Influence of Alloying Elements and Melting Conditions on Graphite Morphology and Matrix in Fe-C and Ni-C Alloys

Fe-C 及び Ni-C 合金の黒鉛形態と基地組織に対する合金元素と溶解条件の影響

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Chapter 1 Introduction

It is well known that the spheroidal graphite cast iron has a better comprehensive mechanical property (strength, toughness, wear resistance, etc.) compared to the flake graphite cast iron, and the main applications are the automobile parts such as the chassis, the crank shaft and the suspension, and the industrial machinery products namely the cast iron pipe and the construction machinery. However, the invention of the spheroidal graphite cast iron was totally by accident. In 1947 Morrogh \textsuperscript{1-3}) added Ce and in 1948 Gagnebin \textsuperscript{4) added Mg to the cast iron, and the spheroidal graphite cast iron was invented as a new kind of material with a superior mechanical property. Since then, the spheroidal graphite cast iron has been used as a main material of the cast iron, and much research work has been conducted in order to explain the formation mechanism of the spheroidal graphite phase in it.

The mechanical property of the cast iron is determined both by the graphite morphology and the matrix. However, the chunky graphite often appears in the heavy spheroidal graphite iron castings as a result of the significant undercooling during the eutectic solidification. On the other hand, the spheroidal graphite iron castings are produced from the B-contained steel scrap, which changes the matrix from a pearlite matrix to a ferrite matrix when Cu exists. Both of the two aspects will lead to a decrease of the mechanical property of the high-strength spheroidal
graphite iron castings. In this study, a series of researches were carried out in order to investigate the influence factors and the controlling methods of the formation of the chunky graphite morphology and the ferrite matrix in the spheroidal graphite cast iron.

The formation sequence of the chunky graphite in the heavy castings was not clear. In this study, the investigations were carried out both in the Fe-C and the Ni-C alloy by comparing the relationship between the graphite morphology and the thermal analysis curves.

In past research, many parameters were found to affect the graphite morphology and the matrix in the cast iron, such as the kind of the addition elements and the melting conditions \(^5,6\). However, there are few reports which describe the relationship between the graphite and the matrix in the cast iron because of the difficulty caused by the phase transformation in the matrix after the eutectic solidification. Ni-C alloy was employed in this study to investigate in detail the effects of the cooling rate, the atmosphere and the holding time on the graphite morphology. Meanwhile, as there is no phase transformation in the Ni-C alloys, the crystallographic orientation of the matrix around the graphite was also studied by EBSD observations.

About the influence of alloying elements on the matrix of cast iron, there has been a significant number of studies \(^7-15\) showing that Cu was a pearlitization element both in the flake and spheroidal graphite cast irons. However, the actual influence of Cu on the matrix of the flake graphite cast iron was not clear \(^7,16\). In this study, the iron alloys with almost the identical C and Si contents were used, and the influences of the alloying
elements of Cu, Mn and P on the matrix of the flake and the spheroidal graphite cast irons were discussed. Pearlitization effect of Mn and P was found in both irons, while that of Cu was found only in the spheroidal graphite cast iron. For the flake graphite cast iron, Cu has a ferritization effect. To investigate the mechanism of the different effects of Cu, the distribution of Cu was studied in both irons, and the Cu film around the spheroidal graphite was confirmed using a special etching method.

In order to obtain the high-strength spheroidal graphite cast iron, Cu is often added in the production process. However, an unusual phenomenon was reported by many researchers that the matrix is ferrite in the Cu-alloyed spheroidal graphite cast iron when B is contained \(^{17,18}\). In this study, the interaction between B and Cu was also investigated, and its counteraction was discussed.

References

8) A. De Sy: Cu and Technology, 6 (1967) 12-23.

9) A. De Sy: Modern Castings 41 (1962) 390-399.


Chapter 2
Background Studies

2.1 Spheroidal graphite

2.1.1 Formation conditions of spheroidal graphite

Spheroidal graphite cast iron was invented by Morrogh et. al. in 1947 \(^{1-3}\) and Gagnebin et. al. in 1948 \(^4\). In a hypereutectic Fe-C alloy with less than 0.02 mass\%S (abbreviated as \%) and an alloy with 0.02\%S, more than 0.02\%Ce and 0.04\%Mg were added respectively and thus, the spheroidal graphite cast iron was investigated for the first time. Morrogh \(^5\) reported in 1955 that more than 0.04\%Mg should be added to the melt even if the content of S is less than 0.015\%, and the vermicular graphite will appear when the additive amount of Mg is insufficient. Therefore, the sulfur and the oxygen in the melt should be strictly controlled in the melting process. In the research of Loper et. al. \(^6\) showed that the graphite morphology is flake when the ratio of Mg and S is smaller than 1.0 and is spheroidal when it is greater than 3.0, and is CV graphite when the ration is between 1.0 and 3.0.

Nevertheless, there have been some reports that the spheroidal graphite could also form without the addition of the spheroidizing element, such as Mg or Ce. Buttner et. al. \(^7\) indicated in his research that the wettability of the melt on a graphite crucible becomes worse when Mg is added. In the
study after, Keverian et. al 8) produced the spheroidal graphite cast iron using the vacuum induction furnace without adding the spheroidizing element. The spheroidal graphite was confirmed in the alloy at the cooling rate of 60K/min, and they indicated that the effect of the spheroidizing elements of Mg and Ce is to remove the interface active elements, such as sulfur and oxygen, from the melt. Other research 9) also approved that the spheroidal graphite could form with the vacuum induction furnace.

The spheroidal graphite obtained with the addition of the spheroidizing element or the vacuum melting precipitates directly from the melt regardless of the composition is of the hypereutectic or of the hypoeutectic. The evidence is that when rapidly cooled, the spheroidal graphite which should be surrounded by the austenite shell connects directly with the eutectic ledebrite 10-12). In addition, the number of the spheroidal graphite increases with the centrifugal force of the centrifugal casting 13). What’s more, the undercooling in the eutectic solidification in the spheroidal graphite cast iron is significant than in the flake graphite cast iron 11),14). There was also research showing that when the cooling rate increases, the vermicular graphite changes shape to the spheroidal graphite 15).

