Macrosegregation

Macrosegregation refers to variations in composition that occur in alloy castings or ingots and range in scale from several millimeters to centimeters or even meters. These compositional variations have a detrimental impact on the subsequent processing behavior and properties of cast materials and can lead to rejection of cast components or processed products. Macrosegregation is present in virtually all casting processes, including continuous, ingot, and shape casting of steel and aluminum alloys, iron casting, casting of single-crystal superalloys, semisolid casting, and even growth of semiconductor crystals. Because of the low diffusivity of the solutes in the solid state and the large distances involved, macrosegregation cannot be mitigated through processing of the casting after solidification is complete.

The cause of macrosegregation is relative movement or flow of segregated liquid and solid during solidification. Most alloy elements have a lower solubility in the solid than in the liquid phase as is shown by phase diagrams. During freezing, the solutes are therefore rejected into the liquid phase, leading to a continual enrichment of the liquid and lower solute concentrations in the primary solid. This segregation occurs on the scale of the microstructure that is forming, which often consists of dendrites having arm spacings of the order of 10–100 μm. It is therefore termed microsegregation, and results in a nonuniform cored solute distribution in the dendrite arms. Consider now a small volume element that contains several dendrite arms and the liquid between them, i.e., an element inside the liquid–solid (mushy) zone. The flow of solute-rich liquid or the movement of solute-poor solid in or out of the volume element will change the average composition of the volume element away from the nominal composition. Since solute can be advected over large distances, macrosegregation results. Positive (negative) segregation refers compositions above (below) the nominal alloy composition, and all macrosegregation averages out to zero over the entire casting.

There are numerous causes of fluid flow and solid movement in casting processes:

(i) Flow that feeds the solidification shrinkage and the contractions of the liquid and solid during cooling.

(ii) Buoyancy-induced flows owing to thermal and solutal gradients in the liquid. The thermal and solutal buoyancy forces can either aid or oppose each other, depending on the direction of the thermal gradient and whether the rejected solutes cause an increase or a decrease in the density of the liquid.

(iii) Forced flows owing to pouring, motion of gas bubbles, applied magnetic fields, stirring, rotation, vibration, etc.

(iv) Movement of small (equiaxed) grains or solid fragments that have heterogeneously nucleated in the melt, separated from a mold wall or free surface, or melted off dendrites. The solid can either float or settle depending on its density relative to the liquid.

(v) Deformation of the solid network owing to thermal stresses, metallostatic head, shrinkage stresses, or external forces on the solid shell such as those from the rolls in continuous casting of steel.

Efforts to prevent macrosegregation are all aimed at controlling fluid flow and movement of solid. Examples include adjustments to the alloy composition or thermal gradients to induce a stable density stratification in the liquid; application of nozzles, baffles, porous materials, or electromagnetic fields to redistribute the flow; controlled deformation such as soft reduction during continuous casting of steel to squeeze highly enriched liquid away from the centerline of slabs; and modifications to the grain structure to change the resistance to flow through the solid network or the prevalence of equiaxed grains.

Models of macrosegregation are generally aimed at understanding the basic mechanisms involved, quantitatively predicting its occurrence and severity, and performing parametric studies for casting process control and improvement. Such models are by nature very complex and require large computing resources, because they must consider virtually all aspects of a solidification process simultaneously. Phenomena to be considered include heat transfer, solute transport, fluid flow, and solid movement at the (macroscopic) scale of the casting, as well as phase equilibrium, structure formation, segregation, and flow at various microscopic scales. Any factors that affect the flow and the microstructure will also influence macrosegregation. Although these models have reached a high level of sophistication, there are still several macrosegregation phenomena that have not been adequately predicted, and the application of such models to the multicomponent alloys and complex three-dimensional geometries encountered in industrial practice is only beginning.

1. *Examples of Macrosegregation in Alloy Casting*

1.1 Ingot and Continuous Casting of Steel

Figure 1 shows a schematic diagram of the macrosegregation pattern in a steel ingot (Flemings 1974). Negative segregation appears as a zone in the bottom third of the ingot. It is associated with equiaxed dendrites, formed early in the solidification process and relatively poor in solute, that have settled in this region. Positive segregation near the centerline, and particularly at the top (hot top segregation), arises from buoyancy- and shrinkage-driven interdendritic fluid flow during the final stages of solidification. The A-segregates, also called freckles in other applications, are pencil-like chains of equiaxed crystals that are

