MACROSEGREGATION refers to spatial variations in composition that occur in metal alloy castings and range in scale from several millimeters to centimeters or even meters. These compositional variations negatively impact the subsequent processing behavior and properties of cast materials and can lead to rejection of cast components or processed products. It is present in virtually all casting processes, including continuous, ingot, and shape casting of steel, cast iron, aluminum and copper alloys, casting of single-crystal superalloys, semisolid casting, and growth of semiconductor crystals. Macrosegregation is especially important in large castings and ingots. 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 shown by the partial equilibrium phase diagram in Fig. 1. During solidification, 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 to 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, that is, an element inside the liquid-solid (mushy) zone. In the absence of any solute transport into or out of the volume element, the average composition of the mixture inside of the volume element will remain constant at the nominal alloy composition, \( C_0 \). However, if liquid or solid having a solute concentration different from the one of the liquid or solid inside of the volume element flows into the volume element, the average composition of the mixture in the volume element will change away from the nominal alloy composition. Since such flow generally occurs over large distances, the casting becomes macroscopically segregated. Positive (negative) macrosegregation refers to compositions above (below) the nominal alloy composition. All macrosegregation must average out to zero over the entire casting.

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

- Flow that feeds the solidification shrinkage and the contractions of the liquid and solid during cooling
- Buoyancy-induced flows due 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.
- Flows due to capillary forces at liquid-gas interfaces
- Residual flows from pouring
- Flows induced by gas bubbles
- Forced flows due to applied electromagnetic fields, stirring, rotation, vibration, and so on
- 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.

- Deformation of the solid network in the mushy zone due to thermal and shrinkage stresses, head pressures, or external forces on the solid shell

Efforts to prevent macrosegregation are aimed at controlling liquid 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; changing the cooling rate or the alloy composition to decrease the dendrite arm spacing and hence increase the resistance to flow through the solid network; and increasing the prevalence of equiaxed grains in a casting, for example, by inoculation or stirring, in order to obtain a more uniform and dense solid distribution.

**Macrosegregation Induced by Flow of the Liquid**

Liquid flow through the mushy zone, where the developing solid network can be assumed to be rigid and fixed, is the most common cause of macrosegregation. Such macrosegregation can be best understood by considering the local solute redistribution equation (LSRE) derived by Flemings and coworkers (Ref 1–3). This equation is based on a solute balance on a small-volume element inside the mushy zone, as illustrated in Fig. 2. As in a standard Scheil-type analysis (see other articles in this section of the Volume), local solute diffusion in the solid phase is neglected, and the liquid inside the volume element is assumed to be well mixed and in equilibrium. Then, the solute concentration in the liquid, \( C_L \), is given as a function of temperature by the liquidus line of an equilibrium phase diagram (Fig. 1) according to \( C_L = (T - T_m)/m \) (where \( T \) is the temperature, \( T_m \) is the melting point of the pure solvent, and \( m \) is the slope of the liquidus line).
the different densities of the solid and liquid, respectively. In one dimension, mass conservation yields that the liquid velocity needed to feed the solidification shrinkage is given by:

\[ v_T \left( \frac{1 - \Delta \rho}{\rho_L} \right) = -v_T \frac{\beta}{1 - \beta} \]  

(Eq 3)

Note that shrinkage-driven flow is in the direction opposite to the isotherm velocity, that is, in the direction of decreasing temperature toward regions of higher solid fraction. Only if the alloy expands upon solidification, \( \beta < 0 \), and \( u_{\text{shrink}} \) has the same sign as \( v_T \).

Figure 3 illustrates the meaning of some of the quantities appearing in the previous equations. Since the liquid solute concentration is uniform along isotherms, liquid flowing in or out of the volume element in the direction of the isotherms has the same solute concentration as the liquid inside of the volume element. Therefore, liquid flow parallel to the isotherms in the mushy zone does not induce macrosegregation.

Defining a flow factor, \( \xi \), as:

\[ \xi = (1 - \beta) \left( 1 - \frac{v_T}{v_L} \right) \]  

(Eq 4)

Equation 1 can be integrated to yield a modified Scheil equation:

\[ \frac{C_L}{C_0} = (1 - f_s)^{(k-1)/k} \]  

(Eq 5)

where \( k \) and \( \xi \) are assumed to be constant. No macrosegregation occurs if the flow factor is equal to unity and the standard Scheil equation is recovered. There are two obvious cases for which \( \xi = 1 \): (no macrosegregation):

- No shrinkage (\( \beta = 0 \)) and no liquid flow normal to the isotherms (\( u_n = 0 \))
- No liquid flow other than the one required to feed the solidification shrinkage in one dimension: \( u_n = -v_T \beta (1 - \beta) \) or \( u_n = u_{\text{shrink}} \)

For \( \xi \neq 1 \), macrosegregation occurs, since the liquid concentration, \( C_L \), varies differently from that predicted by the standard Scheil equation. Based on Eq 5, three different macrosegregation mechanisms and outcomes can be identified (assuming, for the purpose of this discussion, that \( k < 1 \)):

1. Negative macrosegregation: \( \xi > 1 \) or \( u_n/v_T < -\beta (1 - \beta) \), or equivalently, \( u_n < u_{\text{shrink}} \).
   The solid fraction, \( C_L \), is lower than for \( \xi = 1 \), indicating that negative macrosegregation will result. For the case of \( \beta \geq 0 \), this condition is met if the liquid flows in the direction of decreasing temperature toward regions of higher solid fraction (\( u_n < 0 \)) and with a speed (absolute value of velocity) that is greater than \( |u_{\text{shrink}}| \).