According to the comprehensive review by Lux et. al. 16, 17) in 1972, the low content of sulfur and oxygen and the significant undercooling are the necessary conditions for the formation of the spheroidal graphite. This review showed that the content of sulfur and oxygen not more than 10ppm is a necessary condition for the formation of the spheroidal graphite. In addition, the spheroidal graphite forms more easily at a higher cooling rate.
After that, many studies on the indispensable conditions for the formation of the spheroidal graphite have been carried out in detail. Subramanian et al. \(^{18}\) studied the relationship of the activities of sulfur and oxygen and the graphite morphology using the thermodynamic calculation in the Ce, Mg or Ca added Fe-C-Si melt, and the result is shown in Fig. 2.1. In Fig. 2.1, the formation field of the spheroidal graphite and CeS is identical, where the activities of sulfur and oxygen are below \(2.3 \times 10^{-3}\) and \(3 \times 10^{-7}\) respectively. In other area, namely out of the formation field, CeS, Ce\(_2\)O\(_2\)S\(_2\) or Ce\(_2\)O\(_3\) forms with the increase of the activity of oxygen, and Ce\(_3\)S\(_4\) or Ce\(_2\)S\(_3\) with the increase of the activity of sulfur. The formation of these sulfides or oxides indicates that the vermicular graphite or the flake graphite forms as a stable phase. However, this figure only applies to the situation in which the melt is slowly cooled, while the deviation occurs when the melt is rapidly cooled. Argo et al. \(^{19}\) studied the change of the cooling rate \(R_1\) on the graphite morphology in the Mg-treated unidirectionally solidified Fe-C melt. The result showed that the spheroidal graphite forms when rapidly cooled at a low Mg content. Stefanescu \(^{20}\) investigated the effect of the Ce content and the G/R value (G means the temperature gradient in the melt at the S/L interface) on the graphite morphology, and the result is shown in Fig. 2.2. The graphite morphology changes from flake and vermicular to spheroidal with the increase of the Ce content and the G/R value. These researches mentioned above are mainly discussed on the spheroidizing element-added alloys. Nevertheless, the research with the pure Ni-C alloy and Fe-C alloy was also carried out. According to the research work of
Hellawell \textsuperscript{21)}, in the unidirectionally solidified pure Ni-C alloy, the graphite morphology was of the fine graphite at the solidification rate of 100mm/h while the spheroidal one formed when the solidification rate was more than 240mm/h. Lux et. al. \textsuperscript{22}) reported that in the pure Ni-C alloy solidified at 600mm/h, the spheroidal graphite formed in the solid part while the flake-like graphite appeared in the liquid part. The research of Nakae et. al. \textsuperscript{23}) showed that at the solidification rate of 150mm/h, the graphite is fine flake-like, and the liquid/solid interface is stable, as shown in Fig. 2.3. When the alloy was changed to the Ni-C-Mg, the growth model of the graphite changed from the continuous one to the discontinuous one at 150mm/h, and the existence of the spheroidal graphite was confirmed in the discontinuous graphite morphology. In addition, Nakae et. al. \textsuperscript{24}) also suggested that the spheroidal graphite could form both in the Fe-C alloy and the Fe-C-Mg alloy cooled at the rate of 1000K/min for the Fe-C alloy. Their study also showed that the addition of Ce could promote the formation of the spheroidal graphite even at a slow cooling rate of 5K/min. While for the high-purity Fe-C and Fe-C-Si alloy, the spheroidal graphite could form at a high cooling rate without the addition of the spheroidizing element.
Fig. 2.1 Graphite morphology control diagram

Fig. 2.2 Influence of G/R ratio and residual Ce content on graphite morphology transition in cast iron.
2.1.2 Solidification of spheroidal graphite cast iron

The eutectic structure could be divided into two types. The eutectic of metal/metal is the normal eutectic and that of metal/nonmetal like the Fe-C alloy and the Al-Si alloy is the abnormal eutectic. Most of the cast irons are the Fe-C-Si alloys, and so is the spheroidal graphite. Therefore, the eutectic in the spheroidal graphite is also abnormal eutectic.

Here we consider a eutectic alloy composed of metal and metal. In this binary alloy, the phase $\alpha$, the phase $\beta$ and the liquid could coexist at one point at the eutectic temperature, therefore, the degree of freedom is 0. Then, the eutectic temperature is constant. The change of the solid/liquid interface morphology of this binary alloy with the eutectic solidification

<table>
<thead>
<tr>
<th></th>
<th>Ni - C</th>
<th>Ni - C - Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 K/min</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>200 K/min</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 2.3 S/L interfacial microstructure of Ni-C and Ni-C-Mg samples solidified at different rates.
rate is shown in Fig. 2.4 27). When the solidification rate is low, the solid/liquid interface is flat while is of cellular or dendrite at the high solidification rate. However, the solid/liquid interface is not flat even at a low solidification rate in the case of the Fe-C alloy, which is the metal/nonmetal system and the eutectic is classified as the anormalous eutectic. Fig. 2.5 shows the unidirectionally solidified structure 28). The morphology of the graphite is flake and the head stretches into the melt in the Fe-C alloy, and is of spheroidal, surrounded by austenite and does not contact with the melt directly in the Fe-C-0.2mass%Ce alloy. This phenomenon is known to all, and is also approved by Lux by quenching the spheroidal graphite cast iron in the process of the eutectic solidification. The eutectic structure of the quenched alloy is shown in Fig. 2.6 29). The structure which austenite surrounds the spheroidal graphite (or Si in the Al-Si alloy) is called the “halo” 29). This is “one way nucleation” and is a unique phenomenon in the Al-Si eutectic and the Fe-C eutectic. The spheroidal graphite which formed in the melt is surrounded by austenite during the quenching. In other words, the spheroidal graphite is in direct contact with the melt before the eutectic solidification, and is surrounded by austenite and separates from the melt after the eutectic solidification begins. This structure is analogous to the graphite head in the Fe-C-0.2mass%Ce alloy. It could be understood that the growth of the flake graphite depends on the diffusion of carbon from the melt directly and through austenite shell indirectly, while the growth of the spheroidal graphite could only depend on the diffusion of carbon through austenite
shell. This is believed to be the primary cause why the graphitization in the spheroidal graphite cast iron is more difficult than that in the flake graphite cast iron. The difficulty of the graphitization will cause the undercooling in the melt, and thus causes the formation of the chill and the shrinkage. That is why the chill and the shrinkage are much easier to form in the spheroidal graphite cast iron than in the flake graphite cast iron, while has no relationship with the CE value \(^{30, 31}\).