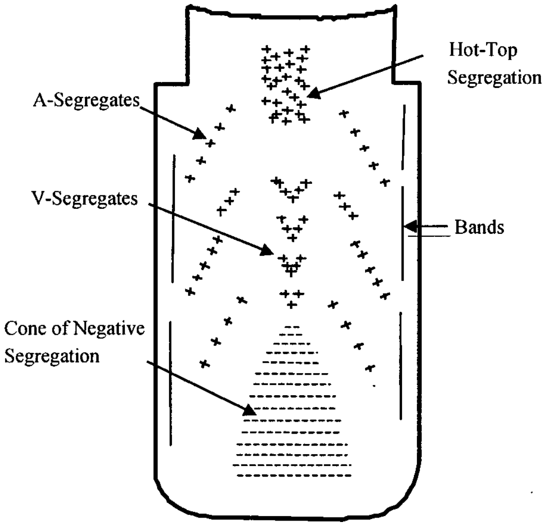

Figure 1
Schematic of the macrosegregation pattern in a steel ingot.

highly enriched in solute. They are the result of buoyancy-driven solutal convection through the columnar dendritic zone in the same direction as, but at a faster speed than, the isotherm velocity. The pencil-like shape of the A-segregates is related to the convection patterns. The V-segregates in the center of the ingot arise from equiaxed crystals settling in the core and forming a loosely connected network that can easily rupture owing to metallostatic head and liquid being drawn down to feed solidification shrinkage. Fissures then open up along shear planes oriented in a V-pattern, and are filled with enriched liquid. Finally, the banding pattern along the sidewalls of the ingot is believed to be because of unsteady heat transfer or flow early in the solidification process.

Many of the solidification phenomena, structural features, and macrosegregation patterns in continuous casting of steel are similar to ingot casting if one measures time with respect to a reference frame that moves with the strand. Axial segregation and V-segregates, although less pronounced, may be seen in longitudinal sections of continuously cast steel. A sulfur print showing a typical centerline segregation pattern in a slab is shown in Fig. 2. Here, an important additional factor influencing the segregation is bulging of the slab owing to inadequate roll containment close to the bottom of the liquid pool. The bulging draws enriched liquid down into the center of the slab where it freezes.

1.2 Direct-chill (DC) Casting of Aluminum Ingots

Centerline segregation is also observed in DC casting of aluminum ingots, and is generally attributed to thermosolutal convection and/or settling of equiaxed grains. A typical macrosegregation profile over an ingot cross-section is sketched in Fig. 3. An important additional feature apparent in Fig. 3 is the strong positive segregation at the chilled ingot surface, which is termed inverse segregation. It is a result of shrinkage-driven flow of enriched liquid toward the

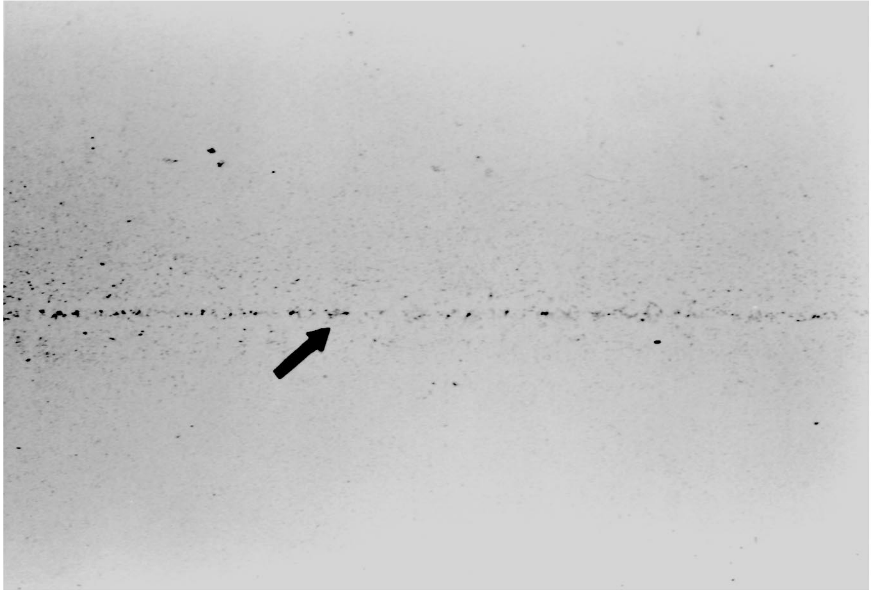

Figure 2
Sulfur print showing centerline segregation in a continuously cast steel slab (courtesy of IPSCO Inc.).

