Colour Metallography of Cast Iron

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Preface

Cast iron, as a traditional metal material, has advantages of low total cost, good castability and machinability, good wear resistance and low notch sensitivity, and is still facing tough challenge in quality, property and variety of types etc. Experts and engineers studying and producing iron castings all around world extremely concern this serious challenge. Over more than 30 years, a great of research work has been carried out on how to further improve its property, expand its application and combine cast iron technology with some hi–techs (for example, computer technology). Nevertheless, cast iron is a multi–element and multi–phase alloy and has complex and variety of structures and still has great development potential in structure and property. For further studying and developing cast iron, theoretical research work is important promise, and the study on solidification process and control mechanism of graphite morphology is fundamental for improving property of cast iron and developing new type of cast iron.

Metallography of cast iron normally includes two sections: liquid phase transformation and solid phase transformation. The book, Colour Metallography of Cast Iron, uses colour metallography technique to study solidification structures of cast irons: graphite, carbides, austenite and eutectics; and focuses on solidification processes. With progress of modern solidification theory, the control of material solidification process becomes important measure for improving traditional materials and developing new materials. Solidification structure not only influences mechanical and physical properties of cast iron, but also affects its internal quality. The book uses a large amount of colour photos to describe the formation of solidification structures and their relations. Crystallization phenomena, which cannot be displayed with traditional metallography, are presented and more phase transformation information is obtained from these colour metallographic photos.

Except for focusing on the effect of high carbon phases in cast iron, in this book, special attention is also paid to the effect of austenite on solidification, graphite morphology, and quality of cast iron; at the same time, the study on the solidification behaviours in the region around eutectic cells and its effects on mechanical properties of cast iron, are also emphasized.


Chapter 1

Introduction (1)

Cast iron is a multi-element eutectic alloy containing mainly iron, carbon and silicon. The composition of industrious cast irons varies, according to their types, in following range: w(C)=2.4%–4.0%, w(Si)=0.8%–3.2%, w(Mn)=0.2%–2.0%, w(P)=0.05%–1.2%, w(S)=0.01%–0.15%. Sometime, in order to obtain certain special property, additional alloys are added into cast iron.

Based on the different forms of carbon precipitated: graphite or carbide, and macro fracture, cast iron is classified as grey iron, white iron and mottled iron. In grey solidified cast iron, according to graphite shape, the iron is divided into grey (flake graphite) iron, vermicular graphite iron and spheriodal graphite iron. Malleable iron is in between white iron and grey iron; white iron blank belongs to white solidified iron; after heat treatment, finished malleable iron product becomes grey iron due to carbon’s converting to graphite.

Different types of cast irons follow different crystalline structure changes during solidification. Nevertheless, no matter which type of irons, during solidification, all the cast irons have similar crystallization phenomena, and follow the common rules of crystallization, such as the liquid structure of cast iron, non-equilibrium solidification conversion between grey and white solidification etc. These phenomena occur not only in spheriodal graphite iron, but also in vermicular graphite iron and white iron.
1.1 Liquid structure of cast iron

During phase transformation from liquid to solid, the structure of molten cast iron has significant effects on the phase crystallization, formation of solidification structure and defects of cast iron.

As in other liquid metal, under normal superheat state, the atoms in liquid iron are short-range ordered. Cast iron is a multi-element Fe-C alloy; the existing state of carbon in liquid iron is an important feature of liquid cast iron structure. Study has shown that there exist undissolved carbon molecules (C\(_n\), C\(_{m}\)) all called C\(_n\) and carbon cluster (C\(_{am}\)) built up with those carbon molecules C\(_n\). Even though all the elements are melted, cast iron liquid is also not a single phase liquid, but a multi-phase solution (or suspensoid liquid).

1.1.1 Fe\(_5\)C molecule

From thermodynamics, the hypothesis, there existing Fe\(_5\)C molecules in molten Fe-C, is tenable, because the formation energy of Fe\(_5\)C is less than that of graphite and Fe-C is more stable, which cause Fe\(_5\)C clusters easier to form in the carbon-rich region. In addition, containing w(C)=6.67%, Fe\(_5\)C is easier to form than graphite containing w(C)=100%. When liquid iron has high temperature, the necessary carbon concentration for forming graphite is relatively high, thus graphite is more difficult to exist. There are many different forms of carbide structures; the iron carbide in liquid iron is Fe\(_5\)C. But, it is not a solid crystal; it is a short range ordered atomic region in liquid iron, similar to the structure of cementite.

1.1.2 Carbon cluster (C\(_n\))

Carbon cluster is a micro group consisting of several carbon molecules, C\(_n\). When molten iron is stewed at high temperature for a long time, carbon cluster can decompose to carbon molecules, C\(_n\), and further decompose to carbon atoms. Only at this time, the Fe-C solution presents an ideal state of Fe-C solution.

