Colour Metallography of Cast Iron

By Zhou Jiyang, Professor, Dalian University of Technology, China
Translated by Ph.D Liu Jincheng, Fellow of Institute of Cast Metal Engineers, UK

*Note: This book consists of five sections: Chapter 1 Introduction, Chapter 2 Grey Iron, Chapter 3 Ductile Iron, Chapter 4 Vermicular Cast Iron, and Chapter 5 White Cast Iron. CHINA FOUNDRY publishes this book in several parts serially, starting from the first issue of 2009.

Chapter 1

Introduction

1.5 Colour metallography technique of cast iron

Colour metallography possesses better differentiation ability and is more sensitive to segregation, grain orientation and stress state than black-white metallography. It adds functions to traditional metallography and displays wide application perspectives.

Colour metallography technique belongs interference film metallography. By using chemical or physical methods, a thin interference film can be formed on the surface of alloy metallographic specimen; with the aid of extinction effect in thin film interference, the microstructures are displayed with different colours. Colour metallography methods producing interference film include polarized light, chemical deposition, constant potential, vacuum coating, ion sputtering and heat tinting. Among them, chemical deposition (also called etching method) is simple, convenient, therefore obtains wide application.

The colour metallography technique used in this book is a hot alkaline etching display method, belonging category of chemical deposition interference film. In this method, metallographic sample is put into hot sodium hydrate solution and heated. When solution reaches a certain temperature, hold the sample for certain time at the temperature, take out, clean and dry it; microstructures with different colours can be observed under microscope. In the early time, this method was used in alloy steel, white iron to colour carbide and phosphide, and in the study of segregation within grain in grey iron. From the middle of 1980s, the author and other researchers have continuously improved and perfected this hot alkaline etching method and gradually developed this method into a method for studying the solidification structure and phase transformation of cast iron.

1.5.1 Principle of hot alkaline etching method

Using chemical method to deposit a thin film onto a metal surface, an optical interference effect occurs through the film. This is the fundamentals of optics for hot alkaline method displaying colour.

Optical phase has important effect on destructive interference effect; the phase condition of destructive effect is influenced by inherent optical parameter of metal structure, and more importantly is determined by thickness of a film. Different film thickness produces different destructive effect. For example, under white lighting, if a certain film thickness of metal structure is just destructive with blue light wavelength (440 µm), thus, reflected light consists of mixed lights without blue light. At this time the reflected light is not a white light, but displays another wavelength colour. Under the same principle, different film thicknesses are produced on the same structure with un-uniformed composition caused by segregation; thus different locations of the same phase can display different colours.

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Hot alkaline etching method can cause cast iron to produce different thickness films on the sample surface with different local composition and structure. When the metallographic sample is merged into alkaline solution, SiO$_2$ formed by Si in cast iron will react with NaOH following:

$$2\text{NaOH} + \text{SiO}_2 = \text{Na}_2\text{SiO}_3\cdot\text{H}_2\text{O} \quad \text{(colloid)}$$

The picronitric acid in alkaline solution, C$_6$H$_4$(NO$_2$)OH,
simultaneously reacts with NaOH:

\[ C_6H_2(NO_2)_3OH + NaOH = C_6H_2(NO_2)_3ONa + H_2O \]

Sodium metasilicate \( Na_2SiO_3\cdotH_2O \), as colloid, is absorbed and deposited onto the surface of sample and formed a thin film. For silicon rich region containing more \( SiO_2 \), the film forms quicker and thicker; for silicon poor region, the formed film is thinner. In the end, films with different thickness are formed. Except for \( Si \), segregation of other elements also accelerates the forming of different thick films.

1.5.2 Characteristics of colour metallography with hot alkaline etching

Based on author’s many years of practical experiences, colour metallography using hot alkaline etching technique in studying solidification of cast iron has following advantages:

