2.5 Crystallization of the LTF during final stage of eutectic solidification of grey iron

In the final stage of eutectic solidification, eutectic cells grow gradually into large sizes; the liquid iron between the cells enters the last stage of solidification. At this time, the region of the remaining liquid iron is called last to freeze volume, LTF in short, as shown in Fig.2-39. It is difficult to quantitatively and strictly define the boundary of the LTF, since crystallization conditions (composition, cooling rate and the melt state etc.) in the LTF is obviously different to other regions, leading to difference in solidification structure which influences subsequent solid phase transformation. Because the LTF situates in the boundaries of eutectic cells, the structure, purity, inclusions and density or compactness in the LTF exert important effects on the mechanical properties of cast iron.

Fig. 2-39: The LTF during the final stage of eutectic solidification

2.5.1 Crystallisation characteristics of the LTF

(a) Heat dissipation and solidification conditions

The volume fraction of the LTF is very small, and the LTF are surrounded by solidified metal, as solidification in a hot metal mould. In addition, the graphite projecting into the LTF has good thermal conductivity, can transfer heat out the regions; thereby the liquid iron in the LTF has relatively fast solidification velocity.

(b) Strong segregation in liquid composition

The element concentrations in the LTF are very different from that of mother iron liquid; the carbide formation elements such as Cr, Mn, V and Mo etc. are enriched; while graphitization elements, Si, Cu, Ni and Al are significantly depleted.

(c) More inclusions and complicated melt state

The final liquid to solidify often has more non-metallic inclusions and low melting point metals, which influence the solidification of the LTF. When the LTF is large, it is prone to forming micro shrinkage porosity.

All the cast irons have such characteristics.

2.5.2 Crystallization of the LTF

According to the chemical composition, nucleation state and cooling condition (section thickness), the solidification of the LTF has following several situations:

(a) Eutectic cells continue to grow

The graphite flakes in eutectic cells continue to project to and branches in the LTF; at the same time, following graphite, austenite continues to epitaxially grow, forming zigzag shape and interpenetrating with neighbour eutectic cells, see Fig. 2-40. Hereafter,
the LTF gradually becomes smaller and smaller, until all the liquid is depleted, no any other structure forms.

(b) Graphite precipitation

If the volume fraction of the LTF is larger and there exist graphite nuclei in the region, new graphite nuclei are possible to form and grow in carbon atom rich area. The graphite presents independently in the LTF, see Fig. 2-41; while the formed austenite is connected with the austenite in eutectic cells and difficult to be distinguished.

(c) Austenite epitaxial growth

When the carbon is depleted or reduced to a lower value, due to lack of condition for graphite nucleation and growth, graphite stops growing; but austenite continues to grow and extend to remaining liquid until all the liquid is finished. At this time, the eutectic cell boundary is wider, clear and easy to be distinguished, as illustrated in Fig.2-42.

(d) Carbide precipitation

The positive segregation elements (such as Cr, V and Ti) enriched in LTF reduce the temperature interval between $T_{EG} - T_{EM}$ (see Fig.1-21). When the content of those elements is high, it is prone to forming intergranular carbides. At this time, thick section thickness seems not to significantly reduce the tendency of carbide formation in the LTF, since the slow cooling of thick section will aggravate segregation. Thick section castings without Cr, V, Ti will not occur intergranular carbides, since under the slow cooling, the point $S$, the end of solidification, is above the $T_{EM}$ line.

When the cooling rate is increased, the solidification process is accelerated, the temperatures of the end of solidification, $T_{ES}$, is quickly decreased below $T_{EM}$, as illustrated in Fig. 1-17(d), thus promoting carbide formation.

For iron melt containing low carbon equivalent and high content of positive segregation elements, it is prone to forming eutectic carbides between eutectic cells, as shown in Fig. 2-43.