With measurements of X-ray, neutron diffusion and speed of sound for Fe-C alloy melt at temperature 20°C above its liquidus, it is found that when w(C)>1.8%, the atomic distance \(r_1\) between the nearest neighbor atoms and the number of the nearest neighbor atoms \(N_1\) show an increased trend, see Fig.1-1. When w(C)>1.8%, the distance of neighbor atoms remains constant, but the number of the nearest neighbor atoms increases continuously. At w(C)=3.0%–5.5%, the distance and number of neighbor atoms are kept constant. When w(C)>3.5%, there are more of carbon-rich short range ordered regions, implying iron melt becomes more viscous due to the increase of carbon. A measurement of viscosity is shown in Fig.1-2. It is seen that the viscosity is increased with the increasing of carbon content. Entering in short-range ordered region, the melt forms colloidal distribution system of carbon group. In Fe-C system melt with w(C)>3.5%, there exist micro groups of carbon, (C\(_n\))\(_{am}\). In the temperature range of 1,300–1,400°C, the diameters of carbon region of (C\(_n\))\(_{am}\) are about 1–10 nm; the calculated amount of carbon groups is about 2.7×10\(^7\)/mm\(^3\). The size and amount of carbon groups of (C\(_n\))\(_{am}\) depend on carbon content, melt temperature and holding time at high temperature. The diameter of carbon group of (C\(_n\))\(_{am}\) is increased with increasing carbon, decreasing of silicon and superheated temperature. Carbon clusters (C\(_{am}\)) have obvious effect of nucleation centre for graphite, and also have influence on the nucleation of austenite and Fe-C. Figure 1-3 shows their relationship. It is seen from Fig.1-3 that undissolved molecule groups of C\(_n\) make the nucleation of austenite easier, because with increasing of (C\(_n\)), the actual composition of iron melt is off-set to eutectic region, thus promoting eutectic austenite to precipitate. If iron melt is superheated high enough and kept for long enough, (C\(_n\))\(_{am}\) is gradually decomposed into C\(_n\) or C\(_{am}\), even C atoms; at this time, graphite and austenite all are difficult to

**Fig.1-1: Relationship of nearest neighbor atomic distance \(r_1\) and nearest atom number \(N_1\) to carbon content in liquid alloy**

**Fig.1-2: Relationship between carbon content and viscosity of Fe-C alloy**

**Fig.1-3: Relationship of carbon cluster (C\(_n\)) to carbon molecules, C\(_n\), and transition of carbon atoms with formation of graphite, Fe-C and austenite**
nucleate, however, Fe₃C is easy to form. Therefore, above a certain temperature, the iron melt is beneficial to form Fe₃C, at this time Fe₃C is more stable than graphite. Below this temperature, Fe₃C is unstable and has spontaneous tendency to decompose to Fe and C. This critical temperature is influenced by chemical composition and other factors. When there exist strong carbide promoting elements, they will influence (Cₙ)ₙ group transformation trend towards graphite or Fe₃C. Thus, it cannot say that the existence of carbon groups in iron melt will all promote nucleation of graphite or cristallization of carbide under any condition.

1.1.3 Heredity in cast iron
During re-melting of cast iron, some information in structure, composition and physical characteristics of charging materials are retained and transmitted to following re-crystallized crystal, this is named heredity in cast iran.

The heredity in cast iron includes three respects:
(a) Retention of structure information
Its characteristic is some structure features (such as types of carbon atom groups, size and non-uniformity of grains, micro-multiphase structure etc.) are inherited during subsequent transition from furnace charge to molten iron and casting. This phenomenon happens often in melting practice. For example, if more steel scrap and white iron charges are used, chilling tendency is increased; this is because original Fe₃C molecules are retained in melt as nucleis for carbides. Similarly, using high percent of pig iron containing large amount of coarse graphite, the undissolved carbon group (Cₙ)ₙ will result in precipitation of coarse graphite. By using chilling process, poured ferrosilicon to 0.5–2 mm thick plates to make fast cooling inoculant. Comparison experiment showed that the fast cooling ferrosilicon has significantly improved result: the width of chill is markedly reduced and fading time is prolonged. This is because containing extremely fine and uniformly distributed phase structure in this type of ferrosilicon produces active effect on inoculation[9].

(b) Heredity of composition
Except for common elements, charging materials often contain some trace element, such as Pb, Ti, Sb, Sn, As, Bi etc. and alloy element Ni, Cu, Cr, Mo, and V etc. Those elements come from pig iron, scrap steels and various mixed scraps. For example, using scrap Zn and Al plated automotive steel plates as chargers may cause increased Zn and Al content. Some elements are retained in castings during melting and cause various heredity effects: strong carbide promoting elements cause increased shrinkage, crack and chilling tendency; trace surface active elements promote some abnormal graphite shape such as Widmannstaetten and spiky graphite; gaseous elements are prone to blowhole defect. Therefore, improving the purity of charging materials is a key factor to obtain quality cast iron[9].

(c) Retention of physical characteristics
It is rather possible that physical characteristics (viscosity, surface tension), chilling tendency, shrinkage, blowhole and crack tendency all have heredity and these characteristics are related to charge materials. When bad charge materials are used, certain of these characteristics is retained; after changing charging materials this phenomenon disappears. The principle of heredity of physical characteristics is retention of information in structure and composition. Because the dispersed particles in iron melt are the genetic factors (or media); the inherited dispersed particles from charge materials become potential crystallizing nuclei[9].

Measures for improving bad heredity include changing charge materials, using a combination of different materials and superheating iron melt. Among them superheating is an effective measure. Using X-ray measurement, it is found that when melt is superheated to 1,550 °C, the structure of the melt changes obviously and its micro uniformity is improved significantly[9].