(1) Can display solidification development process

The solidification development process displayed by colour metallography with hot alkaline etching method is achieved with etching austenite. The negative segregation of \( Si \) in austenite is displayed by etching austenite. \( Si \) is an element enriching in austenite. According to the phase diagram, the early crystallized austenite forms at high temperature containing lower carbon content; high temperature is beneficial for enhancing diffusion rate of \( Si \); while low carbon can decrease the repulsion force of \( Si \rightarrow C \), thus, is favorable for \( Fe \rightarrow Si \) forming strong chemical bond, causing \( Si \) atoms easily to migrate towards the inside of austenite grain. Therefore, the earlier the austenite forms, the higher the \( Si \) content; the later the austenite forms, the lower the \( Si \) content. Beside, the \( Si \) content of austenite has a direct relation with colours. At constant etching condition, \( Si \) directly influences the film thickness, thus displays different colours. The relations between \( Si \) content and qualitative or semi-quantitative measurement by colours for some actually examples are shown in Fig. 4.37 and Table 4.3 (in Chapter 4). By connecting and relating the time austenite starting to solidify, \( Si \) content and the displayed colours, Table 1.3 is obtained. Since etching process and colour photo developing conditions are different, the obtained general colour tones of metallographic photos are different (see Fig. 1.25), but the colour variation sequence is the same with the variation of \( Si \) content. Some time, certain colour is not obviously displayed; after a longer time etching or using solution with higher alkalinity, all the colours in Table 1.3 can be observed. If etching time is short, the colours presented in Table 1.3 will not start from serial number 1. The shorter the etching time, the lower

![Fig. 1.25: Relation between Si content of solidified structure and colour under different colour tones.](image-url)

<table>
<thead>
<tr>
<th>Number</th>
<th>Colour</th>
<th>Silicon content</th>
<th>Time to solidify</th>
<th>Etching time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yellow</td>
<td>high</td>
<td>early</td>
<td>long</td>
</tr>
<tr>
<td>2</td>
<td>Blue green</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Purple</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Orange red</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pale yellow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pale blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Brown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Cream white or pale yellow</td>
<td>low</td>
<td>late</td>
<td>short</td>
</tr>
</tbody>
</table>
the produced colour sequence moves to. Thus, as long as control the etching time in alkaline solution, gradually etch and show the colour, operate in steps, the colour variation can be observed at a particularly selected position. With increasing etching time, colour changes following sequential number 9→1. Then, check the colour in Table 1-3 and find the colour which is the same or close to it to determine the solidification time at that position and to compare with solidification progress of other positions. In addition, using this technique, it can also study solidification according to colours, rather the fixed position. The region having the same colour will start to solidify at the same time: the closer to the region shown by the serial number 1, the earlier the time starting to solidify. Therefore, the solidification information on nucleation, growth and relations between solidification structures can be obtained from the types, distribution and shape characteristics of colours.

(2) Can display solidification structure existing at high temperature and transformation phases at room temperature simultaneously

Using hot alkaline etching, except for colouring solidification structure, room temperature structure of cast iron can also be displayed.

According to electrochemical etching principle \[35\], whether the structures in iron and steel materials are etched or not, depend on their polarity, that is, the height of stable potential in solution. The phase having low potential becomes anode (positive) and is etched; the phase having high potential becomes cathode (negative) and is protected. Under effect of acid reagent, the room temperature structures in iron and steel, such as ferrite, martensite, austenite solid solution all have lower stable potential and are etched as anode. While, stable potential of carbides and nitrides is relatively high and, as cathode (negative) they are protected. However, when iron and steel specimens are put into alkaline solution, these phases’ electrochemical behaviours are changed. Originally, carbides, nitrides and phosphides are cathode (negative) phase in acid solution; but in caustic alkaline solution, their potential is even lower than that of matrix phase. Thus, they become anode (positive) and are preferentially etched. While solid solutions, such as ferrite, martensite and austenite etc, become negative phase in alkaline solution. According to anode deposition mechanism of interference film, there are no interference films deposited on these cathode (positive) region, thus these structures are not easy to be coloured in normal alkaline solution.

In addition to caustic alkali, a certain amount of picronitric acid is added in hot alkali solution. Picronitric acid is a kind of weak acid which can increase concentration of \(H^+\) in the solution, change the stable potential of anode and electrochemical polarisation, causing cathode, which originally cannot be coloured, to be coloured. Experiments \[36\] have confirmed that if the reagent is well prepared and etching time and temperature is properly controlled, these cathode phase structures in alkali solution can also be coloured and displayed. If no picronitric acid added in the hot alkali solution, pearlite, ferrite and carbide structure cannot be displayed.