In grey iron containing high content of alloying elements, the carbides are also distributed, except in eutectic cell boundaries, in honeycomb structure inside eutectic cells, see Fig. 2-44; this is because there exists remaining iron liquid in the honeycomb structure, which solidifies in later stage. All this is resulted from the characteristics of eutectic cells of grey iron. Besides, carbides in grey cast iron are also situated between austenite dendrites, see Fig. 2-45. Therefore, the carbides in grey iron are more dispersed than that in spheroidal graphite iron.

If carbide formation elements are pushed to centre area of castings, a large amount of ledeburite is formed in the centre of castings (see Fig. 2-46). At this time, white solidification is formed inside the castings, called inverse chill.
Precipitation of phosphorus eutectics

The solubility of phosphorus in austenite is drastically decreased with increase of carbon. In high carbon cast iron, phosphorus almost does not dissolve in austenite. Therefore, during solidification, phosphorus does not enter solid all at, and all the phosphorus is kept in the final remaining liquid.

As solidification progresses, the phosphorus concentration becomes higher and higher, so that in the end, the phosphorus enriched liquid crystallizes as Fe₃P or phosphorus eutectics formed with Fe₃C.

There exist stable and meta-stable Fe–C–P system phase diagrams, see Fig. 2-47. If Fe₃C presented in the LTF, meta-stable ternary Fe–Fe₃C–Fe₃P is formed; If graphite is precipitated in the LTF, stable ternary Fe–G–Fe₃P is formed; If there are no conditions for the formation of graphite or Fe₃C in the LTF, the precipitated is binary phosphorus eutectic Fe–Fe₃P. In previous literatures, Fe–Fe₃C–Fe₃P was named ternary phosphorus eutectic, but Fe–G–Fe₃P was listed as binary phosphorus eutectic; the graphite in the phosphorus eutectic was listed into eutectic graphite. Actually, there should exist two types of ternary phosphorus eutectics: Fe–Fe₃C–Fe₃P and Fe–G–Fe₃P. When the solidification condition in the LTF is beneficial for the formation of both Fe₃C and Fe₃P, combined binary and ternary phosphorus eutectics are formed.

Phosphorus eutectics are often distributed in eutectic boundaries in network shape; when phosphorus is high, the phosphorus eutectics become continuous network, as illustrated in Fig. 2-48.

The relationship between melting point of P-rich liquid and P content can be obtained from Fig. 2-47. The lines CL₁UE₁ and CL₂UE₂ represent eutectic lines for meta stable and stable Fe–C–P systems respectively; L₁ and L₂ are ternary eutectic points (lowest temperature); the corresponding composition and temperature are:

<table>
<thead>
<tr>
<th>Eutectic point</th>
<th>Constituent</th>
<th>Composition</th>
<th>Eutectic temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>Fe–Fe₃C–Fe₃P</td>
<td>w(P)=6.75%, w(C)=1.9%</td>
<td>955°C</td>
</tr>
<tr>
<td>L₂</td>
<td>Fe–G–Fe₃P</td>
<td>w(P)=8%, w(C)=1.7%</td>
<td>977°C</td>
</tr>
</tbody>
</table>

As solidification progresses, the amount of liquid in the LTF is gradually reduced and the concentration of phosphorus is gradually increased; the solidification temperature of remaining liquid is reduced gradually following Fig. 2-49, after reaching L₁ (or L₂), it is raised again.
load, the tips will develop into crack initiations that cause the frames to fracture prematurely. The author observed the microstructures of thirty tensile samples and found that there occur zigzag shaped metal frames in most of the samples having low strength (30–50MPa). The metal network frames of eutectic cells in type D graphite cast iron are mainly meniscus frames (see Fig. 2-51); maybe, this is the reason that type D graphite cast iron has higher strength.

(b) Detrimental effect of precipitate phases

Precipitate phases, such as graphite, carbides, phosphorus eutectics and inclusions in the LTF all are brittle phases; their morphology and amount have direct influence on the strength and brittleness of the metal frames. The isolated particles (such as TiC, TiN) have less detrimental effect; but continuous network, angular or lathy precipitates (for example phosphorus eutectics and cementite) will cause significant detriment to properties. Figure 2-52 shows crack propagations along carbides.