1.2 Fe-C phase diagram

1.2.1 Theoretical basis of coexistence of Fe-Fe₃C and Fe-C phase diagrams
When carbon in Fe-C alloy exceeds its solubility in iron liquid, the excessive carbon will present as graphite or carbides in the alloy.

(a) Fe-Fe₃C phase diagram
Iron and carbon can form a series of carbides[9], except for cementite Fe₃C (also called θ carbide), there exist possible FeC, Fe₂C, Fe₃C, Fe₄C, Fe₂Cₓ, Fe₃Cₓ, Fe₅Cₓ, Fe₆Cₓ, Fe₇Cₓ and Fe₈Cₓ. Among them, many are transition phases, or stable only when with impurity elements; the Fe₃C called ε carbide and the Fe₅Cₓ called X carbide are transformed from θ carbide under particular conditions. However, for most instances, the transition temperature (230 °C) from θ → X, ε, is very low, the transition rate is very slow, it is difficult to form FeCₓ and Fe₃C. Thus, in most instances, the thermostability of Fe₃C is higher than that of both X, ε carbides and cementite is most stable. In addition, cementite is an interstitial intermetallic compound; carbon atoms exist only in the interstices or spaces of iron crystal lattice. When forming cementite, iron atoms need not to diffuse away from nuclei, thus the formation of cementite is not difficult. Therefore, cementite is considered as a phase, and from this consideration, the measured iron-carbon phase diagram is the widely used Fe-Fe₃C phase diagram. Nevertheless, cementite is not fully stable, holding for a long time at high temperature, cementite will decompose following Fe₃C → 3Fe+4C and form graphite. Compared with graphite, cementite is still a metastable phase. All these indicate that all the transitions in Fe₂Cₓ phase diagram are conditioned, that is, the cooling rate is not unlimitedly slow; it is a relative equilibrium. Therefore, the structures in the diagram are not the most stable, can be called metastable and are in relative equilibrium.

(b) Fe-C (graphite) phase diagram
Under suitable conditions, carbon in iron and carbon alloy with carbon above 2.14% can be crystallized as graphite. Carbon precipitating as graphite can be realized through decomposing from cementite and also from iron melt or precipitating from solid solution; then, the alloy is further crystallized and solid phase transformed following Fe-C (graphite) phase diagram. Since graphite has much lower free energy than cementite, from thermodynamics, Fe-C (graphite) phase diagram is the most stable equilibrium state, and the most possible phase diagram to exist. Nevertheless, from kinetics analysis, it is quite possible that transformation follows Fe-Fe₃C phase diagram.
1.2.2 Superimposed Fe-C (graphite) and Fe-Fe₃C phase diagram

Adding Fe-Fe₃C metastable phase diagram onto Fe-C (graphite) stable phase diagram forms a superimposed phase diagram as shown in Fig.1-4[9]. This diagram is drawn from thermo-dynamical calculation and has very small error compared with experiment results. According to the latest literature, solid line represents iron-graphite phase diagram, dash line represents iron-cementite phase diagram (opposite to previous expression), when dash line and solid line overlap, solid line is used.

Comparing Fe-Fe₃C diagram with Fe-C (graphite) diagram, it can be seen from Fig. 1-4 that under the same temperature, the solubility of graphite in melt and austenite is less than that of cementite. The equilibrium eutectic and eutectoid reaction temperatures of austenite-graphite are 6 °C (eutectic) and 13 °C (eutectoid) higher than that of austenite-cementite, respectively; The equilibrium eutectic and eutectoid carbon contents are 0.1% and 0.11% lower than that of austenite-cementite, respectively.

1.2.3 Fe-C-Si ternary phase diagram

In addition to iron and carbon, cast iron contains larger amount of silicon and certain amount of manganese. Since containing much more silicon than manganese, normal cast iron is simplified as Fe-C-Si ternary system alloy. In the Fe-C-Si ternary system alloy, high carbon phase can exhibit as graphite and cementite; thus, there exist stable and metastable Fe-C (graphite)-Si and Fe-Fe₃C-Si ternary phase diagrams.

If silicon content of Fe-C-Si system is constant, iron-carbon quasi binary phase diagram is established, see Fig. 1-5. Comparing the silicon contents in Fig. 1-5, it is known that silicon has following effect on Fe-C phase diagram:

(a) Reduce the carbon of eutectic and eutectoid point, that is, reduce the solubility of carbon in eutectic and austenite.

(b) Change eutectic and eutectoid temperature. With increasing silicon, the equilibrium temperature is raised, and the temperature of metastable system is decreased, see Fig. 1-6. Silicon also raises the eutectoid temperature markedly, which is significantly beneficial for formation of ferrite.

(c) Create three phase coexistence region in the phase diagram.

The eutectic region consists of liquid + austenite + graphite; the eutectoid region consists of austenite + ferrite + graphite.

(d) Reduce the austenite region. For high silicon Fe-C alloy, when w(Si) > 10%, the austenite region is markedly reduced, or almost vanished.

The effects of silicon are all beneficial for the formation of graphite, causing metastable Fe-Fe₃C system change towards stable Fe-C (graphite) system.