The above features are beneficial for studying high temperature solidification and solid phase transformation. For example, from Fig. 1-26 and Fig. 3-47(in Chapter 3), it can be seen clearly that as-cast pearlite occurs at the last region to solidify and the lower ausferrite formed during austempering has certain inheriting relationship with its originally solidified structure, as shown in Fig.1-27.

(3) Can visually and quickly display segregation of cast iron.

Cast iron is a kind of metal material containing large amounts
and various types of solute elements, with serious positive and negative segregation. The hot alkali method can be used to quickly display face distribution information of elements in macro or micro region.

(4) Presented information is very sensitive
Experiments have shown that the variation in composition, which cannot be identified with electron probe, can be displayed with different colour using hot alkaline method.

(5) Operation is simple and convenient; no special experimental apparatuses needed
The disadvantage of this method is that it cannot display the precipitation process (nucleation and growth) of graphite; it can be complemented if combining with liquid quenching method. In addition, if colours can be pre-calibrated by electron probe, this method is possible to be developed from qualitative to semi or full quantitative display.

1.5.3 Operational procedure of colour metallography using hot alkaline etching method
The important contents of hot alkaline etching process include etching reagent, etching temperature and time; these all result in decisive influence on colour effect. Figure 1-28 is an actual example showing the influence of etching time on colour development.

![Figure 1-28](image-url)

(a) 5 min, (b) 10 min, (c) 15 min, (d) 25 min, (e) 35 min, (f) 45 min (with polarized light)

**Fig: 1-28 Relation between colour evolution and etching time (etching solution 1)**
Preparation of etching reagent

The composition of hot alkaline reagent consists of sodium hydrate (NaOH), potassium hydrate (KOH), picronitric acid and distilled water. Table 1-4 lists several actual formulas of the etching reagents. Reagent number 1 has moderate alkalinity and reaction is mild; the displayed colours show good gradation of colours and good colour transition; the reaction is slow, etching time is long and it is easy to operate. Formula number 2 and 4 have strong alkalinity, reaction is violent, sharp colour can be obtained in a short time. When sample has low silicon content, number 2 and 4 are more suitable. Reagent number 5 is more violent in reaction, its etching time is relatively short, and especially suitable for ductile iron containing Al. Reagent number 3 is weaker in alkalinity than number 1, needs lower temperature, suitable for naked-eye observation of macro solidification morphology with low magnification.

Table 1-4: Formula of hot alkaline etching reagent and etching process

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Distilled water (mL)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH (g) 28</td>
<td>KOH (g) 1</td>
<td>Picronitric acid (g) 4</td>
<td>200</td>
<td>95–100</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>3</td>
<td>8</td>
<td>200</td>
<td>95–100</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>4</td>
<td>200</td>
<td>65</td>
<td>10–65</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>160</td>
<td>40</td>
<td>200</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>28</td>
<td>56</td>
<td>28</td>
<td>200</td>
<td>95–100</td>
</tr>
</tbody>
</table>

Preparation procedure of the etching reagents is as follows: first add NaOH into water, stir to accelerate dissolution; then add picronitric acid, stir to make solution uniform. After fully dissolved, heat the solution (best to heat in a constant temperature bath) to required temperature, then put sample in the solution. Place the polished face up to protect from scratching. After holding the sample at the constant temperature for required time, take the sample out, wash with distilled water, then wash away water with absolute ethylalcohol. Dry the sample, then the sample can be used for observation.

(2) Etching and display process

Important etching parameters are etching temperature and time. At constant temperature etching time exerts significant effect on film forming rate. With extension of time, colour gradually changes (see Fig.1-28) and displays solidification development progress. The colour changing sequence in the same position is: brown, blue, pale blue, pale yellow, yellow brown, orange, blue green, red yellow.

The promise for satisfied result is well controlled etching solution temperature. The higher the temperature, the shorter the etching time. Often, in order to obtain good colour contrast for different samples or obtain the same or similar colour for a certain phase, constant temperature is used by changing etching time. For certain structure, the time demanded for displaying special colour is related to composition of cast iron, (particularly silicon content). So, the corresponding relation is varying with variation of cast iron composition.

For samples difficult to etch, first use normal etching reagent to pre-etch to increase surface activity. This can accelerate film formation.

