Using nucleators to control freckles in unidirectional solidification

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Abstract

Buoyancy-induced fluid flow, which is responsible for most forms of macro-segregation and channel-type segregates in castings, is not directly controllable. If left uncontrolled, natural convection will contribute to non-uniform distribution of alloy constituents and grain structure during solidification of a casting. Non-uniform distribution of chemical composition and physical structure in an alloy casting can significantly affect the reliability of mechanical components. Therefore, materials with acceptable defects can be produced only by trial-and-error and their acceptability is determined by costly inspections. We present a novel technique to control the formation of chimneys and resulting freckles in the mushy zone during the solidification of ammonium chloride that is cooled from below. This is done by placing metallic nucleators in particular arrangements on the bottom cooling plate. With this technique, freckles in a casting might be avoided and/or be forced to form where stresses are expected to be lower during use of the part.

The objective of this study is to investigate the effects of the arrangement, spacing, and size of the nucleators on finger formation, plume structure, and the solidification process. Results showed that it is possible to obtain a relatively large area free of channel-segregates in a metal analog directionally solidified upward by placing nucleators in certain arrangements at the bottom of the casting. The outcomes of this study will serve as a baseline for subsequent investigations that will examine the solidification of binary alloys, and could be used to test and develop mathematical and numerical models.

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1. Introduction

During solidification of binary solutions, the solubility of components is usually lower in the solid as compared to the liquid, thus, solute is usually rejected at the solidifying solid liquid interface. This solute rejection enriches the local liquid causing concentration gradients, and thus, density gradients in the liquid. As a result of thermal and solution-related buoyancy forces, several different kinds of convection have been observed in many experiments such as; salt-finger convection, plume convection and double-diffusive layer convection [1]. Convection can influence the solidification process and affect the strength, hardness, and corrosion resistance of the final casting. Advection and diffusion during solidification can result in segregation and non-uniform distributions of chemical and physical composition in final products. Segregation and variations in grain size in an alloy casting can negatively affect the properties of the casting. Freckles or channel-segregates are a type of macro-segregation that usually extends along the length of a casting vertically [2]. Freckles have been observed in many experiments [3]. Using an aqueous ammonium chloride solution, an analog system for binary metallic alloys, it was shown that the freckles are generated by plume convection in the mushy layer.

As crystals grow in the initial stages of solidification, they reject lighter water-rich fluid and an attendant double-diffusive instability yields a large number of ascending water-rich fingers adjacent to descending salt-rich fingers. Worster mathematically identified two instability mechanisms, 'Boundary-Layer' and 'Mushy-Layer' modes [4]. In the boundary-layer mode the fluid within the interstices of the mushy layer is stagnant and the instability occurs above the mushy layer in the fluid region. Salt-finger convection occurs as a result of this mode and is confined to the compositional boundary-layer. The solid-fraction does not get perturbed in this mode. On the other hand, the mushy layer mode is related to the solid-fraction perturbations. It was shown that this mode is the cause of the formation of the plumes. As the mush grows thicker and the critical condition in the mush is exceeded, chimneys in the form of vertical channels start to appear in the mush and plumes of lighter fluid flow upward through the chimneys into the liquid. With continuing upward solidification, the number of fingers reduces to a smaller number of robust plumes. With increasing time, the channels deepen, while the strength of the related plumes increases, enabling plumes to ascend to the top of the container.
Chen et al. implemented a linear stability analysis and they speculated that the plume convection was a result of the sub-critical instability under the perturbation of nonlinear salt-finger convection rather than mushy layer modes of instability [5].

Buoyancy forces which are mainly responsible for the formation of chimneys and freckles are not easily controllable. Some researchers have investigated process control options to suppress freckle and chimney formation in unidirectionally solidified ingots of ammonium chloride solution.

Kou et al. performed a numerical analysis which was confirmed by experiments to predict macro-segregation in rotated vacuum arc remelted ingots of Sn–Pb [6]. Due to upward concavity of the liquid and solid interfaces, Pb-rich segregates formed in the center of the ingot. This concavity caused the denser Pb-rich inter-dendritic liquid to flow downward and radially inward towards the centerline. This indicated that during solidification process, there was a remelting of the dendrites which, in fact, left a freckle along the centerline. Centrifugal forces due to the rotation of the ingot prevented the denser Pb-rich fluid to flow toward the centerline creating a more uniform composition profile radially. In fact they mentioned that by choosing a proper rotational speed of ingot, the freckles could be significantly reduced. It was also shown that at a high solidification rate, the macro-segregation was slight and centrifugal force had little effect on the macro-segregation.