(c) Effect on solid phase transformation

The positive segregation elements (Mn, Cr, Mo and V etc) enriched in the LTF increase austenite transformation undercooling and refine transformed structure (see Fig. 2-53), thereby increase properties of the material. However, if these elements are too much enriched in the LTF, thus leading to formation of carbides and phosphorus eutectics; at this time, the detriment effect will exceed positive effect.
2.6 Segregation in cast iron

Similar to other alloys, segregation in cast iron has macro segregation and micro segregation.

Macro segregation is a non-uniform distribution of chemical compositions in macro scale, which is caused by long range flow of liquid in casting and redistribution of solute elements in large area.

Micro segregation is called short range segregation; which is a phenomenon of chemical composition non-uniform in grain scale. According to their forms, segregation is divided into cellular, dendrite and inter-granular segregation. Micro segregation of solidification is the result of solute redistribution, depending on the diffusion process of micro area.

Micro segregation in cast iron is more obvious than macro segregation. The non-uniform distribution of elements during solidification often causes structural diversity, for example, the region with high silicon is prone to forming ferrite, Mn, Cr, Mo enriched regions prone to carbides, and phosphorus segregation regions prone to phosphorus eutectics etc. In addition, segregation also affects solid phase transformation during cooling or heat treatment, since segregation caused by non-uniform distribution of alloying elements will result in difference in stability and hardenability of austenite. Therefore, segregation in cast iron has always been paid attention.

2.6.1 Measurement of micro segregation

Micro segregation is caused by redistribution of solute elements in an alloy. For most of the alloys, distribution coefficients of solutes, \( K_s \), are all less than 1. For alloys with \( K_s < 1 \), solutes are rejected from grains, causing constitutional difference between inside and outside grains.

An important parameter measuring micro segregation is segregation coefficient \( K_s \), which is a ratio of centre solute concentration to edge concentration in dendrite (or eutectic cell). The value of \( K_s \) indicates the degree of difference in solute concentration inside and outside of a grain.

\[
K_s = \frac{\text{Solute concentration in the centre of dendrite (or eutectic cell)}}{\text{Solute concentration in the boundary of dendrite (or eutectic cell)}}
\]

Definition:

\( K_s = 1 \) no segregation

\( K_s < 1 \) positive segregation. Solute concentration in the boundary of dendrite (or eutectic cell) is higher than in the centre of dendrite (or eutectic cell)

\( K_s > 1 \) inverse segregation. Solute concentration in the boundary of dendrite (or eutectic cell) is lower than in the centre of dendrite (or eutectic cell)

Similarly, segregation ratio \( S/R \) can also be used to describe the segregation degree of solute elements:

\[
S/R = \frac{\text{Solute concentration in the boundary of dendrite (or eutectic cell)}}{\text{Solute concentration in the centre of dendrite (or eutectic cell)}}
\]

\( S/R > 1 \) positive segregation

\( S/R < 1 \) inverse segregation

The relation between the two equations:

\[
K_s = \frac{1}{S/R}
\]

The solute elements in above equations refer to common elements (Si, Mn, P, S), alloying elements (Cu, Ni, Mo, Cr, V, Ti, etc.) and other elements studied in cast iron, except Fe.

Table 2-6 lists the \( K_s \) for the elements in cast iron. Due to different measurement conditions, the data from different literatures have quite big difference. It is seen from Table 2-6, the graphitizing elements (Si, Ni, Cu, Co, Al) have \( K_s > 1 \) and belong to inverse segregation elements; carbide formation elements have \( K_s < 1 \) and belong to positive segregation elements. Sulphur and phosphorus do not belong to carbide formation elements, but present positive segregation.