References

Grey Iron is a type of cast iron with grey color fracture and carbon precipitated as flake graphite. According to its chemical composition in Fe-C phase diagram, grey iron is categorised into three types: hypoeutectic, eutectic, hyper-eutectic irons. In order to satisfy strength demand, most engineering grey irons are hypoeutectic composition. However, for achieving combinations of good castability, strength, conductivity and dumping capacity, eutectic and even hyper-eutectic grey irons attracted more and more attention in research.

In a hypoeutectic cast iron with carbon saturation degree (the ratio of carbon content in the iron to the actual carbon of eutectic point) $Sc < 1$, the first precipitated phase is primary austenite during solidification; for a hyper-eutectic iron with $Sc > 1$, the first precipitated is primary graphite. For these two type irons, at the second solidification stage, eutectic crystallization will take place. While, a cast iron with $Sc = 1$ only has the second stage eutectic crystallization during solidification. In the last stage of solidification, due to significant difference in composition in the region last to solidify, the formed structures are quite different. For convenient discussion, this solidification is separately listed as the third stage solidification in this book.

Thus, the solidification structures of grey irons comprise primary austenite, primary graphite, eutectics (eutectic graphite + eutectic austenite) and the structure formed around eutectic cells.

### 2.1 Graphite in cast iron

Graphite is an extremely important constituent in cast iron, accounting for about 10% volume in cast iron. Graphite itself has almost no strength, but its shape or morphology, amount and distribution exert significant influence on the properties of cast iron.

Commonly observed graphite shapes are: flake, vermicular or compacted, spheroidal and quasi spheroidal-temper graphite. The former three types are the graphite directly precipitated from liquid
iron, while, the last one is obtained from solid tempering treatment. The cast irons with above types of graphite are correspondingly named grey iron, vermicular iron, spheroidal iron and malleable iron.

Internationally, according to their shape and distribution, flake graphite is classified into A, B, C, D and E five types, see Fig. 2-1.

In China, F type graphite is added based on the classification. Characteristics of the various types of flake graphite are listed in Table 2-1, among them, Kish graphite (type C) and star-like graphite (type F) belong to primary graphite, the rest types precipitate during eutectic stage and belong to eutectic graphite.

![Fig.2-1: Classification of flake graphite](image)

<table>
<thead>
<tr>
<th>Graphite</th>
<th>Type</th>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flake graphite</td>
<td>A</td>
<td>uniform distribution, random orientation</td>
</tr>
<tr>
<td>Rosette graphite</td>
<td>B</td>
<td>Rosette grouping, random orientation</td>
</tr>
<tr>
<td>Kish graphite</td>
<td>C</td>
<td>Coarse and large primary graphite flakes with small flakes around</td>
</tr>
<tr>
<td>Interdendritic dot-like graphite</td>
<td>D</td>
<td>Randomly orientated interdendritic undercooled short flake graphite</td>
</tr>
<tr>
<td>Interdendritic flakes graphite</td>
<td>E</td>
<td>Interdendritic orientated undercooled short flake graphite</td>
</tr>
<tr>
<td>Star-like graphite</td>
<td>F</td>
<td>star or spiky graphite mixed with short flake graphite</td>
</tr>
</tbody>
</table>

**2.1.1 Crystal structure of graphite**

In nature world, there are two types of carbon: crystalline carbon (graphite, diamond) and amorphous carbon (coke, coal etc.). Graphite is a hexagonal crystal structure, comprising six prismatic faces and two close-packed basal planes; its crystal structure is illustrated in Fig. 2-2. The plane between layers is called basal plane (0001), the plane perpendicular to the basal plane is a rectangular face, called prism face (10\(\bar{0}\)). The orientation parallel to the basal plane is crystallographic orientation [10\(\bar{0}\)], called \(\alpha\)-axis; the orientation perpendicular to basal plane is crystallographic orientation \([0001]\), called \(c\)-axis. The atom distance within the layer (basal plane) is 0.142 nm; the distance between layers (basal planes) is 0.335 nm. Within each layer the carbon atoms are packed in hexagon; each carbon atom is bonded with three nearest-neighbor atoms by 400–500 kJ/mol connecting energy, a kind of energy between atoms, similar to that of metallic bond. The adjacent layers are connected by a weak attractive force—Van der Waals force—the interaction force between molecules. The huge difference in bonding forces makes graphite strong anisotropy. Due to a very weak bond between layers, it is easy to split and slip between layers. Consequently, the strength and hardness in basal plane are markedly higher than that in prism plane; while, the electrical resistivity is opposite, the resistivity in basal planes is much lower than that in prismatic planes.