Sample and Hellawell showed that slow rotation of a cylindrical ingot about an inclined axis retarded the formation of chimneys and associated macroscopic composition changes during solidification of an ammonium chloride solution; however, for higher rotational speed some chimneys were formed at the mold walls [7]. They concluded that for freckles to form there must be a convective circuit within the bulk liquid and inter-dendritic liquid and there must be a flow of more dense solution into the dendritic network around the chimneys. This flow is to feed the plumes; therefore, any interruption in this convection circuit could suppress the chimney formation. In another set of experiments, Sample and Hellawell reported that the mush-melt interface had been pitted to various depths by slowly punching a pointed quill into the mushy zone [8]. These artificially created channels had failed to propagate and form chimneys and had been overgrown and closed within 2–4 min. However, they could create a new plume and from that a new chimney by lowering down an open capillary to within 1–2 mm of the growth front and sucking some liquid up the tube. They also observed that blocking an established chimney by a quill, could close the chimney and prevent the formation of the plume at that location.

By solving complex and strongly coupled governing equations, Neilson and Incropera supported the findings of Sample and Hellawell [9,10]. They indicated that the quality of unidirectionally solidified binary alloys may be enhanced through intermittent rotation of the mold which restricts freckling to the centerline and outer radius of the casting.

Experimental observations showed that low-amplitude vibrations to the test section reduced the mushy zone thickness and the number of chimneys for all concentrations of an ammonium chloride solution cooled from below [11]. It was also mentioned that chimney suppression was influenced by vibration amplitude rather than frequency of oscillation.

Small nucleators were used to create and measure velocity and temperature distributions of plumes during the solidification process of ammonium chloride [12–15]. It was shown that by placing small nucleators in a particular arrangement on the bottom plate of the test section, the plumes can be formed right above the nucleators. In order to obtain the velocity fields and temperature maps of the plumes using MTV and PIV techniques, one should know the location of the plumes prior to the test. Therefore, placing nucleators seems to be the only solution.

With the exception of the described studies, little has been done to consider means by which freckling may be inhibited by placing the nucleators in particular arrangements. The objective of this study has been to investigate the effects of the arrangement and size of the nucleators on the plume structure and the solidification process of an ammonium chloride (26% wt) solution in water. We will also show that it is possible to obtain a relatively large area free of chimneys. Results from this study will serve as a baseline for a subsequent investigation that will study the solidification of binary alloy, and could be used to provide experimental verification for mathematical and numerical models.

2. Experimental setup

The test section was essentially that described in Refs. [12,13] and consisted of 1/4” quartz glass measuring 52 × 89 × 100 mm placed over a stainless steel base plate (430 stainless steel). The cooling of the fluid within the test section is achieved with the use of the base stainless steel plate as a heat transfer medium. The plate is exposed to a coolant bath on one side and aqueous ammonium chloride on the other within the test section (Fig. 1).

During initial experimental trials, it was observed that convective plumes due to the density instability develop within the test section in a random manner. However, each experimental trial would yield approximately 11 chimneys within the test section. Two different sets of nucleators are used in these experiments. Small nucleators measuring 1.59 × 1.59 × 3.19 mm and big nucleators measuring 3.19 × 3.19 × 3.19 mm are made of Neodymium rare earth magnets. Nucleators are chosen to be magnets so that they can be arranged and placed easily on the stainless steel bottom plate. Further details of the experimental setup can be found in Ref. [15].

3. Results

3.1. Effect of size and arrangement

To examine the effects of size and arrangement of nucleators on the solidification of aqueous ammonium chloride, two different arrangements are used in the following experiments. The first arrangement as shown in Fig. 2a with small nucleators is the same as Wirtz used in his experiment. The second arrangement as shown in Fig. 2b with small nucleators is used for the purpose of comparison with that of Wirtz [12].