Fig. 2.4 Coupled growth model in eutectic solidification
Fig. 2.5 Structures of the interface in Fe-C-S and Fe-C-Ce alloy (2 mm/h).

Fig. 2.6 Model of eutectic morphology of quenched spheroidal graphite cast iron at eutectic solidification.

Fig. 2.7 shows the eutectic solidification mode of the spheroidal graphite cast iron. Before the eutectic solidification, the spheroidal graphite is in direct contact with the melt, and at the beginning of the eutectic
solidification process, austenite begins to surround the spheroidal graphite, and the growth rate of the spheroidal graphite only depends on the diffusion of carbon through the austenite shell. Meanwhile, the austenite shell also grows to be thicker and its growth rate is much faster than that of the spheroidal graphite. As the growth of the austenite shell continues, the growth rate of the spheroidal graphite becomes slower and slower, and at the end of the eutectic solidification, the graphitization of the spheroidal graphite is very difficult. The thickness of the austenite shell is calculated with the equilibrium diagram of the eutectic composition. As the volume fraction of the graphite is 7%, the thickness of the austenite shell is 1.4 times that of the radius of the spheroidal graphite, which is a barrier to the diffusion of carbon. Therefore, reducing the thickness of the austenite shell is beneficial to promote the growth of the spheroidal graphite. To achieve this purpose, it is effective to increase the number of the spheroidal graphite. For example, when the number of the spheroidal graphite is doubled, the radius and the spheroidal graphite and the thickness of the austenite shell could be reduced by 21% \(^{31}\). Suppose the volume fraction of the spheroidal graphite does not change. When the diameter of the spheroidal graphite reduces by half, the number of the spheroidal graphite increases by 8 times, which was confirmed by the optical microscope. For this reason, the inoculation is very important to promote the graphitization process.
Generally speaking, the growth of the eutectic is the “coupled growth” as shown in Fig. 2.4, which means the two phases and the liquid coexist and the two phases grow together. The field of the “coupled growth” of the common normal eutectic alloy is symmetric as shown in Fig. 2.8. Referring to the solidification model in Fig. 2.4, when the degree of undercooling is small, the solid/liquid interface is flat on the macroscopic level, which means the solidification rate is low. However, with the increase in the solidification rate, the degree of the undercooling becomes greater, and the interface changes to be dendrite or cellular.
Fig. 2.8 Coupled growth zone of normal eutectics at eutectic solidification

In the case of the anormalous eutectic, the eutectic grows in a different pattern, which is not symmetric as that of the “normal eutectic”, and the “couple zone” leans to the nonmetal side, as shown in Fig. 2.9. The “planar” in the figure is a concept on the macroscopic level, while on the microscopic level (namely the atomic level), the interface is rough. As already mentioned, the spheroidal graphite does not directly contact with
the melt in the eutectic solidification process. Therefore, the growth pattern of the eutectic of the spheroidal graphite is not the “coupled growth”, and is called the “divorced eutectic growth”. The solidification of the spheroidal graphite is very complicated because the eutectic is “anormalous eutectic” and the growth pattern of the spheroidal graphite is the “divorced eutectic growth”.

![Fig. 2.9 Coupled growth zone and morphology of solid/liquid interface of anormalous eutectics at eutectic solidification.](image)

### 2.1.3 Growth models of spheroidal graphite

a) Circumferential growth model

Schram’s 32) macromolecule spheoidizing model was used by Sadocha 33) to establish the circumferential growth model of the spheroidal graphite at high graphite/melt interface energy. Sadocha reported that although the preferred growth direction of the graphite is the prism <0001>, the
spheroidal graphite remains its shape by rotation, keeping its base plane in contact with the melt when it grows. The growth of the graphite proceeds on many steps in different directions, and the site the graphite contact with the melt is where the crystallization occurs, and the spheroidal graphite is polycrystalline as a result. The surface morphology observation of the spheroidal graphite is shown in Fig. 2.10(b).

b) Cone-Helix growth model

Based on the phenomenon that the whisker graphite grown from the gaseous carbon has a similar structure with that of the cross section of the spheroidal graphite, Double and Hellawell \(^{34,35}\) suggested the Cone-Helix growth model of the spheroidal graphite. Typical graphite fiber morphology is shown in Fig. 2.11(a) and (b), that the angle of the conical tip is \(140^\circ\), and that of the repetitive part is \(21.8^\circ\), identical with that of the angle of the defect of the flake graphite \(^{36}\). Under this growing condition, the graphite grows in the pattern of Fig. 2.11(c), and the interface energy between it and the melt decreases, and is possible to grow from the base plane. Most of the graphite crystals grow from the center in a radial pattern, and in the end, the spheroidal graphite is surrounded by the base planes. And then, the growth of the spheroidal graphite at the surface is in a layer growth pattern from the bicrystals and the low angle grain boundary \(^{36-38}\) of the Conical-Helix growth. Therefore, the surface of the spheroidal graphite is composed of many layers.
2.1.4 Spheroidizing theory

There have been many different theories on the formation of the spheroidal graphite, and most of them were explained by Lux \(^{39-41}\) and recent research \(^{42-44}\). These theories are totally different from each other, and are summarized in Table 2.1.

(a) Circumferential growth model of a graphite spheroid.  
(b) Model of spheroidal graphite surface.

Fig. 2.10 Model of spheroidal graphite surface and circumferential growth.