**2.1.2 Defects in graphite crystal**

There are large amounts of defects or imperfections in graphite crystal, such as lattice distortions caused by interstices or lattice vacancies, staggered pack arrangements of one row or several rows. The crystal defects directly affect growth of graphite.
There are following defects in graphite crystal:

(1) Rotating twin: rotating twins are common defects in graphite crystal; the carbon atomic layers remain parallel to each other. The top and bottom layers rotate an angle around $c$-axis each other (see Fig. 2-3), this angle is called angle $\theta$. The rotating angle complies with the interface response theory to ensure as more atoms as possible corresponding to each other. The most angles forming rotating twins are $22^\circ$, $28^\circ$ \cite{2} or $13.2^\circ$, $21.8^\circ$ and $27.8^\circ$ \cite{3}.

The big difference in bonding force between basal and prismatic planes is the important reason causing rotating twin defects to take place frequently.

(2) Screw dislocation: although the carbon atoms in basal plane are connected by strong covalent bond, there still exist vacancies in certain local regions in the hexagonal network. The resulted plier shaped defects from these vacancies are the bases for screw or spiral dislocations. When there is a shearing stress perpendicular to basal plane, this stress can cause graphite crystal to split along $Q$ plane, leading to screw dislocations. The $CD$ line is the centre of spiral face, as illustrated in Fig. 2-4. There are much less screw dislocation defects than rotating twin defects in graphite crystal.

Double and Hellawell divide screw dislocations into three types, as illustrated in Fig. 2-5.

(a) Circular cone screw: formed by the folded graphite flakes rotating $\theta$ angle round $c$-axis. The rotating angle $\theta$ is calculated by:

$$\theta = 2\pi \cos \frac{\alpha}{2}$$

Where $\alpha$ – apex angle, possible range for spiral pack is $\alpha = 0$–$180^\circ$.

(b) Typical screw: pure screw dislocation perpendicular to plane (0001)

(c) Cylinder screw: apex angle is 0$^\circ$ for this case.

Actual often existing screw dislocations are circular cone screw; the apex angle is between 0–180$^\circ$. Nodularizing elements are embedded in the layers or absorbed in basal plane causing local barrier effect on (10[0]), easily creating screw dislocation. Besides, liquid iron undercooling, especially the undercooling at existence of low S and O-active elements, will significantly increase disturbing sources and accelerate the formation of screw dislocations \cite{4}. 
2.1.3 Conditions of graphite nucleation

Graphite nucleation can be homogeneous or heterogeneous nucleation.

Homogeneous nucleation relies on large amounts of fluctuated micro-carbon atom clusters of \((C_6)_n\), which transform to crystal structure the same as graphite, forming germs or embryos, then finishing nucleation process. Only when a liquid iron reaches enough undercooling, the germs with certain sizes can transform to stable nuclei.

The nature of these micro clusters is not very clear at present, however, they do exist\(^\text{[5]}\). Often, the \((C_6)_n\) clusters in iron melt are in unstable state, forming dynamic equilibrium with carbon-rich liquid regions. When liquid iron reaches high enough undercooling (200–230°C), the smaller sizes of micro cluster \((C_6)_n\) are possible to exist as stable nuclei. Under normal conditions, such high undercooling is very difficult to achieve; therefore, the nucleation of graphite mainly is heterogeneous nucleation.

Heterogeneous nucleation refers to that carbon atoms preferentially attach to the surface of existing particles (substrates) and form nuclei. There exist large amounts of foreign particles in liquid cast iron. For example, in 1 cm\(^3\) of iron melt, just the number of oxide particles can reach five million. That does not mean all the foreign particles can become nuclei of graphite. Becoming a nucleation substrate, foreign particles must satisfy two conditions:

1. Conform to certain relation of lattice mismatch or disregistry: a certain lattice face of the foreign particle (inclusion) substrate has a certain corresponding relation in lattice parameter and orientation with graphite crystal lattice.

   A characteristic parameter of the lattice matching relationship is plane mismatch \(\delta\).