The ammonium chloride solution, which was at room temperature when poured into the container (26% wt NH₄Cl), was cooled from the bottom by a heat exchanger. The thermo-bath circulated constant temperature coolant (−19 °C) through the cooling chamber built under the bottom surface of the container. This caused the stainless steel base plate to be at a constant temperature of −14 °C. The cooling fluid was a 50% mixture of water and generic automotive anti-freeze which was refrigerated by an external cooling bath (Neslab, RTE-140) and pumped through insulated tubing into the cooling chamber. To reduce the heat transfer to the surroundings, the cooling chamber was covered with appropriate insulations.

The cooling provided to the test section would then initiate the crystallization process. The initiation of crystallization usually started around the nucleators and then quickly spread over the bottom plate. Rapid growth of the mushy layer at the initial stages of cooling produces fluid with lower concentration at the bottom of the container [14].

Cooling from the bottom induces a temperature gradient. This temperature gradient imposes a stabilizing density gradient, with cooler and heavier liquid at the bottom. As solidification starts due to cooling below the solution’s equilibrium solidification tem-
perature, ammonium chloride crystals form and water is rejected at the solidifying interface. Solidification enriches the local liquid with water which reduces the mixture density. This lower density eventually overcomes the contributions to density changes made by the temperature gradient, and as a result, the lighter liquid near the nucleators preferentially ascends forming water-rich fingers.

Four minutes into the solidification process small fingers started to form around the nucleators and could be seen rising. At 6 min, more fingers maintained their concentration identity and were able to rise higher. Due to the large Lewis number of ammonium chloride, the water-rich fingers retained their compositional identity and were clearly visible to the top of the test section before they would begin to collapse [3]. Later in time fingers above the nucleators strengthened and became plumes.

In the case of the first arrangement (Fig. 2a) with small nucleators as expected eleven chimneys and plumes were formed above the nucleators. This is consistent with Wirtz's observation [12]. Fig. 3a shows the top view of the mushy zone and as can be seen eleven chimneys (marked with red circles) were formed above the nucleators.

We could not force all chimneys and plumes to be formed above the nucleators using the second arrangement (Fig. 2b) with small nucleators. As can be seen in Fig. 3b, four out of twelve chimneys formed randomly in the test section. These simple tests illustrate that the arrangement of the nucleators plays an important role during the solidification process.

Keeping the same arrangement (second arrangement) but using the big nucleators, plumes and chimneys could be forced to form above the nucleators. Therefore, the bigger nucleator caused a larger perturbation in the density field and a stronger driving force for plume formation. At early stages, fingers that are formed at the mush-melt interface above the nucleators seem to be stronger and thicker than the rest of the fingers. Chen et al. concluded that plume convection was possible if vigorous enough salt-finger convection is present along with a mushy layer of sufficient permeability [5]. Sample and Hellawell reported that they could create a new plume and from that a new chimney by lowering down an open capillary to within 1–2 mm of the growth front and sucking some liquid up the tube [8].

The capillary suction creates the perturbation required for the lighter inter-dendritic liquid trapped in the mushy zone to rise up and break through the mushy zone. Once a small amount of

![Fig. 1. Schematic of the setup.](image)

![Fig. 2. Different arrangements (a) first arrangement, and (b) second arrangement.](image)

![Fig. 3. Top view of the mushy zone for the case of small nucleators (t = 120 min) (a) for the first arrangement, and (b) for the second arrangement.](image)
water-rich liquid starts to move up through the mush, secondary dendrite arms are melted and broken creating the start of a chimney. The nucleators cause a similar chimney, though creating a perturbation from the bottom and at the start of solidification. Fingers are formed above the nucleators due to the fact that the solidification rate is higher around these nucleators. As mentioned before, these nucleators are made of metallic alloys. These nucleators act as fins and they enhance heat transfer from the surrounding fluid to the bottom plate; therefore, they enhance the solidification rate locally around them.

