Chapter 5

White Cast Iron (II)

5.5 Eutectic crystallisation of white iron

When undercooled below the eutectic line $ECF$ in the Fe-C phase diagram, liquid iron will start eutectic transformation (crystallization): eutectic liquid $\rightarrow$ cementite + austenite.

Eutectic crystallisation is an important stage during the crystallization of white iron. At this stage, the nucleation and growth of eutectic cells (consisting of carbide or cementite + austenite) occur. The carbide in eutectic cells (or eutectic carbide) is the main hard and brittle phase structure which has an important effect on the properties of white iron. If there is no primary carbide in the structure, the effect of eutectic carbide is more prominent.

5.5.1 Thermodynamics and kinetics of eutectic crystallisation

Whether a eutectic melt follows the meta-stable system to crystallise as carbide + austenite, or follows the stable system to crystallise as graphite + austenite eutectic, is dependent on the nucleation and growth of the two high carbon phases (carbide and graphite), namely, on thermodynamic and kinetic conditions. Figure 5-23 shows the comparison of thermodynamic driving forces of the two eutectics. The two lines in the lower section of the figure represent the free energy of the two eutectics respectively and $G_L$ is the free energy of the undercooled iron melt. It is easy to see that the iron melt has the highest free energy and the graphite-austenite has the lowest free energy; so, following a stable system, the thermodynamic condition favours the crystallisation of graphite-austenite eutectic from the iron melt.

However, compared to forming graphite, forming carbide needs much less carbon atom diffusion; thus, when the cooling rate is fast, forming carbide – austenite has faster growth velocity and the kinetic conditions favour a meta-stable system of crystallisation. Figure 5-24 shows the relationship between growth velocity and temperature for the two eutectics [12]. When an iron melt is undercooled between 1,148–1,153°C, only graphite can nucleate and grow; if rapidly undercooled below 1,148°C, both (Fe$_3$C + austenite) eutectic and (graphite + austenite) eutectic are possible

$G_L$—Free energy of undercooled liquid iron, $G_{cm}$—Free energy of cementite, $G_r$—Free energy of austenite, $G_{gr}$—Free energy of graphite

Fig. 5-23: Comparison of free energy of formation of the two eutectics

Fig. 5-24: Relationship between (graphite + austenite) eutectic, $(\text{Fe}_3\text{C} + \text{austenite})$ eutectic and temperature [12]
to nucleate, but the growth velocity of (Fe₃C + austenite) eutectic exceeds that of (graphite + austenite) eutectic, which causes the iron melt to crystallise totally as white iron. It is known from this that a rapid cooling rate (or undercooling) is an important factor in determining whether crystallisation follows a meta-stable system or not.

Addition of carbide-forming elements will increase the tendency of an iron melt to form (Fe₃C + austenite) eutectic and promote chill formation from thermodynamics and kinetics. Therefore, the alloyed irons containing medium or high contents of Cr, Mn, V, W and Nb all solidify as white irons, even under slow cooling conditions.

5.5.2 Eutectic growth of normal white iron

The eutectic crystallisation of a white iron is a crystallisation process in which cementite + austenite eutectic (eutectic cells) form the main structure. According to the principle of eutectic crystallisation, the formation of a second phase on the leading phase and their restricted cooperative growth is the key to eutectic cell formation.

Based on the morphology of cementite and austenite in eutectic, Richard divided the eutectic structure of normal white iron into two types [19]: honeycomb ledeburite and plate cementite.

(1) Honeycomb eutectic (often called ledeburite)

Honeycomb ledeburite consists of eutectic cells in which many austenite rods, along [001], are embedded into cementite plates (or blocks) based on (001) plane. The eutectic cells show a lamellar or plate shape; their length and width are far greater than their thickness. Therefore, under microscope, only the transverse sections of the austenite rods are observed; after etching, they show as dark round spots on a white substrate (cementite). The two-dimensional image of honeycomb ledeburite is illustrated in Fig. 5-25.

The formation process of ledeburite is shown in Fig. 5-26 [20]:

(a) At the beginning of the eutectic, cementite nucleates first as the leading phase. For a hypoeutectic white iron, the nucleus substrates of eutectic cementite are very small and difficult to find [5]. For a hypereutectic white iron, the debris or fragments of primary cementite or their extent sections are good nuclei for eutectic cementite. The Fe₃C embryos have obvious anisotropy, thus Fe₃C plates grow easily along the heat flow direction [21], and the base planes grow quickly into a flat, plate-shape. Because of the orientation relationships, which exist between certain crystal planes of cementite and austenite [22]: (104)₆C//(101)γ and (010)₆C//(310)γ, austenite is in close contact with plate-like Fe₃C and is easy to grow following a plate crystal growth mode, thus forming the earliest plate structure.

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(b) Due to non-uniform adsorption, constitutional undercooling and carbon enrichment of the liquid iron between lamellar austenite plates, the $\text{Fe}_3\text{C}$ crystals situated in this region become unstable\textsuperscript{[20]}. This provides an opportunity for austenite dendrites to change their growth direction from previous $\alpha$-axis to $\epsilon$-axis and to grow laterally.

(c) The flat plates of austenite dendrites also branch and grow laterally, perpendicular to the $\alpha$-axis. They extend into the gaps between laterally branched cementite plates, because the carbon content there is lower. Thus, laterally branched austenite and laterally grown cementite grow together co-operatively.

At the beginning, laterally growing austenite branches according to the plate mode, then gradually grows in a rod-shaped form. Bunin\textsuperscript{[5]} considered that the transmission mechanism from plate-brancing to rod is related to accumulated impurities in front of the eutectic; the formed undercooling also promotes further growth of the protruding section on austenite. According to research by Park\textsuperscript{[23]}, laterally growing austenite which shows a rod-shape is the result of the effect of silicon. Si promotes dendrites to branch and offers more interdendritic grooves. When the silicon content exceeds 1%, austenite changes from plate-branching to rod shape.