   According to planar lattice corresponding model by Bramfitt\(^\text{[6]}\), the mathematical expression for plane lattice mismatch is:

   \[
   \delta = \sum \left( \frac{|d_{(hkl)} - d_{(hkl)}| \cos \alpha}{d_{(hkl)}} \right) \times 100\%
   \]

   Where,

   - \(d_{(hkl)}\) — atomic spacing of foreign nucleus along \([UVW]\) direction, \(UVW\) is the low-index direction of foreign nucleus in \((hkl)\).
   - \(d_{(hkl)}\) — the inter-atomic spacing of graphite along \([UVW]\) direction, \(UVW\) is the low-index direction of graphite in \((hkl)\).
   - \(\alpha\) — angle between heterogeneous nucleus and graphite in \([UVW]\) direction.

   The smaller the mismatch of the two substances \(\delta\), the stronger the nucleation ability between them. The general relation is\(^\text{[7,8]}\):

   - \(\delta < 6\%\) has the strongest nucleation ability
   - \(6\% \leq \delta < 12\%\) has nucleation ability
   - \(\delta > 12\%\) has a weak nucleation ability

   Mismatch \(\delta\) (%) between a certain special lattice face of some substances and the (0001) face of graphite is listed in Table 2-2.

   Except for a small lattice mismatch, the good matching relationship also means that the two substances have the same lattice structure, similar or proportionally similar lattice constants; the two substances have different lattice structure, but have similar atom pack arrangements and close or proportionally similar lattice constants on certain lattice plane. It is obvious that if the substrate and growing crystal are the same substance, the growing crystal has the best nucleation condition.

2. Satisfy interfacial energy requirement between heterogeneous nucleus and graphite: only when the foreign particles can be wet by graphite, graphite can form nuclei on the foreign substrates.
According to the most recent study \[12\], the interfacial energy between iron liquid - nucleus \(\sigma_{LN}\) must be higher than the interfacial energy between iron liquid - graphite \(\sigma_{LG}\). In addition, \(\sigma_{LN}\) needs to be higher than the interface energy between nucleus-graphite \(\sigma_{NG}\). Only under these conditions, it can be sure that the two phases have stable coherence and adhere each other. At this time, the small mismatch can fully play a role for nucleation. Thus, only lattice match is not enough to fully explain the efficient nucleation; the energy requirement between melt - nucleus interfacial energy needs to be satisfied.

Nevertheless, no all the inclusions existing in the centre of graphite satisfy above principles, since inclusions in the centre of graphite may comprise several inclusions. However, one kind of inclusions satisfying lattice mismatch and interfacial energy requirement with graphite is enough. At most cases, the nuclei of graphite are about 1–2 \(\mu\text{m}\) \[10\].

### 2.1.4 Mechanism of graphite growth

The nucleation of graphite influences the amounts of graphite nuclei, while the growth process determines the final morphology of graphite. The different morphologies of flake, vermicular even spheriodal graphite are not coming from different types of nuclei, but from different growth processes.

The growth dynamical mechanism of graphite is closely related to melt undercooling and crystal defects of graphite.

There exist three mechanisms of graphite growth (that is, graphite forms nuclei and grows independently along (1010) face; the steps on (1010) face can only advance to the edge of crystal. Due to the weak connecting force (bond) between a single atom and (1010) face, graphite growth is very difficult, even almost impossible to grow with this type of mechanism.

(2) Rotating step growth: graphite deposits on the rotating twin steps, the (1010) face grows by step expanding laterally. Since the deposited atom has two touching faces, this growth is more stable than the two dimensional growth and has large growth probability.

(3) Screw dislocation growth: carbon atoms deposit on the edge of steps caused by screw dislocation, the steps continuously expand, sweeping the crystal plane. The angle-velocity sweeping crystal plane at dislocation centre is faster than that in the region far from the centre, giving rise to spiral, tower-tip-like crystal surface. Due to having three touching surfaces, carbon atoms enter step without need of forming a new surface.

Two-dimensional growth and rotating step growth mechanisms adapt prism face (1010) growth, the growth velocity \(v_c\) and undercooling \(\Delta T\) follow exponential rule:

\[

v_c = \mu_c e^{b\Delta T}

\]

Where \(\mu_c\), \(b\) — coefficients

When graphite basal face (0001) grows, carbon atoms deposit on the steps of screw dislocations, the growth velocity \(v_c\) of basal face and undercooling \(\Delta T\) follow parabolic relation:

\[

v_c = \mu_c \Delta T^2

\]

Where \(\mu_c\) — coefficient.