3.2. Effect of spacing

To examine the effect of spacing between nucleators on plume structure, two different arrangements were used in the following experiments. Either one pair (Fig. 4a) or two pairs (Fig. 4b) of nucleators was used. In the case of two pairs, we made sure that pairs of nucleators were far enough apart (h > 30 mm) so that one pair did not influence the other. Different experiments were carried out by changing the spacing L between the nucleators. It was observed that when the two nucleators were close to each other the plumes generated above them were always phase locked with 180° phase difference (Fig. 5). The reason for phase locking was due to the coupling between nearby jets. Entrainment of fluid and counter-propagating shear flow produce dynamical instabilities, and results in synchronization of phases of the nearby plumes [16]. Phase locking of the plumes (with 180° phase difference) suggests that the two adjacent plumes have the same Reynolds number and they are identical. Referring to the previous statement, one can conclude that two nearby plumes are fed by the same source of flow within the mushy zone which is split equally among them.

Some of the experimental results are summarized in Table 1. The forth column explains whether two plumes were generated or only one was formed on each pair of nucleators. The fifth column shows whether the two generated plumes were phase locked or not and the sixth column illustrates the time the phase locking occurred (before this locking time, two fingers or two plumes existed with no relationship between their phases). The last column represents the shortest distance d between one of the plumes formed on the pair of nucleators and a next adjacent plume (Fig. 4a).

From Table 1 and other observations, the results given in the following section were obtained.

3.2.1. A pair of small nucleators

If the distance between nucleators of each pair was less than 6 mm only one plume was formed on one of the nucleators. The transition from fingers to plume formation was either oscillatory or non-oscillatory. In the oscillatory mode, initially two fingers were formed above the nucleators; then later in time, one of the fingers would disappear while the other remained. Sometimes, the one that disappeared grew back. This process only repeated itself once or twice, with the surviving finger becoming a plume later in time. Fig. 6 shows the sequence of images for the oscillatory mode of the test # 5. Initially two fingers were formed above the nucleators then later the finger on the left nucleator disappeared while the other on the right nucleator was still ascending (t = 12 min). Then (t = 16 min) the one that had disappeared grew back again on the left nucleator. At t = 18 min this finger started to get weaker again and disappeared at t = 20 min. The surviving finger became a plume on the right nucleator.

In the non-oscillatory mode two fingers grew initially and later one disappeared and the other one remained and later formed a plume until the end of the experiment.

Most of the time, for distances 6 < L < 12 mm, two plumes formed above the nucleators. If the distance between the next adjacent plume and one of these plumes was larger than d = 12 mm, then the plumes on the pair of nucleators were always phase locked with 180° phase difference and had the same amplitude of oscillation until the end of the experiment. Once another plume randomly formed close to the pair of plumes, the phase between the pair of plumes would no longer be locked and they were out of phase until the end of the experiment. The coupling of nearby plumes becomes complicated with the existence of the third plume.

3.2.2. A pair of big nucleators

The results for pairs of big nucleators are similar to those of small ones, except that the minimum distance between nucleators for one pair to generate two separate plumes becomes shorter (L = 5 mm). This indicates that for the bigger nucleators it is more probable to obtain two separate plumes. The summery of these conclusions is written in Table 2. As ammonium chloride solution crystallizes, the height of the mushy zone increases, which reduces the weight percentage of NH4Cl in the liquid. The height of the mushy zone with respect to time for some of the tests in Table 1 is provided in Fig. 7. It is clear from this figure that all the experiments carried out had the same solidification growth rate.

In order to verify the previous conclusion regarding the phase locking of two adjacent plumes, an experiment was carried out...
by placing 7 big nucleators in the longitudinal centerline of the container with 11.1 mm distance apart.

As usual, initially ($t = 6$ min) some fingers which are stronger than the rest of the other fingers, as a result of being more water-rich, were formed above the nucleators and can be seen in Fig. 8a. These fingers became plumes at $t = 20$ min, however some remained out of phase. Fig. 8b shows these plumes at $t = 30$ min for which some were out of phase and the amplitudes were different. At $t = 35$ min these plumes started to become equal in amplitude, but with a $180^\circ$ phase difference with respect to each other. This is shown in Fig. 8c. At $t = 40$ min these 7 plumes are equal in amplitude but $180^\circ$ out of phase. They remained phase locked until the end of the experiment. Fig. 8d shows this phase locking at $t = 70$ min.