1.2.4 Effects of alloy elements on iron-carbon phase diagram

Multi-system Fe-C phase diagram is extremely complicated. For studying cast iron solidification, the first concern is the effect of alloy elements on the liquidus and eutectic temperature of austenite. The effect trend of commonly used alloy elements on the equilibrium temperature \( t_{EM} \), \( t_{EG} \) of stable and metastable systems is shown in Fig. 1-7[12]. The rules of the effect of alloy elements on \( t_{EM} \), \( t_{EG} \) are: graphitizing elements (Si, Ni, Cu, Co) simultaneously depress metastable eutectic temperature \( t_{EM} \), and raise stable eutectic temperature \( t_{EG} \), giving rise to \( t_{EM} - t_{EG} \) region.
enlarged. Elements (Cr, V) stabilizing carbide raise metastable eutectic temperature \( t_{EM} \), and depress stable eutectic temperature \( t_{EG} \), giving rise to \( t_{EM} - t_{EG} \) interval reduced.

1.3 Non-equilibrium solidification of cast iron

1.3.1 Establishment of Fe-C-Si solidification phase diagram

Actual iron castings have lots of impurities in their chemical composition, and the melt nucleation state is very complicated and the cooling rate is fast. Therefore, their crystallization conditions are significantly different from that of equilibrium phase diagram based on thermodynamic calculations or Fe-C equilibrium phase diagram measured in the special environment (very slow cooling rate, 0.5–2.5°C/min, using very pure material, under vacuum melting). These differences cause cast iron, during solidification under non equilibrium conditions, easily change from stable Fe-C (graphite) system to metastable Fe-Fe\(_3\)C system crystallization.
Thereby, equilibrium phase diagram is not applicable to the solidification analysis for practical iron castings.

For realistic analysing the solidification structure of cast iron, with using charge materials, melting process and cooling condition near to practical foundry situation and with the cooling curves measured by thermal analysis, R. W. Heine[13] established Fe-C (or carbon equivalent) phase diagram. Based on this diagram the relationship between temperature, composition and microstructure was established. Because the phase diagram only considered the relationship in the liquid-solid transition region, it is called solidification phase diagram. Since those cooling curves were measured under more realistic circumstance, the solidification phase diagram is not a phase diagram under equilibrium state, rather a description for forming temperature and composition of solidification structures (austenite, graphite, carbide and eutectic) with considering various realistic conditions.

Figure 1-8 is the Fe-C-Si stable and metastable solidification phase diagrams. The conditions for establishing the diagrams are that the thermal analysis cup should satisfy: (a) the cooling time 4–6 minutes for iron melt cooling from 1,300–1,000 °C, (b) main frequency induction melting, (c) use pig iron, scrap steel and ferrosilicon as charge materials, (d) the melt is superheated to 1,500–1,540 °C and held for a certain time; (e) add $\omega(\text{C})=0.005\% -0.02\%$ when measuring metastable system solidification cooling curves.

Austenite liquidus, graphite liquidus, carbide liquidus, eutectic temperature, eutectic point composition in the Fe-C-Si solidification phase diagram all change with the variation of melting process, melting treatment and cooling rate[13,14].

(a) Austenite liquidus temperature $t_{AL}$

Carbon equivalent, superheat temperature, holding time, charge materials, oxidative atmosphere during melting, even the type of furnace, slag and furnace lining are all the factors causing the $t_{AL}$ line movement in the solidification phase diagram. With the increasing of melt oxidative atmosphere, $t_{AL}$ shows a gradually increased trend, see Fig. 1-9.

Under oxidative atmosphere and superheated to above 1,450 °C and held for a long time, (corresponding to line 12 in the figure), the regression equation for $t_{AL}$ is:

$$t_{AL}(^\circ \text{C})=1594.4 - 102.2[\omega(\text{C}) + 0.25\omega(\text{Si}) + 0.5\omega(\text{P})]$$

If under reductive atmosphere and superheat temperature lower than 1,450 °C and held for a short time, (corresponding to line 6 in the figure), the regression equation for $t_{AL}$ is:

$$t_{AL}(^\circ \text{C})=1,450 - 92.06[\omega(\text{C}) + 0.25\omega(\text{Si}) + 0.5\omega(\text{P})]$$

Iron melt inoculation and nodularization before pouring also change $t_{AL}$. After treatment by adding Mg and Ce, the $t_{AL}$ calculation of the melt is:

$$t_{AL}(^\circ \text{C})=1,569 - 97.3[\omega(\text{C}) + 0.25\omega(\text{Si}) + 0.7\omega(\text{Mg}) - 11.25\omega(\text{Ce})]$$

(b) Eutectic temperature $t_E$

Factors causing austenite liquidus to raise (superheating, holding for long time or melting under oxidative atmosphere) all increase the value of iron-graphite eutectic point. Increasing Mg, Ce, the eutectic carbon equivalent (CE) of nodular iron raises from 4.40% to 4.45%. Most of processes reducing austenite liquidus raise austenite-graphite eutectic temperature and decreases CE value at the same time; while factors which decrease austenite-graphite eutectic temperature all increase CE value of the eutectic, in the end, move CE to the carbide eutectic value.