Summarizing the relationship of prism face growth velocity \(v_c\), and basal face growth velocity \(v_c\) with undercooling \(\Delta T\), the cross of the two curves is called critical undercooling \(\Delta T_c\); when \(\Delta T > \Delta T_c\), \(v_c > v_c\) and when \(\Delta T < \Delta T_c\), \(v_c < v_c\). When graphite grows under an ideal state without lattice defects, carbon atoms are packed in the form of single crystal graphite flake with the same crystalline orientation. Kozlov observed that without influences undercooling and subversive elements, the equilibrium shape of graphite is flake \[15\]. In the same way, Nakae also found that the graphite in a pure Fe-C-Si alloy is a straight, thin and long shape \[16\].

However, the actual growth state of graphite is very different from the ideal state. There exist various defects in the actual crystal germs or embryos, these defects destroy the neat arrangement of graphite lattice, causing braches and many crystalline orientations.

---

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mismatch (\delta) (%)</th>
<th>Reference</th>
<th>Substance</th>
<th>Mismatch (\delta) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphite</td>
<td>0</td>
<td></td>
<td>CaS</td>
<td>8.3</td>
<td>[10]</td>
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**Fig. 2-6: Three mechanisms of graphite growth**

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Serial Report

May 2009
2.1.5 Branches in graphite growth

There are two types of graphite branches [17], as illustrated in Fig. 2-7: graphite branches along $a$-axis, basal plane (0001) split; $c$-axis branches, prism plane (1010) split.

The factors affecting the types and severity of graphite branching include types of graphite defects, undercooling and austenite growth near to the graphite.

1) **Crystal defects:** the defects existing in graphite directly influences the types of formed branches. The packing of carbon atoms on rotating twin steps is equivalent to splitting of graphite along basal plane forming $a$-axis branch. If carbon atoms pack on the step of opening of screw dislocation, because the one end of step is fixed at dislocation line, steps grow around dislocation line, resulting in $c$-axis branch perpendicular to basal plane (0001).

2) **Undercooling:** undercooling is a important factor influencing branching of graphite. The relationship [18] between shape factor $K_F$ and undercooling $\Delta T$ derived from fundamental theory of crystal growth is:

$$K_F = \frac{Q \rho \Delta T}{K \sigma}$$

Where, $K_F$ — is crystal shape factor ($S/V$) ratio of surface area $S$ of a crystal to its volume $V$;

$Q$ — formation heat of graphite crystal;

$\rho$ — density of graphite;

$K_e$ — eutectic temperature;

$M$ — relative molecular mass of graphite;

$\sigma$ — surface energy of touch surface between graphite and melt;

$\Delta T$ — undercooling.

In above equation, except for $\Delta T$, other parameters are all constants. Thereby, $K_F$ is increased with increasing of undercooling. Large $K_F$ means that graphite branching is further severe. Since only large amount of branches can increase the ratio of surface area $S$ to volume $V$.

3) **Austenite near to graphite:** the austenite near to graphite can inhibit graphite branching.

The types and severity of graphite branching is directly related to final graphite morphology. Their relationship is summarised in Table 2-3.

2.2 Crystallization of primary graphite

2.2.1 Crystallization thermodynamics of primary (type C and F) graphite

When hypereutectic iron melt of composition $X$ is undecooled to temperature 1 in Fig. 2-8, the composition of the melt changes to $X_\alpha$ and its free energy is $G_\alpha$. At this time, the free energy of the melt is $\Delta G$ higher than that of the mixture of the melt and graphite. Thus, the mixture of the melt with graphite precipitated is more stable, causing primary graphite to precipitate from the iron melt.

The growth of primary graphite is driven by chemical potential gradient resulted by carbon concentration difference, since in the region near to primary graphite, carbon is poor, the carbon content is $X_\alpha$. While, in the region far from graphite, the melt remains its original composition $X$. The difference in carbon concentration results in carbon chemical potential gradient, causing carbon atoms to diffuse towards the growing crystal, graphite will continuously precipitate until the remaining melt reaches composition $X_\alpha$. At this time, the remaining melt with composition $X$ is in equilibrium with precipitated graphite.