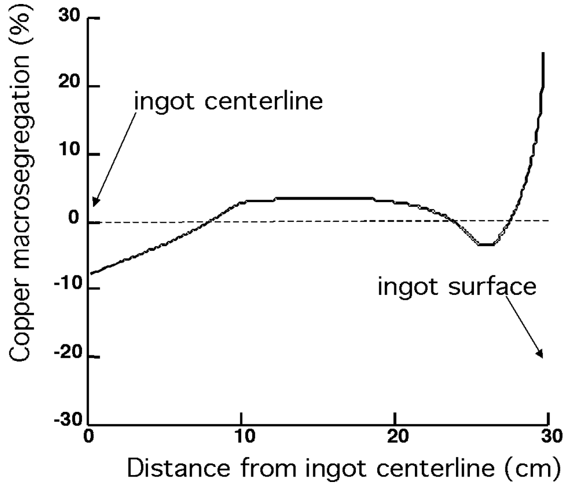

Figure 3
Typical macrosegregation profile in a round DC cast aluminum ingot.

outer face. The liquid may actually exude out of the solidifying shell and freeze onto the surface of the ingot. This macrosegregation is often so severe that it is later removed by scalping the ingot.

1.3 *Investment Casting of Superalloys*

A common macrosegregation defect that occurs in directional solidification of superalloy investment castings is freckles, which are shown in Fig. 4. During solidification of nickel-based superalloys, a number of light elements (such as aluminum and titanium) are rejected into the liquid, and some heavy elements such as tungsten are preferentially incorporated into the solid, leading to strong solutal buoyancy forces in the mushy zone. Despite the presence of a stabilizing thermal gradient, these buoyancy forces can trigger convection cells, leading to open channels in the mush through which liquid streams upwards into the superheated region of the mold. Later, these channels are filled with dendrite fragments, which are then observed as freckle-like chains of equiaxed crystals in the otherwise single-crystal columnar structure. Components with freckles are rejected.

2. *Modeling of Macrosegregation*

The first models for macrosegregation (Kirkaldy and Youdelis 1958, Flemings and Nereo 1967, Mehrabian *et al.* 1970) considered only the flow of interdendritic liquid through a fixed dendritic solid network. Flow in the single-phase bulk liquid region and movement or deformation of solid were not treated explicitly. By performing a mass balance on a small "mushy" volume element that contains both solid and liquid, while accounting for possible in-/outflow of liquid and the different densities of the two phases, a modified form of the well-known Scheil equation can be derived as follows:

$$\frac{\mathrm{d}f_l}{\mathrm{d}C_l} = -\frac{(1-\beta)}{(1-k)}\left[1+\frac{\mathbf{v}\cdot\nabla T}{\varepsilon}\right]\frac{f_l}{C_l} \qquad (1)$$

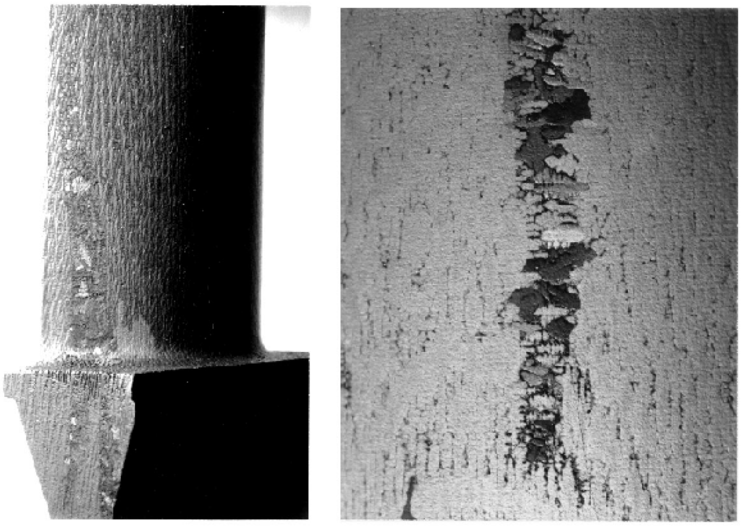

Figure 4
Freckles in a single-crystal nickel-based superalloy prototype blade (left) and close-up of a single freckle (right) (courtesy of A. F. Giamei, United Technologies Research Center).