The mass content of silicon in normal white irons usually exceeds 1%, therefore eutectic structures are mainly honeycomb ledeburite. The edge growth of $\text{Fe}_3\text{C}$ and austenite and the lateral growth of austenite rods perpendicular to $\text{Fe}_3\text{C}$, form the eutectic with pseudo-regular structure\textsuperscript{[22]}. Since the edge growth is faster than the lateral one, the shape of ledeburite eutectic cells is different from that of graphite-austenite eutectic cells in grey iron (or in VG iron); it is not spherical, but a plate-like shaped structure with length and width both larger than thickness. Only under the conditions of very severe undercooling (for example, a cooling rate of $10^4$–$10^5$K/s) can the iron form spherical ledeburite eutectic cells\textsuperscript{[5]}. The degree of branching of the two phases in ledeburite becomes serious with increasing cooling rate, see Fig. 5-27. Among them, the increased austenite branches result in the formation of many densely distributed small austenite rods; while the increase of the leading phase, cementite reduces the size of eutectic cells. Treatment with ferro-boron can refine primary austenite dendrites; this increases branching of the eutectic austenite, therefore, decreases the diameter of honeycomb cells (the transverse section of austenite rods), and also increases the eutectic cell count.

If primary austenite is well developed and the interdendritic interval is very narrow, the eutectic liquid in the interdendritic region is prone to crystallise in the form of a divorced eutectic. At this time, eutectic cementite precipitates as thin plate-shapes, see Fig. 5-28. Therefore, a honeycomb eutectic structure cannot be seen in the interdendritic region.

(2) Plate-like cementite eutectic

Rickard et al\textsuperscript{[19]} first observed plate-like cementite eutectic in hypoeutectic white iron with low silicon ($\omega(\text{Si}) = 0.1\%$). The features of this eutectic are: cementite, as thick plates, alternatively distributed in the intervals of primary dendrites, and eutectic austenite often grows on primary austenite, thus it is difficult to distinguish from each other; the austenite and cementite look like a divorced eutectic structure. Different from honeycomb ledeburite, this eutectic has no rod-like branch on the side and cementite grows mainly along the $\alpha$-axis. However, the $\alpha$-axis growth velocity is significantly decreased and a lateral growth thickening of the plate occurs. The comparison of the two eutectic structures is illustrated in Fig. 5-29.
Although the exact reasons for the formation of plate-like cementite are not yet totally clear, it was recognized that their formation is related to melt undercooling and composition. Rickard found that for a low carbon equivalent iron melt with additions of Te and Sb, under superheating condition, that this type of eutectic structure could be obtained. The silicon content has an important effect on the growth of the two phases of the eutectic; lower silicon can reduce the tendency of lateral rod-like branching of cementite. Phosphorous causes austenite and cementite to transform in a divorced eutectic mode and makes cementite grow to network-like blocks. Phosphorous has very low solubility in solid iron and is easily enriched in the growth front of cementite, thus retarding the diffusion velocity of Fe and C atoms towards cementite, and decreasing the growth velocity of cementite. In addition, the surface activity of phosphorous reduces the interface tension between cementite and liquid, retards co-operative growth of eutectic austenite and cementite, thus benefiting the crystallisation of plate-like cementite eutectic. When the mass percent of Mn reaches 5%, it was found that the amount of honeycomb ledeburite decreases and plate-like cementite increases.

Research on the influence of various types of eutectic on the mechanical properties of white iron have shown the following: because the austenite in plate-like cementite eutectic is connected and the cementite has a non-continuous, isolated distribution, a white iron with plate-like cementite eutectic has better strength than a white iron with honeycomb cementite eutectic. Nevertheless, a white iron with honeycomb cementite has better feeding properties than an iron with plate-like cementite, thus it is not prone to produce shrinkage-induced crack/tear defects.

5.5.3 Solidification and eutectic crystallisation of high Cr white iron

(1) Solidification analysis of Fe-Cr-C alloy system

(a) Liquidus surface projection and solidification structure: Fe-Cr-C phase diagram is a tool to analyse the solidification process of high Cr system white iron. Using thermal analysis, Jackson obtained the liquidus points of Fe-Cr-C system alloys with various compositions and drew a liquidus surface projection, see Fig. 5-30. The diagram is composed of 5 faces: ferrite, austenite, \((\text{Cr}, \text{Fe})_2\text{C}_6\), \((\text{Cr}, \text{Fe})_7\text{C}_3\), and \((\text{Cr}, \text{Fe})_3\text{C}\) type carbides. Point B is the intersect of three liquid phases, but not the lowest temperature point; along the BC groove down to Fe-C eutectic point, that is the lowest point of the alloy. Under equilibrium conditions, according to C and Cr content, the types of primary phases can be determined:

- For medium to high C and high Cr, the primary phase is \(K_2\), \((\text{Cr}, \text{Fe})_7\text{C}_3\),carbide;
- For low C and low Cr, the primary phase is \(\alpha\) or \(\gamma\);
- For low C and high Cr, the primary phase is \(\alpha\);
- For high C and low Cr, the primary phase is \(K_2\), that is \((\text{Cr}, \text{Fe})_3\text{C}\), carbide;
- For medium C and medium Cr, the primary phase is \(\gamma\);
- For medium C and high Cr, the primary phase is \(K_2\), \((\text{Cr}, \text{Fe})_3\text{C}\),carbide.

![Fig. 5-29: Comparison of honeycomb eutectic and plate-like cementite eutectic](image)

![Fig. 5-30: Liquidus surface projection of Fe-Cr-C alloy](image)
temperature in the two diagrams is 3°C, but the difference of C and Cr content is larger; at \( w(C) \) the temperature difference is 1°C. C and Cr contents also have certain differences.

According to the position of line \( w(C) \) (eutectic composition) in Fig. 5-31, the relationship of Cr and C contents to the locations of hypoeutectic, eutectic and hypereutectic regions is illustrated in Fig. 5-32. Different from binary Fe-C alloy, for ternary Fe-C-Cr system, the carbon saturation is not only dependent on C, but also on Cr.