2. Positive macrosegregation: \( 0 < \xi < 1 \) or \( u_n/v_T > -\beta (1 - \beta) \), or equivalently, \( u_n > u_{\text{shrink}} \).
   At the same solid fraction, \( C_L \) is higher than for \( \xi = 1 \), indicating that positive macrosegregation will result. For the limiting case of \( \beta = 0 \), this condition is met if the liquid flows in the direction of increasing temperature toward regions of lower solid fraction (\( u_n > 0 \)) but with a velocity that is lower than the isotherm velocity (\( u_n < v_T \)). For \( \beta > 0 \), this condition can be met even if the liquid flows in the direction of decreasing temperature toward regions of higher solid fraction (\( u_n < 0 \)), since \( u_{\text{shrink}} \) is negative.

3. Remelting: \( \xi < 0 \) or \( u_n > v_T \).
   This condition is met if the liquid flows in the direction of increasing temperature toward regions of lower solid fraction and with a velocity that is higher than the isotherm velocity. Based on Eq 1, such flow results in the solid fraction decreasing, rather than increasing, with decreasing temperature. This means that remelting occurs and that open (solid-free) channels can form inside the mushy zone. Once the casting is solidified, the macrosegregation inside of these channels is positive.

The direction and magnitude of the liquid flow velocities in the mushy zone depend on numerous factors. For a given driving force, the permeability of the mush is the single most important parameter that limits the flow (Ref 4). In general, the permeability decreases with increasing solid fraction. A smaller dendrite arm spacing also reduces the permeability. The following examples illustrate in more detail the aforementioned macrosegregation mechanisms.

**Inverse Segregation.** Near a chill face, the positive macrosegregation shown in Fig. 4 is often observed (Ref 5). This so-called inverse segregation (Ref 6) is a consequence of the second macrosegregation mechanism discussed previously. At an impenetrable chill face, the liquid velocity vanishes (\( u_n = 0 \)). Furthermore, for a finite shrinkage, \( u_{\text{shrink}} \) is negative. Therefore, the condition \( u_n > u_{\text{shrink}} \) is always satisfied at the chill face, and positive macrosegregation results. If a gap is present between the mold and the casting, the solute-rich interdendritic liquid can be pushed into the gap by metallostatic pressure. This is termed exudation and results in even higher positive macrosegregation at the surface. In direct chill casting of aluminum ingots, this macrosegregation can be so severe that the exuded surface layer must later be removed by scalping the ingot.

**Macrosegregation due to Nonuniform Shrinkage Flow.** The first macrosegregation mechanism listed previously has been demonstrated for the casting geometry shown in Fig. 5 (Ref 5). The casting is chilled from the bottom, such that the isotherm velocity is generally in an upward direction. The downward liquid flow is caused solely by shrinkage. However, due to the reduction in the cross section of
the casting near midheight, the liquid must flow at a higher downward velocity in this region. Hence, the condition \( u_n < u_s \) \_\text{shrink} is satisfied in this region (since both velocities are negative), and the negative macrosegregation seen in Fig. 5 and 6 forms (Ref 5).

**Macrosegregation due to Buoyancy-Driven Flow.** The first and second macrosegregation mechanisms can be observed simultaneously if the liquid flow pattern in the mushy zone is of a recirculating nature. This has been demonstrated for the horizontally solidified aluminum-copper casting shown in Fig. 7 (Ref 5). Here, a counterclockwise recirculating flow pattern is induced in the liquid by thermal and solutal buoyancy forces. Shrinkage-induced flow is negligibly small in this case. Figure 7 shows that the flow in the bulk liquid region penetrates into the mushy zone. In the upper part of the mushy zone, the flow is in the direction of decreasing temperature \( (u_n < 0) \). According to the first macrosegregation mechanism, such flow causes negative macrosegregation. Negative macrosegregation was indeed measured in the upper part of the casting, as shown in Fig. 8. Conversely, in the lower part of the mushy zone, the interdendritic liquid flows in the direction of increasing temperature \( (u_n > 0) \), back into the bulk liquid region. This causes positive macrosegregation according to the second mechanism. This was again verified by the measurements (Fig. 8). Note that there is no macrosegregation at the midheight of the casting, because there the liquid flow is primarily parallel to the isotherms.

Buoyancy-driven flow is also responsible for the positive macrosegregation seen in the riser of large steel castings and ingots, as shown in Fig. 9. In steel casting, the interdendritic liquid is often lighter than the bulk liquid and flows up. This up-flow is in the direction of increasing temperature \( (u_n > 0) \), since the riser is the last part of the casting to solidify. Consequently, positive macrosegregation results according to the second mechanism.