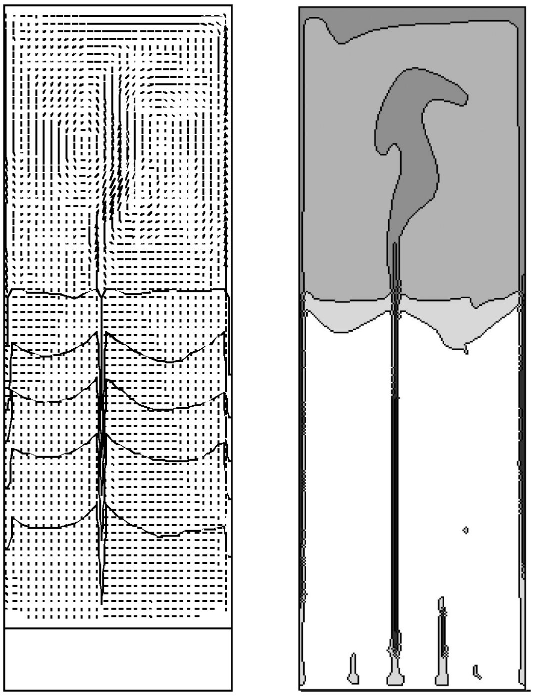

Figure 5
Simulated velocity vectors (left) and macrosegregation pattern (right) showing freckle formation during directional solidification of a single-crystal nickel-based superalloy.

where f_l is the fraction of liquid; C_l is the solute concentration in the liquid; $\beta = (\rho_s - \rho_l)/\rho_s$ is the solidification shrinkage, in which ρ_l and ρ_s are the densities of the liquid and solid, respectively; k is the partition coefficient; $\mathbf{v}$ is the velocity vector of the liquid; ∇T is the temperature gradient; and ε is the rate of temperature change.

The physical significance of Eqn. (1) can be understood as follows: (i) Eqn. (1) reduces to the Scheil equation, implying no macrosegregation, when β and $\mathbf{v}$ both equal zero; (ii) if the liquid velocity alone is zero, for example at an impenetrable chill face, but the shrinkage, β, is finite (> 0), positive macrosegregation will result—this is the so-called inverse segregation mentioned above with regard to aluminum ingots; (iii) Eqn. (1) also reduces to the Scheil equation when the liquid velocity is just that required to feed solidification shrinkage; (iv) flow in the same direction as the shrinkage flow (i.e., down the temperature gradient), but with a greater speed, results in negative macrosegregation; (v) flow with a speed that is less than the shrinkage velocity, and flow that is in the opposite direction, up the temperature gradient towards regions of lower solid fraction, result in positive macrosegregation (such as centerline and under-riser segregation in steel casting); (vi) if the flow velocity up the temperature gradient is so large that the term in the square brackets in Eqn. (1) becomes negative, local melting results, which is the cause of the open channels in the mush that lead to the A-segregates or freckles discussed above.

The interdendritic flow velocities may be calculated from Darcy's law for flow in porous media:

$$\mathbf{v} = -\frac{K}{\mu f_l}(\nabla P + \rho_l \mathbf{g}) \qquad (2)$$

where K is the permeability; μ is the viscosity; ∇P is the pressure gradient; and $\mathbf{g}$ is the gravity vector. The permeability is calculated as a function of the liquid fraction and microstructural parameters such as the dendrite arm spacings (Poirier 1987).

Much progress has been made since this early work to create more general macrosegregation models that account for the flow in the mushy zone and bulk liquid region, the movement of solid, and other effects, as reviewed by Beckermann and Wang (1995) and Prescott and Incropera (1996). In these approaches, a single set of governing equations is formulated that is valid not only in the mushy zone but also in the bulk solid and liquid regions. This set consists of generalized mass, momentum, energy, and species conservation equations that are solved together with phase diagram relationships. The reader is referred to the above reviews for details.

An important advance in modeling the complex transport phenomena leading to macrosegregation in casting is the use of volume or ensemble averaging techniques in deriving the governing conservation equations for solidification systems (Beckermann and Viskanta 1988, Ganesan and Poirier 1990, Ni and Beckermann 1991, Beckermann and Wang 1995). The starting point of this approach is the exact microscopic conservation equations that are valid at a point within a phase and microscopic flux balances and equilibrium conditions that are valid at a point on the solid/liquid interface. These equations are then formally integrated (or averaged) over a representative elementary volume that contains both solid and liquid. The result is averaged or macroscopic conservation equations for each phase and averaged interface conditions that can then be solved on the scale of the casting. The key advantages of averaging are that (i) the macroscopic variables are exactly defined in terms of the microscopic reality; (ii) each term in the macroscopic equations has a clear origin, and terms accounting for the latent heat, permeability, nucleation rate, etc., naturally arise from this procedure; and (iii) most importantly, the macroscopic equations contain microstructural parameters such as the phase volume fractions, grain density, and interfacial area concentration. With respect to the latter issue, Beckermann and Wang (1995) derived a multiphase/-scale model that accounts for the heterogeneous nature of the microstructures present in a solidification system.