![Fig. 5-31: Comparison of the two meta-stable Fe-Cr-C system liquidus surfaces](image)

**Table 5-8: Comparison of parameters in the liquidus surfaces of two meta-stable Fe-Cr-C systems**

<table>
<thead>
<tr>
<th>Critical point</th>
<th>Reaction</th>
<th>Literature</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_1 )</td>
<td>( L + \alpha\delta\text{-Fe} = \gamma\text{-Fe} + M_7C_3 )</td>
<td>[27]</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1,292</td>
</tr>
<tr>
<td>( u_2 )</td>
<td>( L + M_7C_3 = \gamma\text{-Fe} + M_2C )</td>
<td>[28]</td>
<td>1,289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[27]</td>
<td>1,184</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[28]</td>
<td>1,183</td>
</tr>
</tbody>
</table>

The higher the C and Cr, the higher the C saturation degree. The solidification structure of hypoeutectic high Cr white iron (the lower left in Fig. 5-32) is austenite dendrites + eutectic structure. The farther away from eutectic line, the more the primary austenite dendrites and the less the eutectic structure are remained between austenite dendrites. The eutectic structure of high Cr eutectic white iron consists of \( (M_7C_3 + \text{austenite}) \) eutectic cells, in which the carbides display a two-dimensional rose flower pattern. In this microstructure, neither austenite, nor carbide is the predominant structure. The structure in hypereutectic high Cr white iron consists of primary \( M_7C_3 \) (rod-like) + eutectic structure. The solidification structures of hypoeutectic, eutectic and hypereutectic high Cr irons are illustrated in Fig. 5-33.

(b) Influence of C, Cr, Si, Ni and Mo on solidification behaviours: The differential thermal analysis (DTA) curve of an alloy can reflect the precipitation of phases during solidification. Figure 5-34 shows a DTA curve of a Fe-Cr-C alloy.

When \( w(C) \leq 3.18\% \), the primary \( \gamma \)-dendrites precipitate first; while, for a high Cr white iron of \( w(C) > 3.5\% \), the primary phase \( M_7C_3 \) precipitates first. If Cr content is reduced to 7%, a third exothermal peak (C point) on the DTA curve will appear for the iron with high C content, see Fig. 5-34(b); a reaction similar to peritectoid reaction occurs during solidification. The C and Cr contents have important influence on the solidification behaviours of high Cr white iron; the influence of C content on liquid phase temperature \( (T_L) \), eutectic starting temperature \( (T_{EN}) \) and solidification ending temperature of eutectic \( (T_{ES}) \) is shown in Fig. 5-35. With increasing carbon content, \( T_L \), \( T_{ES} \) and \( T_{EN} \) decrease; for a constant carbon content, the higher the Cr, the higher the \( T_{ES} \) and \( T_{EN} \), but \( T_L \) does not change much.

Si, Ni and Mo all decrease \( T_L \), \( T_{ES} \) and \( T_{EN} \); among them, Si has the strongest influence on these critical temperatures. It seems that Ni has no effect on \( T_L \) and \( T_{ES} \). Based on the DTA measurements, it is obtained following equations of \( T_L \), \( T_{EN} \) and \( T_{ES} \) with C, Cr, Si, Ni and Mo:

\[
T_L = 1594.5 - w(C)92.6\% - w(Cr)0.54\% - w(Ni)1.53\% - w(Mo)3.4\%
\]

\[
T_{EN} = 1225.8 - w(C)22.2\% + w(Cr)6.1\% - w(Si)15.3\% - w(Ni)1.35\% - w(Mo)4.1\%
\]

\[
T_{ES} = 1203.5 - w(C)28.8\% + w(Cr)6.3\% - w(Si)10.4\% - w(Ni)1.4\% - w(Mo)17.6\%
\]

According to recent research results \[29\], the effect of Mo on \( T_L \) is larger than those above equations; when the mass fraction of Mo is increased from 0% to 2.3%, \( T_L \) is decreased from 1,246.8°C to 1,231.3°C.

(2) Precipitation of eutectic carbides

The contents of C and Cr have important effect on the amount of eutectic carbides; the influential relationship is shown in Fig. 5-36. For constant C and Cr, with increasing the content of Si and Mo, the amount of eutectic carbides is increased slightly. Ni content
has no influence on the eutectic carbide amount.

Depending on the contents of C, Cr and other alloying elements, the carbides in eutectic structure of high Cr iron can be M₇C₃, M₃C, or duplex M₇C₃ + M₃C, even multiple phase carbides M₇C₃ + M₃C + M₂C, as illustrated in Fig. 5-37. The type, morphology and amount of eutectic carbides have important effect on the wear resistance and mechanical properties, especially the toughness.

The types of eutectic carbides are classified by the amount of C and Cr. When w(Cr) = 7%, w(C) > 2% or w(Cr) = 10%, w(C) > 3%, eutectic carbides are type M₇C₃ and type M₃C; for the alloy with w(Cr) = 10%, 15%, 20% and w(C) < 3% (commercial alloy composition), all the eutectic carbides are M₇C₃ type; when the alloy has w(Mo) ≥ 1%, there exists Mo₂C eutectic.

Fig. 5-33: Solidification structure of hypoeutectic, eutectic and hypereutectic high Cr irons

(b) Eutectic

(c) Hypereutectic

Fig. 5-34: DTA curves of Fe-Cr-C alloys

Fig. 5-35: Influence of C and Cr contents on temperatures during solidification process of Cr white iron
Eutectic M₇C₃ and primary M₇C₃ have different growth behaviour. Under undercooling condition, eutectic M₇C₃ has twin defects and is easy to branch and quickly grows to curve-shaped plate. When undercooling is higher, M₇C₃ grows to fine rod fibers with irregular arrangement and the cross section shows small blocks of multi-grain structure [30,31]; each rod is not independent but grows along [1011] direction connecting one another/each other. Figure 5-38 shows the thermal analysis curves of hypoeutectic and hypereutectic high Cr irons. It is seen from the curves in Fig. 5-38 that for hypereutectic high Cr iron, the recalescence for forming eutectic M₇C₃ is far more significant than that for forming primary M₇C₃, indicating that eutectic M₇C₃ has faster growth rate than primary M₇C₃.