Fast cooling will decrease eutectic temperature significantly, while slow cooling will raise the temperature trend forming
From thermodynamics, when a certain non-eutectic alloy with composition C is supercooled to temperature $t$ and enters the extension region (shade area) of the two eutectic liquidus lines, the two phases all have certain undercooling and can be crystallized simultaneously; therefore eutectic reaction occurs and eutectic structure is formed.

The associated growth region can be classified into two types: symmetrical and non-symmetrical, see Fig. 1-12.

1.3.2 Concept and process of non-equilibrium solidification of cast iron

According to equilibrium solidification principle, the structure of an alloy developed during solidification is only determined by equilibrium phase transformation lines (including liquidus, solidus), has no relation with solidification conditions. Actually, practical castings are always made under certain conditions. External solidification parameters (cooling rate), nucleation state of iron melt, heat, mass and momentum transfer in liquid phase and internal chemical composition (here refer to trace elements no shown in phase diagram) etc., all significantly influence casting solidification structure, not only influence temperature and composition boundary in phase diagram, but also directly change the developed structure. Even the phase which does not exist in equilibrium condition can form. Thus, the structure developed during non-equilibrium is far more complicated than that in equilibrium condition.

(a) Concept of eutectic coexistence region under non-equilibrium state

Cast iron is a typical eutectic alloy; eutectic reaction under non-equilibrium cooling is a key for cast iron non-equilibrium solidification.

Under equilibrium solidification condition, only the melt with just the eutectic composition can obtain 100% eutectic structure. Nevertheless, under non-equilibrium solidification condition, an iron melt with non-eutectic composition can also solidify into typical eutectic structure. This eutectic is called quasi-eutectic. The shade region in Fig. 1-11 is quasi eutectic region. The exact significance of quasi eutectic region is: the composition region in which eutectic structure can be solidified at temperatures below eutectic point, that is, the region of two phase cooperative growth at temperatures below eutectic point.

Quasi eutectic structure is direct result of undercooling.

![Fig. 1-10: Influence of trace element Bi on eutectic temperature $t_E$ (addition of w(Bi)= 0.01%)](image)

**Fig. 1-11: Quasi eutectic region (shade region) under non-equilibrium state**

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The associated growth region can be classified into two types: symmetrical and non-symmetrical, see Fig. 1-12.

- Symmetrical type: the composition of eutectic point is situated in the co-existence region. Normal, uniform lamellar or rod-like eutectic structure is formed, called symmetrical coexistence. Alloys in symmetrical coexistence region are all metal-metal eutectic alloy; the growth rate of the two eutectic phases is more or less the same.

- Non-symmetrical type: the composition of eutectic point is situated outside the co-existence region, named non-symmetrical cooperative growth. Most of the non-symmetrical alloys are nonmetal-metal eutectic alloy (such as Fe-C, Al-Si eutectic systems)

The reason why the quasi-eutectic region is not symmetrical and offset, is that the melting points of the two components, (constituent phases) are different. When fast cooled down below the equilibrium eutectic temperature, the undercooling of liquid phase for the two constituent phases is different; the constituent phase with higher melting point has much higher undercooling than the phase with lower melting point. These cause different
growth rates for the two phases, giving rise to movement of quasi eutectic region. In addition, with undercooling condition, due to concentration fluctuation and different diffusion rate, the phase with lower melting point is easier to nucleate and has faster growth rate. Therefore, this type of alloy obtains hypo-eutectic structure with low melting point phase as primary phase, causing coexistence region deviate to phase with higher melting point.

(b) Non-equilibrium solidification process of cast iron

Practical commercial cast irons are all solidified under non-equilibrium cooling conditions and formed final solidified structures following solidification phase diagram and the concept of coexisting region.

Under supercooling condition, solidification processes for three cast irons with different eutectic degree are analysed and shown in Fig. 1-13. The quasi eutectic region of Fe-C system is deviated to side of nonmetal constituent phase (C or Fe₃C).

● Eutectic cast iron (see Fig. 1-13a): Eutectic liquid is undercooled to temperature 1, and situated to the left of the quasi eutectic region. Austenite is nucleated in undercooled liquid and austenite dendrites are formed. The precipitation of austenite enriches the remaining liquid in carbon and makes it enter the coexisting region; then, austenite-graphite coexisting growth begins. The final solidification structure is shown in Fig. 1-14: isolated eutectic cells (blue green) are distributed around the primary austenite dendrites.

● Hypoeutectic cast iron (see Fig.1-13b): Liquid iron is undercooled to temperature 1 below liquidus temperature; austenite is nucleated. With decreasing temperature, dendrites with poor carbon grow in the liquid and the liquid composition is changing along liquidus. When undercooled to point 2 (to the right of quasi eutectic region), the liquid carbon concentration around austenite dendrites is increased, causing graphite to nucleate; then liquid composition shifts to left to point 3 and enters the quasi eutectic region; thus, eutectic crystallization occurs. The solidification structure is still featured with austenite + eutectic cells of hypoeutectic cast iron, but the dendrites are significantly developed, see Fig. 1-15.