Fig. 2.11 Growth of spheroidal graphite from conical helix crystals.
Table 2.1 Spheroidizing Theories

<table>
<thead>
<tr>
<th>No.</th>
<th>Theory</th>
<th>Researcher</th>
<th>Year</th>
<th>Main Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>“Supersaturated austenite” theory</td>
<td>A. Wittomoser</td>
<td>1950</td>
<td>The graphite precipitates directly from the melt, and is surrounded by austenite, through which carbon diffuses and the graphite grows.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A. De Sy</td>
<td>1953</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>E. Piwowarsky</td>
<td>1950</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>“Carbide decomposes” theory</td>
<td>H. Morrough</td>
<td>1947</td>
<td>Solidified in the form of the chill solidification, and then decomposes and the graphite precipitates.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W. Williams</td>
<td>1947</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>“Undercooling” theory</td>
<td>A. Wittomoser</td>
<td>1951</td>
<td>The nucleus disappears with the addition of Mg, and the growth rate of the graphite in the axes a and c reduces when undercooled.</td>
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<tr>
<td></td>
<td></td>
<td>R. Mehl</td>
<td>1950</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>“Interfacial energy” theory</td>
<td>F. Buttner</td>
<td>1951</td>
<td>The addition of Mg increases the graphite/melt interfacial energy.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y. Ueda</td>
<td>1978</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>“Adhesion” theory</td>
<td>I. Itaka</td>
<td>1950</td>
<td>Mg adheres at the graphite surface and increases the surface tension.</td>
</tr>
<tr>
<td>6</td>
<td>“Condensation” theory</td>
<td>F. Furrum</td>
<td>1952</td>
<td>The graphite condenses to form the spheroidal graphite in the high C and Si density area.</td>
</tr>
<tr>
<td>7</td>
<td>“Dislocation” theory</td>
<td>M. Hillert</td>
<td>1954</td>
<td>The spheroidal graphite forms from the screw dislocation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>L. Qifu</td>
<td>1993</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>“Bubble” theory</td>
<td>S. Karsay</td>
<td>1964</td>
<td>The graphite grows inward in the fine bubble of Mg at the beginning, and then outward.</td>
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<tr>
<td></td>
<td></td>
<td>B. Zhang and Y. kawano</td>
<td>1983</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>H. Itofuji</td>
<td>1995</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>“Nucleus” theory</td>
<td>A. De Sy</td>
<td>1950</td>
<td>The nucleus of the spheroidal graphite is confirmed to be the Mg-Si compound, substance of the spinel structure, the C rich compound, the oxide or the sulfide.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A. Rosenstiel</td>
<td>1964</td>
<td></td>
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<td></td>
<td></td>
<td>M. Jacobs</td>
<td>1974</td>
<td></td>
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<td></td>
<td></td>
<td>L. Ivaklenko</td>
<td>1979</td>
<td></td>
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<td></td>
<td></td>
<td>T. Kusakawa</td>
<td>1976</td>
<td></td>
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<td>H. Horie</td>
<td>1985</td>
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<td></td>
<td></td>
<td>L. Qifu</td>
<td>1993</td>
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</table>
2.2 Chunky graphite

In the center part of the heavy spheroidal graphite iron castings, abnormal graphite often appears, and is called the chunky graphite, as shown in Fig. 2.12. The existence of the chunky graphite causes the reduction in the mechanism properties of the castings, especially in the elongation and the impact value. Therefore, it is necessary to take measures to avoid the formation of the chunky graphite in the castings.

Study on formation mechanism of chunky graphite

Much attention has been paid on the formation mechanism of the chunky graphite, and the most famous study is that of Karsay. Fig. 2.13 is a typical morphology of the chunky graphite. Karsay indicated in his research the formation-promoting elements of the chunky graphite like Ca, Ce, Ni and Si, and the elements of As, Bi, Cu, Pb, Sb and Sn, which will prevent the formation of the spheroidal graphite and promote the formation of the flake graphite. Morrogh showed the maximum amount of the formation-preventing elements of the spheroidal graphite that could be allowed in the production of the spheroidal graphite cast iron as follows.

Al<0.100%, Sb<0.002%, As<0.020%, Bi<0.002%, Cd<0.010%, Cu<3.00%, Pb<0.002%, Se<0.030%, Te<0.020%, Sn<0.15%, Ti<0.10%, Zn<0.10%, Zr<0.10%

These spheroidal graphite formation-preventing elements are in agreement with that of the formation-promoting elements of the flake
graphite. However, an interesting phenomenon is that the chunky graphite formation-promoting elements could be divided into two groups: Ca and Ce are the spheroidizing elements, while Ni and Si are the graphitizing elements.

Fig. 2.12 Chunky graphite at cross section of heavy casting (127mmx127mmx254mm).

Fig. 2.13 Typical morphology of chunky graphite.
Karsay\(^45\) listed the chunky graphite formation-preventing elements of As, Cu, Sb, Sn and Te, which are also the formation-preventing elements of the spheroidal graphite. He studied the relationship between the formation of the chunky graphite and the contents of Si and Sn, and showed the results in Fig. 2.14. The addition of Sn could resist the formation of the chunky graphite when the Si content increases, and for the heavy castings, the Si content should be as low as possible\(^46\).

Karsay also indicated that with the increase of the added amount of the Fe-Si-Sr inoculant, the number of the graphite grains and the chunky graphite volume fraction increases, as shown in Fig. 2.15. This is a strange result and may be because the promoting effect of Si exceeds the restricting effect of Sr on the formation of the chunky graphite.

![Graph showing combined effect of Si and Sn on chunky graphite formation.](image)

Fig. 2.14 Combined effect of Si and Sn on chunky graphite formation.
Nakae agrees with the results of Karsay’s investigation, and did some other study on the influences of the number of the spheroidal graphite grains and the inoculation on the formation of the chunky graphite. Nakae also indicated in his research that the addition of Si will increase the volume fraction of the chunky graphite, while it will also fine and increase the number of the sphroidal graphite grains. This study well explained the phenomenon in Karsay’s result.

Barton reported that the chunky graphite forms at the low cooling rate, and investigated the mechanical properties of the castings with the chunky graphite after the heat treatment. He also indicated that the addition of As could prevent the formation of the chunky graphite.
Church \textsuperscript{49}) investigated the influence of Ca in the ferro-silicon, and reported that at the same Si content, the inoculation promotes the formation of the chunky graphite more than the method of adding Si directly into the melt. In addition, keeping the melt after the addition of Si will prevent the formation of the chunky graphite.