Note: the figure in the table is mass %

Fig. 5-36: Effect of C and Cr on the volume fraction of eutectic carbides [29]

Fig. 5-37: Types of eutectic carbides in high Cr white iron [30]

1 - Hypoeutectic, 2 - Hypereutectic

Fig. 5-38: Thermal analysis curves of hypoeutectic and hypereutectic high Cr irons [30]

The shape of eutectic carbides is closely related to chemical composition; according to different compositions, following shaped carbides can be formed: rod, plate, coral or spheroid.

(a) Carbon saturation: For a high Cr iron with eutectic or near to eutectic composition, the eutectic M₇C₃ is rod shaped and has finest size [32,33]. The carbides in hypereutectic high Cr iron are mainly flake plate shape and grow surrounding primary carbides. The eutectic carbides in hypoeutectic high Cr iron exist in the regions between primary austenite dendrites and solidify last; the formed carbides distributed discontinuously and almost all are flake plate shape. Laird considered [33] that the two morphology carbides can exist in the white irons with three carbon saturations; the only difference is the ratio of the two types of carbides. The experiments by Durman confirmed that with increasing carbon from w(C) = 0.78% to w(C) = 3.40%, at beginning, eutectic carbides distribute between austenite grain boundaries as thin film; then following by forming a discontinuous network, and developed to a continuous network surrounding dendrites. In the end a eutectic cell forms with carbides growing radially from the nucleus; at this time, eutectic carbides show rod shape with hexagonal cross section [34].

(b) Chromium: No matter for hypoeutectic, eutectic or hypereutectic high Cr iron, when w(Cr) = 10%, the two types carbides, M₃C and M₇C₃ are observed and they are flake plate and rod like. And, the faster the cooling rate, the more the M₃C. When the mass fraction of Cr exceeds 10%, all the carbides become M₇C. When w(Cr) > 20%, the amount of plate flake eutectic carbides are gradually decreased; when Cr is increased to w(Cr) = 30% and w(Cr) = 40%, the carbides almost show rod like with blocky grain cross section. The influence of Cr content on the non-uniformity of eutectic carbide particles is shown in Fig. 5-39. It is seen that the white iron with w(Cr) = 30% has the most uniform and finest eutectic carbide particles.

Fig. 5-39: Influence of Cr content on non-uniformity of eutectic carbides [35]
(c) Vanadium: V can refine primary austenite and separate the liquid between dendrites into finer spaces, thus narrow the spaces where carbides grow. In addition, the C-N compounds of vanadium may become nuclei, thus accelerate the refinement of vanadium on carbides.

(d) Nickel: Nickel can dissolve into austenite without limit, coarsen primary austenite, supply spaces for carbides crystallisation, and thus make them coarser.

(e) Molybdenum: In high Cr iron when \( w(Mo) > 1\% \), it is easy to form \( \text{Mo}_2\text{C} \), which comprises eutectic \( (\gamma + \text{Mo}_2\text{C}) \) with austenite, and exists in between the coarse chromium carbides. Figure 5-40 shows that for a white iron with \( w(Mo) = 4.74\% \), there exists a recalescence around 1,150\( ^\circ \text{C} \), which shows that eutectic \( (\gamma + \text{Mo}_2\text{C}) \) forms. When \( w(Mo) = 0.96\% \), no new phase forms\(^{15}\).

(3) Formation of eutectic grains (cells)

In high Cr iron, following primary phase (austenite or carbide) precipitates, a ternary equilibrium transformation happens:

\[
L \rightarrow \gamma-\text{Fe} + \text{M}_7\text{C}_3
\]

The products of transformation are eutectic grains consisting of eutectic austenite \( (\gamma-\text{Fe}) \) and eutectic carbide, that is, eutectic cells. The forming mechanism of eutectic cells in high Cr white iron can be described as follows\(^{9,35,36}\):

The eutectic cells in hypo-eutectic high Cr iron are precipitated in the gaps of austenite dendrites, and their morphology is illustrated in Fig. 5-41. In the centre region of each eutectic cell there are fine carbide fibers with fine grain shaped cross section; the fibers extend from the centre radially as curved flake plates (cross section shows long string/strip shape). When extending to the edge of eutectic cells, the released latent heat is increased, leading to coarse carbides. Within the eutectic cell, eutectic austenite is full between the intervals of carbides. The morphology is similar to that of type B graphite eutectic cell in grey iron; however, the \( \text{M}_7\text{C}_3 \) carbide in the eutectic cell grows slow radially but fast longitudinally along \([0001]\) direction in hexagonal crystal system, forming bunch/sheaf of plates or rods of carbides\(^{37}\). In the end, the long rod or long plate type of carbides together with eutectic austenite form columnar shaped eutectic cells with spherical crown which are non-uniformly mounted/inlaid/distributed in the pre-eutectic austenite matrix. The structure pattern of the eutectic cells is illustrated in Fig. 5-42.

The eutectic cells in eutectic, high-Cr white iron are formed randomly. This is because under equilibrium conditions, there are no pre-precipitated austenite dendrites to act as a substrate for eutectic cell precipitation. However, the structure and morphology of eutectic cells (see Fig. 5-43) are similar to that of hypo-eutectic high-Cr white iron.
The outline of the eutectic cell in hypereutectic high-Cr white iron is similar to that of eutectic and hypoeutectic high-Cr white irons; the difference is that in the centre of the eutectic cells, hexagonal shaped, primary carbide is often observed, see Fig. 5-44. Eutectic $M_7C_3$ grows around primary carbides and there exists a certain connection between them. However, in some sections, eutectic carbide has no relationship with primary $M_7C_3$.[9]

The growth relationship between primary and eutectic carbides in the eutectic cells, in the high-Cr white iron is different from that in the normal white iron. In the eutectic cells in the normal white iron, cementite ($Fe_3C$) is the leading phase, so $Fe_3C$ grows continuously and is interconnected within the eutectic cell. For the high-Cr white iron, it is considered that austenite precipitates first and then $M_7C_3$ is formed in the space between austenite dendrites, where C and Cr are enriched. Since austenite precipitates before carbide, an austenite bridge is easily formed at the tip of carbides, which results in eutectic carbides showing a discontinuous distribution. Powell confirmed[30] that under certain undercooling condition, eutectic $M_7C_3$ easily forms twins, which cause carbide crystals to have angled grooves (cracks); this promotes eutectic carbides to branch in a fibrous manner and accelerates austenite nucleation. Powell also proposed that under the premise of twins existing, eutectic $M_7C_3$, as a facet phase, can act as nuclei for eutectic growth ($M_7C_3$–austenite).