**Channel Segregation.** The third macrosegregation mechanism leads to the formation of so-called channel segregates. One such channel segregation defect is commonly referred to as freckles, an example of which is shown in Fig. 10. Freckles sometimes occur in upward, directional solidification of single-crystal nickel-base superalloy castings. During solidification of nickel-base 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, upward solutal buoyancy forces in the mushy zone. Despite the presence of a stabilizing thermal gradient, these buoyancy forces can trigger convection cells. As the upward liquid flows...
velocities in the mush exceed the isotherm velocity \((u_n > v_T)\), the solid fraction decreases with decreasing temperature, according to the third macrosegregation mechanism. Eventually, this leads to open channels in the mush through which solute-rich liquid streams upward into the bulk liquid region. The numerical simulation results shown in Fig. 11 illustrate these flow patterns (Ref 7). The rodlike channels are no larger than a few millimeters in diameter and have a spacing of, at most, a few centimeters. Later, the channels are filled with dendrite fragments, which are then observed as frecklelike chains of equiaxed crystals in the otherwise single-crystal columnar structure (Fig. 10). The resulting positive macrosegregation in the channels can also be seen in Fig. 11. Channel segregates are also observed in large steel ingots. Here, they are termed A-segregates and occur in the columnar zone of the ingot (Fig. 9). Strong buoyancy forces can cause the liquid to flow upward in the mush with a velocity normal to the isotherms that is greater than the isotherm velocity \((u_n > v_T)\), resulting in remelting. The channels are usually inclined toward the center of the ingot and thus appear as the A-shape illustrated in Fig. 9.

Macrosegregation Induced by Movement of the Solid

The movement or flow of solid during solidification can also induce macrosegregation in castings. Unfortunately, no simple theory, such as the LSRE discussed in the previous section, exists to explain the macrosegregation patterns resulting from solid movement (Ref 8). Therefore, only a few examples are provided to illustrate some of the complex phenomena that have been observed.

The most common form of solid movement is the settling or floating up of small solid pieces formed early in the solidification process. These solid pieces may be dendrite fragments that separated from an existing solid structure or equiaxed grains that nucleated in the bulk liquid. They settle or float depending on their density relative to the liquid. The solid pieces generally have a composition different from the nominal alloy composition, and their movement to different parts of the casting thus induces macrosegregation. One example is provided by the cone of negative macrosegregation that is often observed in the bottom third of steel ingots, as illustrated in Fig. 9. This macrosegregation pattern is confined to the equiaxed zone and is caused by the settling of dendrites that are relatively poor in solute (Ref 9, 10). Buoyancy-driven flow of the liquid also induces negative macrosegregation in the bottom half of steel ingots, but the degree is not as severe as that due to settling of solid (Ref 11). Similarly, negative centerline macrosegregation in direct chill casting of aluminum ingots is sometimes attributed to the settling of unattached solute-poor solid, although shrinkage-driven flow has been found to have a similar effect (Ref 12). On the other hand, the floating of spheroidal graphite (kish) can cause strong positive macrosegregation in the upper part of iron castings.

Another example of solid-movement-induced macrosegregation is given by the V-segregates in the equiaxed region of tall steel ingots. This macrosegregation pattern is also illustrated in Fig. 9 and consists of rodlike solute-rich streaks that appear periodically along the centerline. The V-segregates arise from equiaxed crystals settling in the core and forming a loosely connected network that can easily rupture due 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 (Ref 9, 10).

Macrosegregation can also be induced by deformations of the fully and partially solid regions during casting. One important example is centerline segregation in continuously cast steel slabs (Ref 10). Close to the bottom of the liquid pool, inadequate roll containment can cause the already solidified steel shell to bulge. The bulging draws solute-rich liquid into the center of the slab, where it freezes. This results in a rather sharp and thin line of positive macrosegregation along the center of the slab, as can be seen from the sulfur print in Fig. 12.

Deformation of the solid can also be induced by thermal stresses. This is a particularly common phenomenon in shape casting, due to the restraint that the mold and/or the cores can offer. However, deformation of the solid can also
occur in continuous casting due to uneven cooling. The stresses are able to propagate into the high solid-fraction portion of the mushy zone, where the solid network is already coherent. If the solid network is under compression, interdendritic liquid will be forced to "drain" out of the mush. Conversely, if this part of the mush is in tension, liquid is drawn into it. In either case, complex macrosegregation patterns can result. Under sufficiently severe tension, the solid network will rupture, and the fissure may fill with solute-rich liquid. The resulting cracklike positive macrosegregation in a casting is often referred to as a healed hot tear. If the flow of the interdendritic liquid is insufficient to feed the fissure, an open hot tear will be present in the casting.

Figures 4 to 9 are Fig. 8 to 12 and 7, respectively, in I. Ohnaka, Microsegregation and Macrosegregation, Casting, Vol. 15, Metals Handbook, ASM International, 1988, p136–141

REFERENCES