neither cells nor dendrites have shape factor approaching unity. Similarly the volume fraction of the liquid phase and the hydraulic radius appears to be high only up to less than 10 % length of the mushy for the case of cellular solidification structure. In contrast, for dendritic solidification structure these parameters of the mushy zone is extended up to 30% of its length. Such characteristics
of the mushy zone provides a greater insight into the degree of convection in the mushy zone regions during directional solidification.

Consequently, the convection in the mushy zone of cellular solidification structure is confined to the region closer to the tip of the cells. On the other hand, the convection would occur up to a greater depth in the mushy zone region constituted of dendritic solidification structure. However, the chemical analysis data presented in Fig. 5 shows a large degree of compositional variation in the cellular solidification structure compared to that of dendritic solidification structure. This observation indicates that macrosegregation is predominantly governed by the convection in the bulk melt rather than that in the mushy zone region.

The convection in the bulk melt is examined in terms of fluid velocity that can arise during directional solidification. A parameter, \( \frac{g(C_t-C_o)D_l}{RC_o^{0.5}} \) has been earlier shown to represent fluid velocity on a characteristic distance \( D_l/R \) during natural convection\(^{15}\). In the above expression, \( C_t \) and \( C_o \) are the compositions of the cell/dendrite tip and the liquid far away from the interface respectively, \( R \) is the growth rate, \( D_l \) is diffusion coefficient of the solute in the liquid and \( g \) is the gravitational acceleration. A higher fluid velocity arising as a consequence of intense convection in the melt was demonstrated to result in large longitudinal macrosegregation. On a similar argument Fig. 9 is used to show a variation in effective partition coefficient \( k_e \) (\( C_s/C_o \)) with the fluid velocity parameter \( \frac{g(C_t-C_o)D_l}{RC_o^{0.5}} \) based on data from the present investigation. The data due to Pb-2.2 wt% Sb is also included from the work of Ojha et al\(^5\). This result also indicates that as the growth rate decreases during directional solidification the fluid velocity increases with a consequent increase in convection and mixing in the liquid. The fluid flow rate in plumes in an aqueous solution has been observed\(^{11}\) to be of the order of 1.0 mms\(^{-1}\). In metals these flow rates would be expected to be still higher because of their higher Prandtl number. This would allow sufficient time for a complete mixing, particularly in the range of growth rate conditions used in the present investigation, as these growth rates are much smaller than the expected plume velocities. Therefore the above-described correlation between macrosegregation and the fluid flow velocity due to solute build up at the tip is fortuitous and the results are only demonstrating that the fraction of solutes rejected normal to the growth front is different for different morphologies. The result of the present investigation thus indicates that as the growth rate increases the extent of macrosegregation decreases.

In summary, macrosegregation during directional solidification of alloys occurs as a result of thermosolutal convection in the melt arising from rejection of low density solutes ahead of the interface. This effect greatly influences the composition and configuration of solid/liquid phase and resultant permeability of the mushy zone.

5. CONCLUSIONS

The data generated from the directional solidification experiments of Pb-Sb alloy in the present investigation lead to the following conclusions:

(1) Directional solidification revealed a cellular-dendritic morphology of the primary phase in the growth rate regime varying from 1 to 10 \( \mu \text{ms}^{-1} \) in a temperature gradient of 140 K/cm. The cell to dendritic transition of Pb-5.6 Sb alloy occurred at a growth rate of 1.5\(^{-1} \) \( \mu \text{ms} \).

(2) A low growth rate in the regime of cellular solidification structure exhibited a large degree of macrosegregation. The degree of macrosegregation was less in the regime of dendritic solidification. However, increasing growth rate in this regime resulted in a reduced degree of macrosegregation.

(3) There was a continuous variation in the volume fraction of solid, the shape factor of cells and dendrites and hydraulic radius along the length of the mushy zone. As a result, the permeability of the mushy zone was high only closer to the solid-liquid interface in the mushy zone. These results indicate that the convection in the mushy zone is less than that in the bulk melt ahead the solid-liquid interface.

(4) The fluid velocity during convection represented by a parameter \( \frac{g(C_t-C_o)D_l}{RC_o^{0.5}} \), was related to the effective partition coefficient \( k_e \) and resultant degree of macrosegregation of the alloy.
REFERENCES