● Hypereutectic cast iron (see Fig.1-13c): liquid iron is

Fig. 1-14: Non-equilibrium solidification structure of a eutectic cast iron

Fig. 1-15: Non-equilibrium solidification structure of a hypoeutectic cast iron
undercooled to temperature \( t_1 \), primary graphite is precipitated. Because of graphite precipitation, the temperature of the remaining liquid is decreased along liquidus and its composition is changed to point 2 (to left of the quasi eutectic region). In hypoeutectic region, austenite is nucleated from the liquid and the easiest nucleation sites are around graphite. The growth of austenite again makes the composition of the remaining liquid change back to the coexisting region. Austenite + graphite eutectic growth continues. In the end, a complex structure including primary graphite, austenite and eutectic cells, is obtained, see Fig. 1-16.

Although the most important factor influencing non-equilibrium solidification is cooling condition, that is the undercooling of crystallisation, the effects of variations in internal chemical conditions (impurities, trace elements, segregation and original state of nucleation) can not be neglected. These variations will change diffusion state or dynamics of atomic arrangement at liquid/solid interface.

1.4 Transformation between stable and metastable systems in cast iron

Cast iron possesses stable Fe-C (graphite) and metastable Fe-Fe₃C (cementite) system phase diagrams; high carbon phase can precipitate as C (graphite) also as Fe₃C (cementite). In practical production, for a cast iron with certain composition during cooling process, it cannot get an answer from phase diagrams whether the cast iron will follow stable Fe-C (graphite) system or metastable Fe-Fe₃C (cementite) system to solidify. This depends on crystalline thermodynamic and kinetic factors of graphite and cementite.

During solidification, if cast iron crystallizes as stable system, carbon atoms precipitate as graphite giving raise to grey colour, that is, grey solidification; if cast iron crystallizes as metastable system, carbon atoms combine with iron atoms and form carbides giving raise to white colour, that is white solidification; if it is in between, it is called mottle solidification. Therefore, the transition between grey \( \rightarrow \) white during solidification reflects the transition between stable and metastable systems.

1.4.1 The trend of grey or white solidification

In order to determine whether a cast iron follows grey, white or mottle solidification, except direct observing fracture or microstructure under microscope, it can also gives a estimate and analysis by using cooling-solidification state diagram.\(^{[12,16]}\)

Cooling-solidification state diagram is a diagram in which the cooling curve of a casting is added on stable and metastable Fe-C phase diagrams, see Fig.1-17a. The diagram consists of two parts; one is cooling curve of a casting, the other is phase diagram affected with liquid composition and physical state. The former reflects cooling condition of a casting; the later considers internal factors which influence whether high carbon phase follows stable or metastable system to precipitate. This diagram reflects the actual conditions; therefore, it can be used for clearly predicting solidification trend of a cast iron.

- **Grey solidification:** When \( t_{EU} < t_{ES} \) in a cooling curve is below stable eutectic temperature \( t_{EU} \) and above metastable eutectic temperature \( t_{EM} \) (see Fig. 1-17b), the iron solidifies as grey iron, since cementite is not involved in eutectic reaction. When cooling rate is slower, there are more nuclei in the iron melt, \( t_{EU} \) is higher, undercooling \( \Delta T \) is small, type A graphite is precipitated. If the cooling is fast or nucleation state is poor, it will cause a drop in \( t_{EU} \) and a rise in undercooling \( \Delta T \), (see Fig. 1-17a), and graphite will gradually change from type A to type B and C and form undercooled graphite. Nevertheless, since \( t_{EU} \), \( t_{ES} \) and \( t_{EM} \) are still between \( t_{ES} \) and \( t_{EM} \), the cast iron still belongs to grey solidification.

- **Mottled solidification:** If the cooling curve of a cast iron is like Fig.1-17c, \( t_{EU} \) decreases below \( t_{ES} \), the eutectic solidification follows metastable system first, forming ledeburite eutectics. Soon after, since \( t_{ES} > t_{EM} \) in the cooling curve, grey solidification occurs in the late stage of solidification, giving raising to mixed solidification, forming mottled structure, see Fig. 1-18. When cooling curve follows Fig. 1-17d, another case of mottled solidification happens: the eutectic temperature is higher during solidification, \( t_{EU} > t_{EM} \), solidification follows stable system first, forming graphite + austenite eutectic. However due to certain reasons (such as high alloy content, severe segregation), which cause \( t_{ES} < t_{EM} \) in the liquid around eutectic cell, thereby, carbides form round inter-eutectic cells, resulting in mottled structure, see Fig. 1-19. In making malleable iron blanks, dark spots occurs in heavy section fracture some time, see Fig. 1-20. This belongs to
above mottled structure. Each dark spot is a graphite + austenite eutectic cell solidified as stable system, the white structure between the dark spots is ledeburite solidified as metastable system.

● White solidification: When the \( t_{EU}, t_{ER} \) and \( t_{ES} \) on the cooling curve all drop below \( t_{EM} \), see Fig. 1-17e, solidification all follows metastable system, solidified structures are primary austenite dendrite and ledeburite eutectic cells.

It is not difficult to see the importance of the cooling curve of a cast iron in a sample cup (or a casting) in estimating white or grey solidification trend. The temperature \( t_{EU} \) — the temperature at which the large amount of eutectics precipitate (starting temperature of eutectic \[17\]), also called undercooling temperature \[18\] is an important parameter influencing solidification process, and its value directly determines the solidification process \[17,18\]. The higher the value of \( t_{EU} \) is \[17,18\], the less chance to solidify as white iron the iron melt has.