3. *Results of Macrosegregation Models*

Many attempts have been made to validate experimentally macrosegregation models using transparent metal alloy analogs, simple binary metallic alloys, and multicomponent alloys of industrial interest (Prescott and Incropera 1996). Some models are still at a research stage, while others are already available in commercial software packages.

The simulation of freckle formation in directional solidification of single-crystal nickel-based superalloys is an example of a model application that requires further development. Figure 5 shows the predictions from a two-dimensional, multicomponent micro-/macrosegregation model (Schneider *et al.* 1997) for an intermediate time during solidification. The open channels in the mush through which enriched liquid is streaming upwards are predicted realistically. Extension of such a simulation to actual cast components is difficult, however, owing to the large computer resources required to resolve such small macrosegregation features over the scale of the entire component.

Figure 6 shows an example of a macrosegregation simulation for a large production steel casting that was obtained using a commercial software package (Schneider *et al.* 1998). The left-hand panel of Fig. 6 illustrates the complex convection patterns present in the bulk liquid region and mushy zone during solidification. The right-hand panel shows the predicted carbon macrosegregation pattern in the fully solidified casting, indicting an under-riser segregation problem.

4. *Conclusions*

Modeling of macrosegregation in castings and ingots has made considerable progress since the early 1960s. It is clear that realistic models must take into account the intricate interactions between melt flow, solid

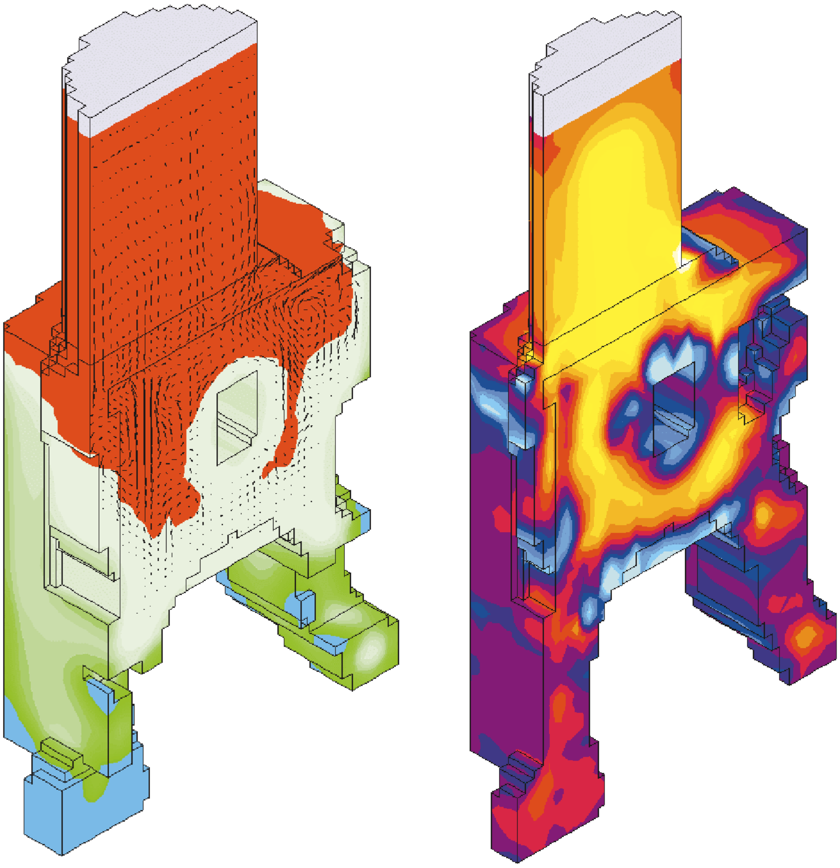

Figure 6
Simulation of macrosegregation formation in a large steel casting, showing liquid velocity vectors during solidification (left) and final carbon macrosegregation pattern (right).

movement, microstructure formation, and multicomponent phase transformations. Macrosegregation owing to interdendritic fluid flow alone can now be simulated for complex, three-dimensional castings, although the resolution of small-scale features such as freckles is still beyond computational capabilities. Much less progress has been made in those cases where grain structure transitions (e.g., columnar-to-equiaxed), movement of free solid, or deformation of mush are significant. As a result, the prediction of macrosegregation in ingot or continuous casting of steel, for example, is still not satisfactory.

See also: Macroscopic Modeling; Micro–Macroscopic Solidification Models; Thermodynamics and Phase Diagrams

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