The size of eutectic cells directly reflects the fineness of eutectic carbides and influences the size of carbide grains in the boundary area of eutectic cells. When the diameter of eutectic cells increases, the released latent heat of crystallisation is increased; resulting in coarsening of carbides in the boundary area and this influences toughness and wear resistance of a high-Cr white iron. The main parameters (see Fig. 5-45) of describing eutectic cell characteristics include: the diameter of eutectic cells, the spacing distance of the boundary areas where eutectic carbides exist and the spacing distance of the area where carbides occupy the centre of a eutectic cell. Factors influencing the diameter of eutectic cells include solidification velocity, Cr content, other alloying elements and the modification agent; among these, Cr content has the closest relationship with the diameter[33]. The lower the Cr content, the larger the diameter of eutectic cells and conversely, with increasing Cr content, the diameter of eutectic cells becomes smaller. When $w(Cr) = 30\%$, the diameter of eutectic cells is the smallest and the eutectic structure is the finest. When $w(Cr) > 30\%$, the eutectic cell size becomes coarser again, as illustrated in Fig. 5-46. It can be seen from Fig. 5-46 that with increasing solidification velocity, the effect of Cr content on the diameter of eutectic cells is gradually weakened.

The influencing rule of Cr content on eutectic cell size corresponds to its influence on the eutectic solidification interval[36]. Figure 5-47 shows the measured solidification interval for $w(Cr) = 6\%–50\%$; when $w(Cr) = 15\%$, the solidification interval is the largest, i.e. 65°C, while $w(Cr) = 30\%$, the solidification interval is the smallest at only 21°C. For an alloy with a large eutectic solidification interval, the growth time is long and thus the final size of eutectic cells is large. For the same reason, eutectic
solidification interval influences B-B, but has no effect on C-C. This is because the central area of eutectic cells precipitates at the earliest stage and thus has no relationship with the eutectic solidification interval.

Molybdenum increases the diameter of eutectic cells. Tenorio found from experiments [29] that for an iron of \( w(Cr) = 15\% \), when the mass fraction of Mo increases from 0 to 2.3\%, the diameter of eutectic cells increases from 38 μm to 46 μm.

5.5.4 Eutectic crystallisation of a W system white iron

Regardless of whether it is a hypoeutectic or a hypereutectic iron, in a W system white iron, for most cases, when entering a eutectic reaction, \( M_6C \) is precipitated first because eutectic liquid contains more W atoms, thus creating better kinetic conditions for \( M_6C \) to form. In addition, below the eutectic temperature the free energy of formation for \( M_6C \) is far below that of austenite, which causes \( M_6C \) to be more stable. If primary \( M_6C \) exists, it is easier to nucleate \( M_6C \) again using \( M_6C \) as the substrate. After precipitation of \( M_6C \), the liquid in front of the solidification interface is depleted in W and C, but enriched in Fe, which creates conditions for austenite precipitation. Due to crystal lattice correspondence, austenite is easy to nucleate on the (111) face of \( M_6C \), which accelerates \( M_6C \) branching and growth along the <100> direction. When eutectic crystallises, austenite and \( M_6C \) show an alternative and co-operative growth mode, but still maintain the crystal characteristics of \( M_6C \) type carbide structure and grow to a fishbone-like eutectic; the growth relationship is shown in Fig 5-48.

For a hypoeutectic W system white iron, with lower W/C, \( M_3C \) type carbides appear in the divorced form in the eutectic structure and are distributed between the austenite dendrites, thus showing a net-work style. If W/C > 6, \( M_6C \) type carbide is formed, which exists as austenite + \( M_6C + M_{23}C_6 \) ternary eutectic and grows in a divorced manner.
In W-Cr system white irons with different Cr content, two types of ternary eutectic can exist:\[38]\; for a W system white iron of \(w(Cr) < 7\%\), the ternary eutectic is austenite + M\(_{3}C\) + M\(_{6}C\); when \(w(Cr) > 7\%\), M\(_{6}C\) is formed and the ternary eutectic becomes austenite + M\(_{3}C\)+ M\(_{6}C\).

### 5.5.5 Modification of the eutectic structure of white iron

For improving the toughness and service life of white iron, in addition to heat treatment to change the matrix structure and morphology of carbides, the alternative method is to control the solidification process, to modify the eutectic structure.

The measures to improve eutectic structure include:

- Refine eutectic cells
- Disconnect eutectic carbides
- Change the morphology of carbides (Plate→rod→spherical shape)

The purpose of refining eutectic cells is to refine eutectic carbides and thus improve the service performance of white iron. For an as-cast white iron for making malleable iron, refining the eutectic cells is to shorten the graphitisation annealing time because fine eutectic carbides significantly increase the interfaces between carbides and austenite and thus accelerate the decomposition process of cementite. The measures of refining eutectic cells is to increase the nuclei number of eutectic cells; therefore, increasing the cooling rate during solidification, adjusting chemical composition, changing the nucleus status and adding heterogeneous nuclei (inoculation) are effective measures of refining eutectic cells.

Breaking the continuity of eutectic carbides is an important measure to improve the toughness of white iron. In normal white iron, the cementite in ledeburite eutectic cells is connected each other and formed net-work between primary austenite dendrites, seriously reducing the toughness of the white iron.

Changing carbide morphology in the white iron is an effective measure to improve the toughness and strength because like the coarse flake graphite in a grey iron, the plate carbides are very brittle and have no strength; serious stress concentration occurs on the tip of carbide plates, and crack is easy to propagate quickly along the sharp tip.