Okada \textsuperscript{50}) reported that the chunky graphite is easy to form in the high-purity alloy, and the addition of 0.02\% Bi or Te will effectively depress the formation of the chunky graphite. Prinz \textsuperscript{51}) investigated the impact factors for the formation of the chunky graphite, and reported Si promotes its formation because it increases the eutectic temperature. This indicates that the elements that could decrease the eutectic temperature will restrict the formation of the chunky graphite. Although in his research, the influences of the number of the spheroidal graphite grains and the thickness of the austenite shell formed around the spheroidal graphite at the solidification were mentioned, detailed investigation was not done.

Barton \textsuperscript{52}) suggested the chunky graphite-free conditions in heavy spheroidal graphite cast iron castings as follows: C < 3.4\% and Si < 1.5\%. Camponanes \textsuperscript{53}) indicated the simultaneous addition of 0.002\%Sb and 0.02\%Ce is the most effective method in restricting the formation of the chunky graphite.

To sum up the previous investigations, Si, Ni, Cu, Ca and Ce are the formation-promoting elements of the chunky graphite. Addition of Sb or Te is an effective counteraction of the influence of Ce \textsuperscript{51-55}). Tsumura \textsuperscript{54}) investigated the influence of the content ratio of Sb and RE on the
formation resistance of the chunky graphite, and found that when the ratio is greater than 0.7, the chunky graphite will form. Kiguchi did research on the formation period of the chunky graphite in detail.

Nakae investigated the formation mechanism of the chunky graphite using the pure Fe-C-Ce alloy, the pure Fe-C alloy and the pure Fe-C-Si alloy. The formation area of the chunky graphite in the Fe-C-Si alloy is shown in Fig. 2.16. This result indicates that the degree of the undercooling increases with the thickness of the austenite shell, and then the carbon diffusion during the solidification of the spheroidal graphite is suppressed. As a result, the graphite begins to grow in the melt, in a continuous and branched manner, and forms the chunky graphite in the end. In order to better understand the continuous morphology of the chunky graphite, the matrix is removed by etching for the three-dimensional observation. This observation was carried out with the SEM in the Fe-C-Ce alloy cooled at 12mm/h of the one-direction solidification, and the morphology of the chunky graphite being like a coral was understood.

Nakae also reported that in the unidirectional solidification experiments, the graphite morphology changes from the spheroidal one to the chunky one when the solidification rate changed from 2mm/h to 4mm/h. The diffusion of carbon through the austenite shell in the alloy with the chunky graphite is much easier than that with the spheroidal graphite due to the difference in the austenite shell thickness. As a result, the solidification rate of the chunky graphite alloy is much faster than that of the spheroidal graphite, and then the degree of the undercooling is also smaller in the
alloy of the chunky graphite morphology. The reason of the graphite morphology change from the spheroidal one to the chunky one lies in the increase of the austenite shell thickness at the end of the solidification process. Therefore, in order to restrain the formation of the chunky graphite, an effective method is to reduce the thickness of the austenite shell. The thickness of the austenite shell of the spheroidal graphite cast iron at the end of the solidification is 1.4 times that of the radius of the spheroidal graphite. Therefore, reducing the spheroidal graphite size will help to reduce the thickness of the austenite shell, which could be realized by increasing the number of the spheroidal graphite. Sb could restrain the formation of the chunky graphite is also because it can increase the number of the spheroidal graphite.

Fig. 2.16 Formation area of chunky graphite in high-purity Fe-C-Si alloy.

(SG: spheroidal graphite; PG: plate-like graphite;
FG: flake graphite; ChG: chunky graphite.)
2.3 Flake graphite

Morphology of flake graphite

The morphology of the flake graphite could be divided into five types according to the ISO standard, as is shown in Fig. 2.17. However, Nakae indicated that the coarse graphite in the C-type graphite forms at the beginning of the solidification process, which is different from the formation of the A-type graphite, and thus should not be considered when dividing the flake graphite morphology. In addition, according to the dividing method of the flake graphite morphology, the E-type graphite is a separate type from the A-type graphite, because the dendrite could be observed in it. However, the E-type graphite morphology could be achieved from the A-type graphite by increasing the cooling rate, and thus should also not be defined as a different type from the A-type graphite. What’s more, the B-type graphite is a production of the morphology change of the D-type graphite to the A-type graphite during the eutectic solidification, and thus should also be considered as a separate type. Based on these considerations, Nakae indicated the morphologies of the graphite are only the A-type graphite and the D-type graphite. The evidence is shown with the unidirectionally solidified flake graphite cast iron, in which the graphite morphology changes from the A-type to the D-type at the solidification rate of 10mm/h. The change of the graphite morphology was observed with the SEM, as is shown in Fig. 2.18. The morphological change solidification rate differs when different alloying-elements are added. For example, the
solidification rate is lower in the low-S-content cast iron and the Ti-added cast iron.

Fig. 2.17 Five different types of flake graphite according to ISO standard.

Fig. 2.18 Change of graphite morphology from A-type to D-type.
2.4 Matrix of cast iron

It is well known that the cast iron is composed of the graphite and the matrix. If the graphitization during the cooling process is not sufficient, the graphite and the cementite will co-exist in the matrix. Two typical kinds of the matrix of ferrite and pearlite will be introduced here in detail.

Ferrite is called the $\alpha$ Fe (the $\alpha$ solid solution) and very soft, and contains a small amount of C. As the cast iron often contains some Si, ferrite is actually Silicon-ferrite, and is harder and more brittle. Therefore, the property of the matrix is affected by the content of Si.

Pearlite is a mixed morphology of cementite and ferrite, which is obtained by the eutectoid transformation of austenite, and is usually in lamellar structure. The morphology of pearlite after the heat treatment is spheroidal. In general, pearlite and ferrite coexist in the matrix of the cast iron. In particular, the coexistence morphology of pearlite and ferrite in the spheroidal graphite cast iron is called the “bull’s eye”.