As mentioned before in the absence of nucleators, experimental trials would yield approximately 11 chimneys within the test section. In this experiment seven plumes were forced to be formed above the row of nucleators therefore the remaining plumes would be free to form randomly within the test section. Two additional plumes seen on the left side of the Fig. 8d were formed randomly within the test area. As can be seen clearly from Fig. 9, 7 chimneys were formed above the row of nucleators. The reason for chimneys not to be exactly on the straight line was due to the fact that the plume formation could occur at any locations around the periphery of the nucleators. The two chimneys on the left side which are not on the row shows the locations of the two plumes described in Fig. 8d.
3.3. Obtaining a relatively large area free of chimneys

In order to enhance the quality of the unidirectional solidified ammonium chloride alloy and to push out the chimneys to the sidewalls, some nucleators were placed at locations specified in Fig. 10 by rectangular elements. In this case ten plumes were formed above the nucleators as can be seen in Fig. 11. More uniform composition profile of the final product (free of chimneys) was obtained in a relatively large area ($66.6 \text{ mm} \times 34.4 \text{ mm}$).

Keeping the same number of nucleators, we carried out the next experiment by placing the nucleators closer to the side walls (schematically shown in Fig. 10 by circles). With exception of one, all of the plumes formed above the nucleators however some more plumes were formed in the middle of the test section as can be seen in Fig. 12. More uniform composition profile of the final product (free of chimneys) was obtained in a relatively large area ($66.6 \text{ mm} \times 34.4 \text{ mm}$).

Fig. 10. Schematic of the locations of the placed nucleators in two different arrangements (yellow squares and red circles) in order to obtain relatively larger area free of chimneys. (For interpretation of the references to colours in this figure legend, the reader is referred to the web version of this paper.)

Fig. 11. Top view of the chimneys for the yellow squares arrangement in Fig. 10. (For interpretation of the references to colours in this figure legend, the reader is referred to the web version of this paper.)

Fig. 12. Top view of the chimneys when nucleators are placed closer to the container side walls, i.e. the red circles arrangement in Fig. 10. (For interpretation of the references to colours in this figure legend, the reader is referred to the web version of this paper.)
seen from the top view in Fig. 12. The total number of 13 plumes formed during the solidification process. For this case, placing more nucleators near the side walls did not change the results. Still we observed some plumes in the middle of the test section. This experiment shows how sensitive the results are to the wall boundary condition, when the nucleators are placed very close to the side walls.

As it was mentioned, the plumes were not exactly formed above the nucleators. In this regard, it must be considered that the pressure of the water-rich flow drops through the mushy zone. The buoyancy effect which is produced by concentration difference between plume and its adjacent solution compensates that pressure drop. Thus, if a region in the mushy zone were far from the plumes formed by the nucleators, the pressure drop of the solution which flows through the mushy zone would be more than the one caused by the buoyancy effect. Consequently, a new plume would be formed to exhaust the water-rich solution out of that region. In other words, every plume covers only a limited area of the mushy zone. Therefore, if one of the plumes does not cover a region in the mushy zone, a new plume would form in that region. This is the case that corresponds to Fig. 12.

It should be noted that for every single arrangement we carried out the experiment three times to make sure that the results are repeatable. The results presented in this study are valid for the case of 26% wt ammonium chloride solution cooled from below with bottom temperature of −14 °C. It is obvious that changing any known parameter would alter these results.

4. Conclusion

Several interesting conclusions have been deduced from the experiments. The most important ones are as follows:

1. The location of plumes and chimneys can be controlled during solidification of ammonium chloride using metallic nucleators.
2. The bigger the nucleator the more probable the plume is formed above it.
3. Plumes are formed above the nucleators because at initial stages of solidification stronger fingers are formed above the nucleators due to the higher solidification rate around them.
4. When the distance between two nucleators was less than 5 mm for big nucleators and 6 mm for small nucleators, only one plume was formed above them. If the distance between nucleators was less than 12 mm the two plumes were always phase locked with 180° phase difference. The reason for phase locking is due to the coupling between nearby jets. Entrainment of fluid and counter-propagating shear flow produce dynamical instabilities, and results in synchronization of phases of the nearby plumes.

5. It is possible to obtain a relatively large area free of chimneys by placing nucleators around the side walls but not very close to them.

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