The process measures for improving the eutectic structure of white iron are:

(a) Adjust chemical composition

Increasing certain alloying elements by a large amount can change the carbide type, leading to a change in morphology. For a Cr system white iron, the carbide type has a close relationship with Cr content. When \(w(Cr) \geq 10\%\) and \(w(Cr)/w(C) > 4\), eutectic carbides change from plate-like Fe(Cr),C to rod-like Cr\(_{6}C\).

In a low Cr white iron, vanadium can change the morphology of carbides. When \(w(V) = 4\%\), carbides are disconnected significantly; when \(w(V)=6\%\), spherical carbides begin to form and when \(w(V)=8\%\), most of the carbides are spherical in shape\[39-41]\.

Tungsten has a similar effect on carbides as chromium and can change the morphology and distribution of carbides. When \(w(W) < 6\%\), the carbides are M\(_{6}C\) type, but maintain a net-work or disconnected net-work. When \(w(W) = 13\%–15\%\), the carbides show a disconnected and isolated distribution, and are mainly M\(_{6}C\) type\[42,1\]; when \(w(W)\) is around 20\%, the carbides are M\(_{3}C\) type and show compacted and isolated blocks (rhombus, polygon, rod, etc.)\[13,14]\.

In normal white iron, the eutectic structure is ledeburite with a honeycomb structure. When \(w(Si)<0.5\%\) and pronounced undercooling occurs, the honeycomb carbide network becomes gradually disconnected\[21\]. However, the effect of silicon on the structure of high chromium white iron is the opposite; appropriately increased silicon can increase the degree of disconnection and significantly improve fracture toughness. This is because when the mass fraction of silicon increases from 0.4% to 1.4%, the crystallisation orientation of eutectic carbide is changed and a scattered structure occurs, thus disconnecting the network.

Practical experience has confirmed that for white iron of \(w(Cr) = 11\%–13.5\%\), when \(w(Si)\) is increased to within the range 1.0%–2.2%, the impact fatigue spalling resistance and impact abrasive wear resistance are better than that of high Cr white iron of \(w(Cr) = 15\%\[44,45]\.

The morphology of carbides in a low-alloyed white iron is influenced by carbon content; controlling the carbon content to a low level of \(w(C) = 2.2\%–2.6\%\) is beneficial for carbide spheroïdisation after treatment by a compound rare-earth modifier\[46]\.

(b) Increase cooling rate

With increased cooling rate, eutectic cells become smaller and carbides are refined; for example, extremely fine rod-like M\(_{6}C\) can be obtained when using a metal mould for casting or at the surface of a weld deposit\[39\]. However, solidification rate cannot change the carbide types, thus it is difficult to change the morphology of the carbides.

(c) Inoculation

According to the type of alloy and application, the purposes of inoculation of white iron include improving toughness and wear resistance, and decreasing annealing temperature and/or shortening the annealing time for malleable iron.

Unlike the inoculation of grey iron, in white iron, carbide refinement is achieved by refinement of primary austenite and making the inter-dendritic area smaller. The inoculant elements used for white iron are V, Ti, B, RE and Al. Among these, the formed inclusions of rare earth with S and O in the liquid iron can act as substrates for primary austenite nucleation, resulting in increased nuclei and refined austenite dendrites. Ti and C form excellent heterogeneous nuclei for austenite, increasing the nucleation rate of austenite. Both V and B carbides are favourable for austenite nucleation.

(d) Modification

This is a treatment, achieved by the addition of a small amount of substance into a liquid iron, to modify the morphology of carbides.

Similar to grey iron, the eutectic crystallisation in white iron also belongs to non-facet-facet (metallic-non-metallic) eutectic. The high carbon phases in the two irons have a similar growth mode: graphite and cementite both have a lamellar structure, and have
strong anisotropy and preferred growth orientation. In addition, during the growth of eutectics, both graphite and cementite are in front of austenite, thus leading the progress of eutectic. Therefore, some of the modification mechanisms and processes used for grey iron can be useful for white iron. For example, the mechanism, in which Mg and rare earth Ce increase undercooling of grey iron and change graphite from flake to spheroidal, also exists in white iron; a rare earth containing modifier can also change the morphology of $M_C$ carbides. Because, for white iron, rare earth metals are also surface active elements which are enriched in the liquid in front of a solidification interface, and these increase undercooling and enhance austenite growth velocity. When the leading phase changes to austenite, it is possible for austenite to bridge at the tip of carbides; the austenite dendrites connect with each other, disconnect the carbide and change carbide from plate to plate strip or rod shaped. Besides, preferred absorption of rare elements on carbide crystals inhibits the growth of $M_C$ crystal along the $a$-direction.

However, in an $M_C$ crystal, atoms are combined by a strong Fe-C covalent bond within each atom layer, but connected by a weak Fe-Fe metallic bond between layers; the anisotropy of interatomic bonds in carbide is far stronger than that in graphite. This results in the growth velocity in $a$-direction being much faster than that in the $c$-direction, meaning that the above rare-earth elements cannot play their modification role easily. This is the reason why the modification of normal white iron cannot be as successful as in grey iron. Nevertheless, changing carbide morphology through modification to improve strength and toughness is very significant and research work on this aspect has been persistently performed by many scholars [47-53].

The eutectic carbides in high Cr white iron show a disconnected, curved-plate shape (or fine fibrous rod shape under high undercooling) and toughness is significantly improved compared with the continuous plate $M_C$ in normal white iron. However, for $M_C$, because of the inherent preferred growth characteristics along the [0001] orientation, it is difficult to change the crystal morphology characteristics in which the length is larger than radial size, thus its toughness is still low. For this reason, the spheroidisation of $M_C$ carbide has been focused on by researchers. Rare earth metals have a certain inhibiting effect on the growth of $M_C$ [49]. For example, the addition of a small amount of Al and rare earth element(s) can make carbides in white iron with $w(\text{Cr}) = 4\%$, become isolated, and when $w(\text{Al}) > 8\%$, carbides can become fully spheroidised [49]. The treatment of high Cr white iron using a modifier containing K and Na, can change the form of $M_C$, occur preferentially between primary austenite dendrites; it is possible for ledeburite eutectic cells to nucleate at different locations and after these eutectic cells grow, $LTF$ regions exist between primary austenite dendrites, as illustrated in Fig. 5-49. The observations by the author also confirm this, see Fig. 5-50.