![Fig. 2-53: Fine pearlite structure in the LTF](image)

**Table 2-6: Segregation coefficient of elements in cast iron, \( K_s \)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Primary austenite</th>
<th>Eutectic cell</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.10</td>
<td>2.50</td>
<td>[65] - [66]</td>
</tr>
<tr>
<td>Si</td>
<td>1.15</td>
<td>1.60</td>
<td>1.17</td>
</tr>
<tr>
<td>Cu</td>
<td>1.10</td>
<td>1.80</td>
<td>1.50</td>
</tr>
<tr>
<td>Ni</td>
<td>1.15</td>
<td>1.50</td>
<td>1.30</td>
</tr>
<tr>
<td>Co</td>
<td>1.14</td>
<td>1.40</td>
<td>1.20</td>
</tr>
<tr>
<td>Mn</td>
<td>0.75</td>
<td>0.63</td>
<td>0.75</td>
</tr>
<tr>
<td>Cr</td>
<td>0.85</td>
<td>0.84</td>
<td>0.60</td>
</tr>
<tr>
<td>W</td>
<td>0.95</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>0.87</td>
<td>0.24</td>
<td>0.40</td>
</tr>
<tr>
<td>V</td>
<td>0.97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>0.69</td>
<td>0.53</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>-</td>
<td>0.60</td>
</tr>
</tbody>
</table>

① The structures when measuring \( K_s \) was not indicated.

Electron probe analyses indicate that phosphorus has serious segregation and non-uniformity. In grey iron with \( w(P)=0.11\% \), phosphorus eutectics can reach 8.23% – 11.29%; the ratio of the P content in phosphorus eutectics to the P content in pearlite can reach as high as 51.4 – 70.6% [64].

2.6.2 Factors affecting segregation in cast iron

(a) Alloying factor

Different alloy elements have different segregation behaviours;
this is dependent on their following attributes:

- Shape of phase diagram: solute element (X) influences the shape of Fe–C–X phase diagram. When horizontal distance between solid and liquid lines is increased, the solute concentration difference between the centre and edge of austenite dendrite is increased, the segregation becomes severe.
- Effects of elements with carbon: graphitising elements (Si, Cu, Ni etc) in cast iron can increase activity of carbon and cause carbon to be rejected from austenite, but enrich themselves in austenite grains and present inverse segregation. While, carbide formation elements (Mn, Cr, V, Mo, etc.) can decrease thermodynamic activity of carbon, and are prone to combining with C rejected from austenite, but enrich themselves in the LTF and show positive segregation.
- Solid diffusion coefficient: solid diffusion coefficient of elements has significant influence on segregation degree. The diffusion coefficient of most elements (except C, N and O) in solid is very small; the diffusion velocity is far lower than the velocity of solidification interface, thereby is very difficult to reach constitutional equilibrium. The smaller the diffusion coefficient in solid, the stronger the segregation. Compared to solid diffusion coefficient, the liquid diffusion coefficient has smaller influence on micro segregation.
- Interactive effect: interactive effect between elements can change segregation tendency. If third constituent makes equilibrium distribution coefficient of a certain element $K_s$ become small (when $K_s<1$), the segregation of the element will become strong.