![Cooling-solidification state curve](image1)

**Fig. 1-17: Cooling-solidification state curve** \[12,16\]

![Mottled structure formed through grey and white solidification](image2)

**Fig. 1-18: Mottled structure formed through grey and white solidification**

### 1.4.2 Factors affecting grey (or white) solidification

The grey solidification of cast iron is the graphitization of carbon during solidification. In a broad sense, the process, in which the non-crystalline carbon, through diffusion and polymerization by high temperature (or high pressure) crystallises into graphite, is called graphitization. In the graphitization, the carbon in iron melt is precipitated as graphite, rather as carbides.

Factors affecting carbon atom precipitation are alloy factors, cooling rate and the nucleation state of iron melt.

(a) Alloy factors

Different alloy elements have different effects on carbon precipitation. Carbide forming elements (such as Cr, Mo, W, Mn) combine with carbon through strong chemical bond, thus strengthen the bond force between iron and carbon atoms, causing C atoms difficult to precipitate. Therefore, if cast iron contains above elements, its white solidification trend is strong. Elements which do not form carbides (Si, Al, Ni, Cu, C) are graphitizers. They weaken the Fe-C bond, promote carbon to precipitate as graphite and improve ability in graphitization.

From the cooling-solidification curve (Fig. 1-17a), it is seen that changing interval of eutectic temperature \( t_{EG} - t_{EM} \) can influence solidification of cast iron as white or grey. This is because the graphitization of carbon atoms is carried out in the temperature interval between \( t_{EG} - t_{EM} \); the larger the interval, the
Fig. 1-19: Mottled structure

Fig. 1-20: Dark spots fracture of white iron, a) macro fracture, b) microstructure

longer the graphitization time. If the time interval is narrower, the temperature of cast iron will soon drops below metastable temperature \( t_{EM} \), the dynamical condition for graphitization is lost, carbon atoms have no time to diffuse and polymerize, causing cast iron to solidify as white or mottled iron. Hereafter, the elements narrowing the eutectic time interval (Cr, V, Ti) will inhibit graphitization, while those elements enlarging the eutectic time interval (Si, Ni, Cu, Co) will promote graphitization. The influence of \( t_{EM} \) is more significant than \( t_{EG} \). The higher the \( t_{EM} \) is, the more beneficial the graphitization is. This is because at high temperature carbon atoms are easier to diffuse and polymerize.

Te, Bi, Mg and Ce have strong chill tendency and are easy to promote white solidification. These elements belong to surface active elements, have low melting point, and are easy to deposit and to be enriched on the base face of graphite nuclei. They chemically react with free \( \sigma \) bond of graphite, forming strong film. This film inhibits carbon atoms to deposit on base face of graphite causing graphite to loss the effect as nuclei. Sulphur has similar influencing mechanism on graphitization of cast iron. Sulphur forms low melting point (950 – 975 ℃) Fe-FeS-Fe\(_3\)C three-element eutectic which is enriched as thin film on the interface of graphite and inhibits carbon diffusion.

Carbon and silicon are both strong graphitizer and the main elements in cast iron. However, their graphitization mechanism is different. Carbon increases the amount of carbon group (C\(_n\)), thus promotes the formation of graphite nuclei. Silicon strongly impairs the connect bond between Fe-C, obviously enlarges the \( t_{EG}-t_{EM} \) interval and significantly increases \( t_{EG} \), thus influences the precipitation of graphite. Therefore, Si has stronger graphitization ability than C. For example, if w(Si)<1.2%, even carbon is increased to w(C)>3.5%, it is still difficult to obtain full grey solidification.

N, H and O elements all influence chill tendency of cast iron in certain degree. Their influence mechanisms are different; and how they affect the chill is not clear. In iron melt, when the resolved oxygen combines with other elements and forms oxides acting as nuclei for non-homogeneous nucleation, the resolved oxygen will promote graphitization. Uncombined oxygen will increases white tendency. The effect of nitrogen is related to its resolved amount, only when exceeding a certain of amount, nitrogen will show unfavorable effect on graphitization. Hydrogen has stronger chilling tendency than nitrogen, when w(H)>10\(^{-4}\%), hydrogen will increase undercooling, obviously inhibit graphitization. The thinner the casting section, the stronger the effect of hydrogen.

Segregation of alloy elements during solidification will increase the formation of eutectic grain boundary carbides. Graphitization elements segregate in solid austenite; while the carbide forming elements are more enriched in liquid. The liquid with rich Cr, V
and Ti etc. will increase $t_{es}$ of residual liquid; while the poorer distribution of Si, Ni and Cu in remaining liquid will decrease $t_{es}$.

It is clear that alloy segregation will narrow the $t_{es}$-$t_{em}$ interval, see Fig.1-21. The closer to the end of the solidification, the more serious the phenomena, as shown with dash line in Fig.1-22. This is because the residual liquid at the end of solidification has a small volume but strong segregation. Due to decreased $t_{es}$, this residual liquid does not solidify even at very late stage, thus, the end temperature of eutectic $t_{es}$ is significantly decreased. The increased $t_{em}$ and decreased $t_{es}$ make the iron melt easy to change from grey to white solidification.