5.6 Crystallisation of liquid in the $LTF$ regions during the last stage of eutectic solidification of white iron

During the last stage of eutectic crystallisation of white iron, the eutectic regions grow gradually and contact each other; in the end, the remaining liquid in the $LTF$ (last to freeze) regions, between eutectic cells, solidifies.

5.6.1 Crystallisation of $LTF$ regions in normal white iron

The eutectic cells (ledeburite) in normal white iron show a long, plate-like, block shape and intersect primary austenite dendrites randomly, thus resulting in a difficulty of identifying the outline and location of $LTF$ regions. In addition, the austenite in ledeburite is prone to connect with austenite in the $LTF$ regions, making it more difficult to identify these regions. Wolf etc. considered [50] that not all nucleus locations of the leading phase in ledeburite, $(\text{Fe}_3\text{C})$, occur preferentially between primary austenite dendrites; it is possible for ledeburite eutectic cells to nucleate at different locations and after these eutectic cells grow, $LTF$ regions exist between primary austenite dendrites, as illustrated in Fig. 5-49. The observations by the author also confirm this, see Fig. 5-50.

Because the distribution law of elements in $LTF$ regions in a white iron is different from that in a grey iron, carbide-forming elements are not enriched in the $LTF$ regions, thus the remaining liquid does not necessarily have a tendency to form carbides.

5.6.2 Crystallisation of $LTF$ regions in high-alloyed white iron

Although the eutectic cells in a high-alloyed white iron do not present a spheroidal shape, they show their own specific morphology; the eutectic cells in high Cr-Mo system white iron show a morphology of a cylinder with a spherical crown, while the eutectic cells in high-W system white iron show a fishbone-like shape, therefore it is possible to identify the location of $LTF$ regions from their special morphology.

Different from grey iron, the alloying elements in high-alloyed white iron, such as Cr, Mn, Mo, W and V, are not first concentrated in $LTF$ regions, but exist in various primary or eutectic carbides. Nevertheless, when forming low melting point
5.7 Segregation of white iron

During the crystallisation of white iron, the non-uniform distribution of elements in various crystallisation phases (that is, micro segregation) has a stronger influence on structure formation, phase transformation and properties after solidification, than for a grey iron. This is because most white irons (except white iron used for making malleable iron) have various, high content, alloying elements and the distribution characteristics of these elements can cause the irons to have complicated structure changes.

5.7.1 Distribution of elements in low-alloyed white iron

The ratio of mass fraction of alloying element M in carbide to that in austenite is referred to as the distribution coefficient of element M: $S^C/\gamma[M]$ where $W^C[M]$ — mass fraction of M in carbide (%) and $W^{\gamma}[M]$ — mass fraction of M in austenite (%).

Similar to the definition $K_s$ in grey iron, the ratio of M mass fraction of an element in the centre of a phase to that at the edge of a phase is named as segregation coefficient $K_s$.

According to their distribution characteristics in carbides and austenite, alloying elements can be divided into two types: elements which increase carbon activity and elements which are prone to form carbides.

The elements that enhance carbon activity, such as Si, Al, Cu, Ni and Co (known as negative segregation elements in grey iron) have the same distribution within the structure of white iron as in grey iron and are concentrated mainly in austenite. These elements first dissolve in primary austenite and then distribute in eutectic austenite. Thus, their content in primary austenite is the highest and that in eutectic austenite is lower, but the content in austenite is always higher than the average in the iron. However, the segregation behaviour of these elements (except Al) in austenite is different from that presented in grey iron during solidification, showing positive segregation characteristics, i.e. lower in the centre and higher at the edge of austenite. Because Si content at the edge is higher than that in the centre of primary austenite, this causes ferrite to form first at the edge of a dendrite during annealing of white iron for making malleable iron, see Fig. 5-51.

eutectics, these alloying elements may remain in LTF regions and precipitate last. For example, for high-Cr white iron with Mo, (when $w(\text{Mo}) \geq 2\%$), low melting point, lamellar eutectics consisting of $\text{Mo}_2\text{C}$ and austenite, ($\text{Mo}_2\text{C} + \gamma$), solidify last in the LTF regions.

Fig. 5-50: Microstructure of the LTF regions in normal white iron

Fig. 5-51: Influence of the positive segregation of Si in austenite in white iron during the annealing process (blue ferrite, brown austenite)
The content of elements Si, Al, Cu, Ni and Co in cementite is lower than the average value in the iron; among these, Si and Al are almost insoluble in cementite. Except for Al, the other four elements Si, Cu, Ni and Co are positive segregation elements in cementite.

The elements that increase carbon activity have a low content in cementite, but are enriched in austenite, thus the distribution coefficient of Si, Al, Cu, Ni and Co is \( S^{\text{Fe}}_{\gamma}[M] < 1 \). Among these \( S^{\text{Fe}}_{\gamma}[\text{Si}] \) is the smallest and \( S^{\text{Fe}}_{\gamma}[\text{Co}] \) is the largest.

The elements that have a higher affinity with carbon than with iron, such as Mn, Cr, W, Mo and V, are distributed mainly in cementite, and have a lower relative content dissolved in austenite. Thus \( S^{\text{Fe}}_{\gamma}[M] > 1 \). Bunin found that Cr and V have a negative segregation in the cementite of ledeburite eutectic cells and the austenite matrix, so their content is higher in the centre but lower at the edge\(^1\); while W, Mo and Mn show positive segregation in both primary cementite and eutectic cementite. Table 5-9 lists the distribution of elements in white iron eutectic cells.