Research on effect of elements on matrix of cast iron

There have been a lot of investigations on the effect factors on the matrix morphology. Meanwhile, a significant number of studies $^{61-69}$ on the influence of Cu on the matrix of cast iron were carried out, showing that Cu was a pearlite-forming element both in the flake and spheroidal graphite cast irons. However, in the book of ‘Cu Addition in Cast Iron’ $^{61}$, Fig. 22 on p. 42 was misquoted for the flake graphite cast iron, while in fact, it is
the data for the spheroidal graphite cast iron \(^{70}\). Therefore, the actual influence of Cu on the matrix of the flake graphite cast iron was not clear, and furthermore, the ASM Handbook \(^{65}\) reported that a Cu content of less than 0.3% does not significantly affect the matrix of the flake graphite cast iron, while for the spheroidal graphite cast iron, it is a pearlite-stabilizing element \(^{64,66,68}\). According to the research done by Karsay \(^{67}\), in the spheroidal graphite cast iron, the pearlite-stabilizing effect of Cu is much more obvious than that of Mn. Nevertheless, in his earlier research \(^{69}\), he did not mention the influence of Cu, while the optimum value of Mn in stabilizing the pearlite in the matrix was reported.

Mn, Cr and Mo are the cementite-stabilizing elements, while Cu and P are the graphitizing elements for solidification. Concerning the pearlite-stabilizing effect of Cu, Ishiguro \(^{71}\) reported that the matrix of the spheroidal graphite cast iron for the 2.8% Cu addition is completely pearlite, and succeeded in observing the existence of the Cu film around the spheroidal graphite on the fracture surface for the first time. Therefore, we considered that the pearlitization mechanism could be explained by the existence of the Cu film around the spheroidal graphite. However, Igarashi \(^{72}\) observed the ferrite matrix and the precipitated secondary graphite on the spheroidal graphite surface in the B-contained 0.5%Cu-alloyed spheroidal graphite cast iron, and indicated that it is due to the existence of B. He also estimated the existence of the Cu film on the spheroidal graphite surface. Furthermore, Tsujikawa \(^{73}\) also tried to find the Cu film based on TEM observations, but failed to confirm its existence.
There have been few recent reports about the influence of Cu on the flake graphite cast iron and the influence is considered to be very weak. In this study, the cast iron with almost the same C and Si contents was used, and the influence of Cu on the spheroidal graphite cast iron and the flake graphite cast iron was discussed. In the flake graphite cast iron, because the pearlite-stabilizing effect of S is very strong \(^{74}\), then the same effect of Cu is difficult to detect. Therefore, the effects of S and Cu on the flake graphite cast iron are separately discussed.

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Chapter 3
Formation Sequence of Graphite in Eutectic Solidification

In order to investigate the formation mechanism of the spheroidal graphite and the chunky graphite, the formation sequence of the graphite of different morphology were investigated both in the Fe-C alloy and the Ni-C alloy by comparing the relationship between the graphite morphology and the thermal analysis curve.

3.1 Investigation in the Ni-C alloy

3.1.1 Experimental materials

In this investigation, the influence of the spheroidizing element on the graphite morphology was studied. Pure Ni metal and high-purity graphite electrode were used, and Ce, Mg and Ca were added to the Ni-C melt respectively. The carbon content was 2.2 mass% in each alloy, which was of the eutectic composition. The objective and actual chemical compositions of the Ni-C alloys are shown in Table 3.1-1 and Table 3.1-2.

3.1.2 Experimental procedure and devices

The Ni-C base melt was produced with an Al$_2$O$_3$-lined high-frequency induction furnace in an Ar gas flow. The melt was then casted into 20mmØ
cylindrical ceramic tubes. After solidification, the Ni-C alloy rods were cut into 90g short rods for getting the thermal curve analysis. Then, the sample was remelted in an alumina crucible, which was installed in a furnace of Fig. 3.1.

The furnace was working in a pure Ar atmosphere, which was realized by a vacuum pump for 3 times to vacuum the furnace chamber under $10^{-4}$ Torr, and then Ar was flowed into this furnace as a protecting atmosphere at 0.25L/min. The alumina crucible was covered with an alumina cap to guarantee the accuracy of the thermal analysis by the thermocouple. There was an 8mmΦ hole at the center, which was used for fixing thermocouple tube at the center of the melt. The heating part of the furnace was connected with a B-type thermocouple, which was connected with a PID controller to ensure the heating temperature of the crucible at 1723K. The sample was heated to 1723K at a heating rate of 15K/min, and held for 90min. Then the sample was cooled at a rate of 40K/min or 20K/min, and the cooling curve was recorded by a digital recorder every 1ms. When the measurement of the cooling curve was finished, the sample was taken out for polishing, and then observed by the optical microscopes and the SEM. For the SEM observation, the surface of the sample was etched by an etchant of HCl and H$_2$O$_2$ at a ratio of 2:1 for 10mins.
Table 3.1-1 Objective chemical composition of Ni-C alloy samples. [mass%]

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>Ce</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>①</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>②</td>
<td>2.2</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>③</td>
<td>2.2</td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>④</td>
<td>2.2</td>
<td></td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 3.1-2 Actual chemical composition of Ni-C alloy samples. [mass%]

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>S</th>
<th>Mg</th>
<th>Ce</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>①</td>
<td>(1.98)</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>②</td>
<td>(2.00)</td>
<td></td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>③</td>
<td>(1.94)</td>
<td></td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>④</td>
<td>(1.80)</td>
<td></td>
<td></td>
<td>0.048</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3.1 Schematic of thermal analysis furnace.
3.1.3 Results

3.1.3.1 Influence of addition element and cooling rate

First of all, the graphite morphologies of the 4 samples of the Ni-C, Ni-C-Mg, Ni-C-Ce and Ni-C-Ca were observed by the optical microscopes and the SEM. The graphite morphologies of these samples solidified at the cooling rate of 40K/min and 20K/min are shown in Fig. 3.2 and Fig. 3.3, respectively.