(b) Process factor

- Cooling rate: according to general solidification rule, as cooling rate increases, the segregation degree inside grains becomes severe, since under low temperature, diffusion of elements becomes more difficult. However, when cooling rate reaches rapid cooling rate ($10^3$–$10^4$K/s), segregation tendency is decreased greatly, even no segregation occurs. This is because, at this time, the temperature of dendrite tips quickly drops to solidus; solid-liquid interface is planar growth rather than dendrite growth, composition in solid becomes uniform. But for casting, the influence is different; the fast cooling thin wall iron castings have less segregation, while slow cooling iron castings (especially spheroidal graphite iron castings) have strong grain boundary segregation. In heavy section iron castings, the austenite boundaries, especially eutectic cell boundaries, have significant tendency of intergranular carbide formation. This is because positive elements have enough time to be repulsed to the LTF and combine with carbon there. For example, Ti is prone to forming titanium carbides, titanium nitrides and titanium carbon-nitrides. Under fast cooling condition of metal mould, it is found that TiC is mainly distributed in pearlite while TiN in ferrite. For slow cooling castings titanium compounds are mainly segregated to grain boundaries as granular particles.
- Liquid flow during solidification: liquid short range convection can improve the degree of solute mixing and thin the diffusion boundary layer at solid-liquid interface, which is beneficial for precipitation of uniform solid, thus reducing segregation.
- Structure factor: fineness of austenite dendrites (or eutectic cells) influences the degree of segregation; extremely fine grain makes the $K_s$ value of solute element close to 1 and reduces the degree of segregation.

2.6.3 Characteristics of micro segregation in grey iron

(a) Strong segregation tendency

Cast iron has relatively more solute elements, the interaction of elements increases segregation degree. Positive segregation elements such as Mn, Cr, V, W and Mo are repulsed to the LTF by solidifying solid and combined with carbon in the LTF, thus making micro segregation further severe. The content of common elements (such as Si, C, Mn, S, P) in steel is significantly lower than that in cast iron; thus their segregation tendency is much less than that in cast iron. For example, Cr in steel has $K_s=0.94$, while in cast iron $K_s=0.70^{(60)}$.

(b) Complicated distribution of solute elements

The large content of solute elements and variety of solidification structures in cast iron make solute element distribution very complicated. For example, although primary and eutectic austenite are all austenite, elements in the two have different segregation coefficient $K_s$. Within one eutectic cell, the solute element concentration is also very uneven. This can be seen from the colour difference in Fig. 2-54. In addition, the composition difference exists in transverse section of dendrite and longitudinal direction as well (see Fig. 2-55).

![Fig.2-54: Segregation within eutectic cell](image)

*small white grey area is the LTF having high positive segregation elements*

(c) Inverse segregation

For most engineering alloys, the segregation characteristics of alloying elements show positive segregation. Differently in cast iron, in addition to positive segregation, some elements present inverse segregation characteristics. The solute elements in cast iron are divided into two types: positive and inverse segregation elements:

- Positive segregation elements: Mn, Cr, V, Mo, W, P, S etc.
- Inverse segregation elements: Si, Al, Cu, Ni, Co.

It is not difficult to see that the segregation characteristics are closely related to their graphitizability and carbide formation tendency (except P and S). Positive segregation elements are
mainly carbide formation elements; while inverse segregation elements are strong graphitizing elements.

The inverse segregation behaviour of silicon and other graphitizing elements in cast iron is caused by higher carbon and silicon content. Low carbon steel is a Fe–C–Si ternary system alloy with lower carbon and silicon content; in the steels of the Fe–C and Fe–Si binary alloy systems, the distribution coefficients of solute element C and Si are $K_{0} < 1$. During solidification, according to the principle of solute redistribution, although C and Si are also distributed in liquid phase, the amount segregated to liquid is relatively small; the Si→C repulsion force is not enough to change the distribution characteristics in which solid is enriched in Fe, and liquid is enriched in carbon and silicon. However, for cast iron with higher C and Si, the silicon in Fe-C-Si system is redistributed in another way. At this time, the Si→C repulsion force is remarkably increased; silicon is replaced from carbon-enriched micro volume, repulsed from liquid by carbon and enters Fe phase preferentially. With growth of dendrites (eutectic cells), Si is continuously dissolved in austenite, and the amount of silicon in liquid is gradually decreased; the segregation of silicon is changed from previous positive to inverse, while the type or sign of micro segregation of carbon remains the same. In liquid, the reason why Si is repulsed by C, not C repulsed by Si is that the valence electrons on 3s3p orbit of Si atom are far from Si nucleus and are shielded with two electron orbits K and L; while for carbon atom, it only has one electron orbit (K) shielding. Therefore, when forming chemical bond with Fe, silicon is superior to carbon. The change of segregation direction of silicon in Fe–C–Si alloy is closely related to carbon content, see Table 2-7. When $w(C) > 0.35\%$, $K_{s} > 1$, the segregation of silicon is changed to inverse segregation. When silicon is increased, the critical carbon content is also increased.