### Table 5-9: Distribution of elements in austenite and cementite in white iron eutectic cells \(^2\) (mass%)

<table>
<thead>
<tr>
<th>Element</th>
<th>In iron</th>
<th>In austenite of ledeburite</th>
<th>In cementite of ledeburite</th>
<th>Dist. coeff. ( S^{\text{Fe}}_{\gamma}[M] )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In centre</td>
<td>In edge</td>
<td>In centre</td>
</tr>
<tr>
<td>Al</td>
<td>0.62</td>
<td>1.09</td>
<td>0.96</td>
<td>1.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.70</td>
<td>1.06</td>
<td>1.20</td>
<td>0.87</td>
</tr>
<tr>
<td>Cu</td>
<td>0.86</td>
<td>1.26</td>
<td>1.41</td>
<td>0.89</td>
</tr>
<tr>
<td>Ni</td>
<td>0.94</td>
<td>1.31</td>
<td>1.46</td>
<td>0.90</td>
</tr>
<tr>
<td>Co</td>
<td>0.93</td>
<td>1.09</td>
<td>1.16</td>
<td>0.94</td>
</tr>
<tr>
<td>Mn</td>
<td>1.06</td>
<td>0.77</td>
<td>0.94</td>
<td>0.82</td>
</tr>
<tr>
<td>Cr</td>
<td>0.94</td>
<td>0.46</td>
<td>0.30</td>
<td>1.50</td>
</tr>
<tr>
<td>W</td>
<td>0.89</td>
<td>0.38</td>
<td>1.03</td>
<td>0.37</td>
</tr>
<tr>
<td>Mo</td>
<td>0.99</td>
<td>0.36</td>
<td>1.26</td>
<td>0.28</td>
</tr>
<tr>
<td>V</td>
<td>0.82</td>
<td>0.35</td>
<td>0.30</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Note: 1: The carbon saturation is nearly 1; 2: Cooling rate of the samples is 0.5℃/s, water quenched after solidified.

#### 5.7.2 Distribution of elements in high Cr white iron

In addition to large amounts of Cr, elements such as Mo, Ni, V and W often exist in high Cr white iron. Their distribution rules are different for different elements.

**Chromium:** In high Cr white iron, Cr is enriched mainly in carbide, partially dissolved in austenite, and only a very small amount of Cr occurs in other carbides and inclusions. The distribution feature of Cr affects the stability of austenite and at the same time influences the type and amount of carbides. Figure 5-52 shows the variation of Cr in different phases\(^3\); with an increase in Cr content, the Cr content in primary austenite, eutectic austenite and eutectic carbide, increases correspondingly. Cr is concentrated mainly in the carbide phases, accounting for 40%–70% (mass) of total Cr; the amount dissolved in austenite in only 10%–20% (mass), therefore the distribution coefficient \( S^{\text{Fe}}_{\gamma}[\text{Cr}] = 4–5 \). Also, the Cr content is higher in primary austenite than in eutectic austenite. For a constant Cr content, with increase in carbon, the amount of carbide is increased, but the Cr content in eutectic carbides is decreased significantly and the Cr content in eutectic austenite is decreased slightly, see Fig. 5-53.

**Vanadium:** V is enriched in Cr-eutectic carbides and only partially dissolved in austenite, \( S^{\text{Fe}}_{\gamma}[\text{V}] = 10 \).

**Nickel:** Ni is dissolved in austenite without limit, so with an increase in Ni content, the amount dissolved in austenite is also increased. Ni does not exist in carbide, thus \( S^{\text{Fe}}_{\gamma}[\text{Ni}] = 0 \).

Molybdenum: Mo segregates to the edge of eutectic cells, increases the Mo content in LTF regions and significantly decreases the solidification temperature of the metal in LTF regions. Thus, carbide size around the edge of eutectic cells becomes coarse\(^4\). Mo is distributed in austenite, carbides and high Mo phases. Among these, Mo content is the highest in high-Mo phases, next in carbides and least in austenite, \( S^{\text{Fe}}_{\gamma}[\text{Mo}] = 1–2 \).

Tungsten: Similar to Mo, W exists in the above three phases respectively. However, the W content in austenite and carbide is low, and is mainly enriched in the high-W phase (M₆C).

The content of other alloying elements in high-Cr white iron is low and therefore these have less effect on the distribution of Cr. The data of distribution examples of V, Ni, Mo and W in high-Cr white iron are listed in Table 5-10\(^5\); these distributions have a certain influence on the microstructure and properties of high-Cr white iron.

### Reference


Table 5-10: Distribution of V, Ni, Mo and W in different phases in high-Cr iron (mass %)

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Primary austenite</th>
<th>Eutectic austenite</th>
<th>Eutectic carbide</th>
<th>High Mo phase</th>
<th>High W phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.48</td>
<td>0.36</td>
<td>0.27</td>
<td>2.83</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>0.94</td>
<td>0.45</td>
<td>0.38</td>
<td>5.26</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1.52</td>
<td>0.70</td>
<td>0.72</td>
<td>7.72</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1.99</td>
<td>1.02</td>
<td>0.91</td>
<td>9.40</td>
<td>—</td>
</tr>
<tr>
<td>Ni</td>
<td>1.06</td>
<td>1.05</td>
<td>0.96</td>
<td>0.00</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1.51</td>
<td>1.60</td>
<td>1.56</td>
<td>0.00</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2.02</td>
<td>2.11</td>
<td>1.98</td>
<td>0.00</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2.49</td>
<td>2.86</td>
<td>2.66</td>
<td>0.00</td>
<td>—</td>
</tr>
<tr>
<td>Mo</td>
<td>0.92</td>
<td>1.12</td>
<td>3.12</td>
<td>3.44</td>
<td>55.5</td>
</tr>
<tr>
<td></td>
<td>1.83</td>
<td>2.40</td>
<td>3.86</td>
<td>6.33</td>
<td>61.5</td>
</tr>
<tr>
<td></td>
<td>2.93</td>
<td>3.31</td>
<td></td>
<td>6.35</td>
<td>79.0</td>
</tr>
<tr>
<td>W</td>
<td>4.01</td>
<td>5.29</td>
<td>5.00</td>
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<td>2.34</td>
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<td>4.42</td>
<td>2.73</td>
<td>3.63</td>
<td>4.86</td>
<td>55.6</td>
</tr>
</tbody>
</table>

Note: Other composition of the sample (mass %) C = 2.0%, Si = 1.0% – 1.2%, Mn = 0.7%, Cr = 16%

[13] Wang Yuzhu, Luo Huasheng, Ge Fengde. Study on carbides and