<table>
<thead>
<tr>
<th></th>
<th>1. Ni·C</th>
<th>2. Ni·C-Ce</th>
<th>3. Ni·C-Mg</th>
<th>4. Ni·C-Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical microscope</td>
<td><img src="image1.jpg" alt="Image" /></td>
<td><img src="image2.jpg" alt="Image" /></td>
<td><img src="image3.jpg" alt="Image" /></td>
<td><img src="image4.jpg" alt="Image" /></td>
</tr>
<tr>
<td>SEM</td>
<td><img src="image5.jpg" alt="Image" /></td>
<td><img src="image6.jpg" alt="Image" /></td>
<td><img src="image7.jpg" alt="Image" /></td>
<td><img src="image8.jpg" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 3.2 Graphite morphology at the cooling rate of 40K/min.
As can be seen, in the samples cooled at 40K/min, the spheroidal graphite and the chunky graphite coexisted in the Ni-C sample and the Ni-C-Ca sample, while there was only the spheroidal graphite in the Ni-C-Ce sample and the chunky graphite in the Ni-C-Mg sample. In the 20K/min samples, the graphite morphology was the same as that in the same sample of 40K/min except in the Ni-C-Ce sample. Chunky was the only graphite morphology in the 40K/min Ni-C-Ce sample. In addition, the chunky graphite appeared in the 20K/min samples were much coarser than that in the 40K/min ones. This is because the low cooking rate allows the carbon atom to have more time to diffuse. The graphite morphologies are summarized in Table 3.2.
Table 3.2 Graphite morphologies in Ni-C alloy samples at different cooling rates.

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Ni-C</th>
<th>Ni-C-Ce</th>
<th>Ni-C-Mg</th>
<th>Ni-C-Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>40K/min</td>
<td>SG*+CHG*</td>
<td>SG</td>
<td>CHG</td>
<td>SG+CHG</td>
</tr>
<tr>
<td>20K/min</td>
<td>SG+CHG</td>
<td>CHG</td>
<td>CHG</td>
<td>SG+CHG</td>
</tr>
</tbody>
</table>

(*SG: spheroidal graphite; CHG: chunky graphite.)

3.1.3.2 Relationship between thermal analysis curve and graphite morphology

The thermal analysis curves of these 4 Ni-C samples were measured. As the slope change of the thermal analysis curve reveals the formation of graphite of different morphology, the differential curves of the thermal analysis curves were analyzed for the confirmation of the slope change, and the results at the cooling rate of 40K/min are shown in Fig. 3.4, Fig. 3.5, Fig. 3.6 and Fig. 3.7, and those at 20K/min are shown in Fig. 3.8, Fig. 3.9, Fig. 3.10 and Fig. 3.11.
Fig. 3.4 Cooling and differential curve of Ni-C alloy at 40k/min.

Fig. 3.5 Cooling and differential curve of Ni-C-Ce alloy at 40k/min.
Fig. 3.6 Cooling and differential curve of Ni-C-Mg alloy at 40k/min.

Fig. 3.7 Cooling and differential curve of Ni-C-Ca alloy at 40k/min.
Fig. 3.8 Cooling and differential curve of Ni-C alloy at 20k/min.

Fig. 3.9 Cooling and differential curve of Ni-C-Ce alloy at 20k/min.
Fig. 3.10 Cooling and differential curve of Ni-C-Mg alloy at 20k/min.

Fig. 3.11 Cooling and differential curve of Ni-C-Ca alloy at 20k/min.
Based on the results of these experiments, in the Ni-C and Ni-C-Ca samples, the spheroidal graphite and the chunky graphite coexisted. Therefore, we will only study these two typical samples.

According to Nakae 1), the tip of the chunky graphite is surrounded by austenite phase during the eutectic solidification, while the thickness of the austenite shell is very thin. Nevertheless, the spheroidal graphite is covered with thick austenite phase during the eutectic solidification, and the thickness increases with time. The tip of the flake graphite could contact with the liquid directly. Therefore, the flake graphite could grow not only depending on the diffusion of the carbon atom from the liquid through the austenite shell to the inner chunky graphite, but also could be realized by the diffusion through the liquid directly.

The growth mode of the chunky graphite facilitates it with a possibility in the heat balance during solidification. On the other hand, the growth mode of the spheroidal graphite is quite different. There is an austenite shell around the spheroidal graphite at the beginning of the eutectic solidification, and this austenite shell also grows thicker with the proceeding of the solidification as already mentioned. When the shell is thick enough, the growth of the inner spheroidal graphite could only be realized by the carbon diffusion through the austenite shell, and it is also the only way that the spheroidal graphite grows. As a result, the carbon concentration in the liquid is getting higher and higher, and in the end, causes a constitutional supercooling in the liquid to form the chunky graphite. Therefore, the formation of the spheroidal graphite and the
chunky graphite could be distinguished from the thermal analysis curve.

The differential curve could be divided into two different periods A and B for the formation of the two different graphite morphologies. There is an obvious horizontal line in A period of the differential curve, which indicates the heat balance was obtained there. Therefore, this is the formation period of the chunky graphite. In B period, the thermal analysis curve drops continuously, indicating the formation of the spheroidal graphite.

Then, the length ratio of these two periods was calculated and compared with the area fraction of the chunky graphite and the spheroidal graphite in the samples. The area fractions of the spheroidal graphite in Ni-C and Ni-C-Ca samples at the cooling rate of 40K/min and 20K/min are shown in Table 3.4, while the ratios of the two periods in the differential curves are shown in Table 3.5.

<table>
<thead>
<tr>
<th>Table 3.4 Area fraction of spheroidal graphite by optical microscopes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area fraction of SG, %</td>
</tr>
<tr>
<td>Cooling rate (40K/min)</td>
</tr>
<tr>
<td>Ni-C</td>
</tr>
<tr>
<td>Ni-C-Ca</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3.5 Ratios of A and B periods in thermal analysis.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling rate</td>
</tr>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>Ratio of thermal analysis curve, %</td>
</tr>
<tr>
<td>curve, %</td>
</tr>
</tbody>
</table>
By comparing Table 3-4 and Table 3-5, we found that the area fraction of the graphite and the ratio of the period in the thermal analysis curve are in good accordance. Therefore, it could be confirmed that the chunky graphite forms before the formation of the spheroidal graphite in the Ni-C alloy.