![Fig. 2-55: Dendrite segregation](image1)

![Fig. 2-56: Ferrite caused by segregation of silicon in the centre of eutectic cell](image2)

Table 2-7: Relation of segregation coefficient $K_{s}$ of silicon with carbon content

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$w(C)$(%)</th>
<th>$K_{s}$</th>
<th>Type of alloy</th>
<th>$w(C)$(%)</th>
<th>$K_{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C15 steel</td>
<td>0.15</td>
<td>0.91</td>
<td>60MnSi2 steel</td>
<td>0.65</td>
<td>1.20</td>
</tr>
<tr>
<td>C35 steel</td>
<td>0.34</td>
<td>1.00</td>
<td>Malleable cast iron</td>
<td>2.60</td>
<td>1.51</td>
</tr>
<tr>
<td>C45 steel</td>
<td>0.48</td>
<td>1.10</td>
<td>Grey iron</td>
<td>3.15</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Once mass fraction of carbon is less than 0.35%, the segregation of silicon has nothing to do with its content, showing positive segregation. The inverse segregation of Cu, Ni, Co and Al is because the atom bonds of these elements forming with iron are far stronger than Fe-Fe bond when carbon exists; the thermodynamic potentials of solid solutions of Cu, Ni, Co and Al forming with Fe are more stable.  

2.6.4 Effect of segregation on structure and property of grey cast iron

At beginning of solidification, the inverse segregation of silicon...
makes the austenite dendrites rich in silicon; the austenite dendrites are prone to forming dendritic ferrite during subsequent cooling. During eutectic solidification, silicon is enriched in the centre of eutectic cells. In iron with higher silicon, ferrite often appears in eutectic centre (see Fig. 2-56), leading to decreased mechanical property. Manganese segregates positively to the boundaries of austenite dendrites (or eutectics), decreases transformation temperature of austenite in the regions, increases its stability and makes the austenite easy to form pearlite. Sulphur segregates to late solidified grain boundaries and forms FeS. When manganese is low, isolated FeS is observed. Phosphorus in cast iron is an element prone to segregation. When mass fraction of phosphorus is 0.05%, phosphorus is possible to form phosphorous eutectics in cast iron [20]. For most iron castings, since phosphorus eutectics are very hard, with hardness of 800–950HV, and brittle, the phosphorus content should be restricted. However for improving wear resistance, phosphorus is often added into cast iron. But when w(P)>0.2%, shrinkage porosity occurs because of solidification shrinkage when phosphorus enriched liquid cools to phosphorus eutectic temperature. When Ni, Cr and Mo elements coexist in cast iron, the combined positive segregations increase the amount and tendency of macro shrinkage porosity [71]. Some low melting point elements (Pb, Bi, Sn and Sb etc.) often segregate to boundaries of dendrites or eutectic cells, causing to form special structures during solidification. Trace lead of w(Pb) > 0.005% can cause network graphite to form round austenite dendrites [72]. Loper found through experiment that for thick section grey iron castings, if slow cooling through high temperature region, Wiedmannstaetten graphite can form [73].

Some low melting point elements (Pb, Bi, Sn and Sb etc.) often segregate to boundaries of dendrites or eutectic cells, causing to form special structures during solidification. Trace lead of w(Pb) > 0.005% can cause network graphite to form round austenite dendrites [72]. Loper found through experiment that for thick section grey iron castings, if slow cooling through high temperature region, Wiedmannstaetten graphite can form [73].

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[32] Ruff G F, Wallace J F. Effects of Solidification Structures on the