![Fig. 2-7: Types of graphite branches](image-url)

(a) Branch along $a$-axis, (b) Branch along $c$-axis, (c) high magnification lattice fringe image of branch along $c$-axis.

![Fig. 2-8: Free energy change of hypereutectic cast iron when precipitated primary graphite](image-url)

2.2.2 Precipitation of primary graphite

The type C and F graphite are primary flake graphite, and present in hypereutectic grey iron. The two dimensional characteristics of primary graphite is less branched, straighter and flatter, coarser and larger. This type of graphite is formed under small undercooling,
and the growth temperature is in the region between liquidus and eutectic temperatures, and diffusion of carbon at this temperature region is fast. In addition, austenite is very difficult to form around graphite. Graphite growth is not affected by austenite; therefore, graphite is easy to grow to C type graphite flakes. When undercooling is increased (for example thin wall casting), graphite branches are increased, forming type F, star-like graphite.

The branching of primary graphite can be classified to two types: small angle and large angle branching \(^{[19]}\). The large branching angle is due to the development of rotating twin defect; the defects cause more growth front and change in growth directions. The formation of small angle branching is depended on solidification conditions (such as the variation of undercooling in solidification front, embedded inclusions etc.)

### 2.2.3 Kish graphite

Kish graphite is a type of special structured graphite, which crystallized in carbon saturated iron melt with flake dendrite growth. The graphite flakes are gathered on the iron melt surface, either mixed with slag and exist in slag layers, or leave melt and float in surrounding.

1. **Structure of Kish graphite:** the crystal characteristics of Kish graphite is flake-like dendrite structure, as illustrated in Fig. 2-9. When observing normally from c-direction, it is seen that the hexagon rings are almost overlapped and have branches; and graphite flakes are connected in layer in a-direction. Kish graphite precipitated from melt first gathers together in melt, and then floats to the surface of the melt, forming bulk or blocky volume. While, the Kish graphite directly formed on the surface gathers and forms surface blocks on the melt surface.

2. **Formation of Kish graphite**\(^{[20]}\): for Kish graphite, oxygen plays an important role in either the nucleation or growth by flake-like dendrite manner. Practices have demonstrated when hypereutectic iron melt is exposed in air, Kish graphite is easy to form; disturbing iron melt, thus continuously creating new surface will accelerate the formation of Kish graphite. The role of oxygen is forming SiO\(_2\) as substrate for Kish graphite nucleation. When iron melt is below 1,400°C, the Kish graphite forms more than in higher temperature, since SiO\(_2\) is not stable above 1,400°C. In the melt with low or no silicon, the precipitation phenomenon of Kish graphite is not observed. This shows that existence of SiO\(_2\) has non-ignored influence on the formation of Kish graphite.

Without oxygen (for example protected by argon gas), the cooling rate is a basic condition influencing the formation of Kish graphite. Kish graphite can only form under slower cooling rate (<180°C/h). At higher cooling rate, the formation of Kish graphite is inhibited, since high cooling rate increases crystal growth defects and accelerates graphite branching trend, causing planar growth change to blocky growth. However, the cooling rate cannot be too slow, if cooling rate is decreased below 50°C/h, massive single crystal graphite will form which is even bigger, thicker and more compacted than Kish graphite.

There exist two types of Kish graphite: (a) severely branched and thin flake graphite. This type of graphite is formed under fast cooling and on the iron melt surface directly in contact with air, often observed during cleaning slag operation or occur on the flowing iron melt surface. (b) less branched, thick and disc-like graphite. This type of graphite is formed under slow cooling and on the iron melt surface in less contact with air, often observed in the slag layers of liquid iron conveying tank or in the Kish graphite layers.

(\textit{Be continued})

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<thead>
<tr>
<th>Branch type</th>
<th>Influencing factor</th>
<th>Degree of branching</th>
<th>Graphite morphology</th>
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<td>More</td>
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<td></td>
<td>Big</td>
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</table>

<table>
<thead>
<tr>
<th>Table 2-3 Relationship between branch types and severity and graphite morphology</th>
</tr>
</thead>
</table>

(a) Observation from \(c\)-direction  
(b) Observation from \(\alpha\)-direction

**Fig. 2-9: Crystal structure characteristics of Kish graphite**