![Eutectic Reaction](image)

**Fig. 1-21: Effect of alloy segregation on $t_{es}$ and $t_{em}$**

![Alloy Elements Segregation](image)

**Fig. 1-22: Alloy elements segregation at late stage of solidification significantly increases the formation of carbides at the grain boundary**

Table 1-2 lists the effect of some common elements on graphitization or white tendency of cast iron solidification.

From above, alloy elements, through changing eutectic temperature (see Fig. 1-7), influencing carbon activity and nucleation state, can influence eutectic solidification. By adjusting the liquid composition, the cooling rate and nucleation state, the cast iron can be transformed from grey to white or vice versa. The factors affecting nucleation state include: chemical composition, charge materials, melting process (furnace, overheating, holding) and inoculation.

Grey or white solidification of cast iron is only, from crystalline thermodynamics, a problem whether iron-carbon alloy follows stable system (Fe-Graphite) or metastable system crystallization(Fe-Fe$_3$C); it does not mean that the crystallization condition is equilibrium or non-equilibrium. Crystallization of graphite does not necessarily occur at equilibrium state; the formation of cementite does not necessarily require non-equilibrium crystalline condition. Nevertheless, under non-equilibrium, cast iron is easy to transfer from stable system to metastable system. In the control of grey or white solidification
process, dynamical factor plays a very important role; adjusting composition, changing cooling rate, improving melting process and liquid treatment are all the engineering applications in this respect.

(Continued)

### Table 1-2: Effects of elements on graphitization or white tendency of cast iron solidification

<table>
<thead>
<tr>
<th>Element</th>
<th>Degree of effect</th>
<th>Content (mass%)</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te</td>
<td>Effect on white</td>
<td>strongest 0.05–0.02</td>
<td>Form thin film absorbed on interface inhibiting carbon atom diffusion</td>
</tr>
<tr>
<td>Bi</td>
<td>second strongest</td>
<td>&gt;0.03</td>
<td>Less sulphides, causing significant less graphite nuclei</td>
</tr>
<tr>
<td>Mg</td>
<td>strong &gt;0.03</td>
<td>Low-melting point sulphide eutectics distributing on solid/liquid interface and inhibiting carbon atom diffusion</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>strong &gt;0.03</td>
<td>Strong carbides former</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>strong &lt;0.02 0.17–0.35</td>
<td>Strong carbides former, reduce temperature interval between stable and metastable systems</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>second strongest</td>
<td>&gt;0.3</td>
<td>Form carbides; reduce temperature interval between stable and metastable systems</td>
</tr>
<tr>
<td>V</td>
<td>second strongest</td>
<td>0.3–5</td>
<td>Form carbides</td>
</tr>
<tr>
<td>Cr</td>
<td>moderate &gt;0.1</td>
<td>Form carbides; reduce temperature interval between stable and metastable systems</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>moderate &gt;1.5</td>
<td>Form carbides</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>moderate &gt;2.0</td>
<td>Form carbides</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>weak &gt;2.5</td>
<td>Form carbides</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>No</td>
<td>Form high-melting point compounds as graphite nuclei, but also susceptible to carbide formation</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>No 0.04–0.1</td>
<td>Not form carbides</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>No &lt;0.7</td>
<td>Not form carbides</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>No 0.05–0.12</td>
<td>Not form carbides</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>weak &gt;0.6</td>
<td>Not form carbides; enlarge temperature interval between stable and metastable systems</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>weak &gt;0.5</td>
<td>Not form carbides; enlarge temperature interval between stable and metastable systems</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>moderate ≤0.3</td>
<td>Form titanium and nitrogen compounds, parts of the compounds act as nuclei for graphite</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>second strongest</td>
<td>&gt;2.2</td>
<td>Promote graphite nuclei</td>
</tr>
<tr>
<td>Al</td>
<td>strong 0.1–8, 22–28</td>
<td>Not form carbides; raise eutectic temperature of stable systems; reduce solubility of carbon in iron melt</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>strongest &gt;1.4</td>
<td>Not form carbides; significantly enlarge the temperature interval between stable and metastable systems; reduce solubility of carbon in iron melt</td>
<td></td>
</tr>
</tbody>
</table>

### About the author

Professor Zhou Jiyang, born in 1936, graduated from the Mechanical Department of the Dalian Institute of Technology (now the Dalian University of Technology) in 1959, majoring in foundry. Then he taught at the University, as a lecturer in 1978, and an associate professor in 1983. At the same year, as a visiting scholar, he went abroad to a Research Institute of Foundry in Germany, affiliated to the Metallurgy Department of Aachen TH. He did his doctoral study program from 1984 to 1986 at Aachen TH. After obtaining his doctor’s degree in June 1986, he worked for the Department Division of Science and Technology, in Germany BUDERUS Company Iron Foundry. After returning to China from Germany in 1987, he continued his teaching career at Dalian University of Technology. He was appointed as professor in 1991 and advisor to doctoral candidates in 1993.

He was a member of council of Foundry Institution of Mechanical Engineering Society (FICMES), and a member of Cast Iron and its Smelting Technical Committee of FICMES as well as Vice President of Dalian Foundry Institute.