In order to compare with that in the Fe-C sample, similar study was also done in the Fe-C sample.

3.2 Investigation in the Fe-C alloy

3.2.1 Experimental materials

In the investigation with the Fe-C alloy, the influence of Ce and Si on the graphite morphology was studied. The base melt was prepared by melting the 99.99% mass high-purity electrolytic iron, high-purity graphite electrode (<20 ppm impurities) and metallic silicon in a high-frequency induction furnace in an Ar atmosphere.

The CE value in the Fe-C alloy was at the eutectic composition of 4.3%. Different amount of Si and Ce was added to the base melt. The objective and actual chemical compositions of the Fe-C alloys are shown in Table 3.6-1 and Table 3.6-2 respectively.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.3</td>
<td>3.5</td>
<td>0.15</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
<td>3.5</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>3.3</td>
<td>4.0</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td>3.3</td>
<td>4.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Table 3.6-2 Actual chemical composition of Fe-C alloy samples. [mass%]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Ce</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>①</td>
<td>3.49</td>
<td>3.58</td>
<td>0.12</td>
<td>0.005</td>
</tr>
<tr>
<td>②</td>
<td>3.48</td>
<td>3.58</td>
<td>0.21</td>
<td>0.005</td>
</tr>
<tr>
<td>③</td>
<td>3.31</td>
<td>4.08</td>
<td>0.13</td>
<td>0.005</td>
</tr>
<tr>
<td>④</td>
<td>3.37</td>
<td>4.10</td>
<td>0.24</td>
<td>0.005</td>
</tr>
</tbody>
</table>

In the thermal analysis curve study, 90g of the sample was melted at 1723K, held for 90min, and then cooled at a rate of 25K/min. Other experimental procedure and devices were the same as those with the Ni-C alloy.

### 3.2.2 Results

The graphite morphology observed by the optical microscopes and the SEM are shown in Fig. 3.12 and Fig. 3.13 respectively. As can be seen, the area fraction of the chunky graphite didn’t change significantly in these 4 samples. The addition of Si had no influence on the chunky graphite area fraction. The thermal analysis curves are shown in Fig. 3.14, Fig. 3.15, Fig. 3.16 and Fig. 3.17. The area fraction of the spheroidal graphite and that calculated in the thermal analysis curve were compared in Table 3.7 and Table 3.8, which also agree well with each other. From the thermal analysis curve, it is clear that in the Fe-C alloy, the spheroidal graphite forms before the chunky graphite.
Fig. 3.12 Matrix and graphite morphology of Fe-C alloy (by optical microscope).

Fig. 3.13 Matrix and graphite morphology of Fe-C alloy (by optical microscope).
Fig. 3.14 Cooling and differential curve of 3.5Si-0.15Ce Fe-C alloy at 25k/min.

Fig. 3.15 Cooling and differential curve of 3.5Si-0.25Ce Fe-C alloy at 25k/min.
Fig. 3.16 Cooling and differential curve of 4.0Si-0.15Ce Fe-C alloy at 25k/min.

Fig. 3.17 Cooling and differential curve of 4.0Si-0.25Ce Fe-C alloy at 25k/min.
Table 3.7 Area fractions of different graphite morphologies measured by optical microscopes.

<table>
<thead>
<tr>
<th></th>
<th>SG</th>
<th>CHG</th>
<th>Ledeburite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $3.5\text{Si-0.15Ce}$</td>
<td>21.5%</td>
<td>78.5%</td>
<td>-</td>
</tr>
<tr>
<td>2 $3.5\text{Si-0.25Ce}$</td>
<td>17.9%</td>
<td>82.1%</td>
<td>-</td>
</tr>
<tr>
<td>3 $4.0\text{Si-0.15Ce}$</td>
<td>22.6%</td>
<td>77.4%</td>
<td>-</td>
</tr>
<tr>
<td>4 $4.0\text{Si-0.25Ce}$</td>
<td>11.1%</td>
<td>82.7%</td>
<td>6.2%</td>
</tr>
</tbody>
</table>

Table 3.8 Graphite fractions calculated in thermal analysis curves.

<table>
<thead>
<tr>
<th></th>
<th>SG</th>
<th>CHG</th>
<th>Ledeburite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $3.5\text{Si-0.15Ce}$</td>
<td>26.7%</td>
<td>73.3%</td>
<td>-</td>
</tr>
<tr>
<td>2 $3.5\text{Si-0.25Ce}$</td>
<td>21.9%</td>
<td>78.1%</td>
<td>-</td>
</tr>
<tr>
<td>3 $4.0\text{Si-0.15Ce}$</td>
<td>28.3%</td>
<td>71.7%</td>
<td>-</td>
</tr>
<tr>
<td>4 $4.0\text{Si-0.25Ce}$</td>
<td>18.2%</td>
<td>72.8%</td>
<td>9.0%</td>
</tr>
</tbody>
</table>

3.3 Conclusions

1. The thermal analysis curve of the eutectic solidification drops continuously both in the Ni-C alloy and the Fe-C alloy.
2. The precipitating sequences of the graphite in the Ni-C alloy and the Fe-C alloy are different.
3. In the Ni-C alloy, the chunky graphite precipitates before the spheroidal graphite, while the opposite in the Fe-C alloy.
4. The increase of the cooling rate decreases the area fraction of the spheroidal graphite in the Ni-C alloy.
5. The addition of Si between 3.5%-4% doesn’t change the chunky fraction significantly in Fe-C samples, while the addition of Ce increases the
chunky graphite area fraction.

Reference

Chapter 4

Influence of Melting Conditions on Graphite Morphology and Grain Number of Matrix

It is well known that the spheroidal graphite cast iron has a better comprehensive mechanical property (strength, toughness, wear resistance, etc.) compared to the flake graphite cast iron.

Ni and Fe are of the same family in the periodic table of elements, therefore, they have similar properties. Moreover, the phase diagram of the Ni-C alloy is much simpler than that of the Fe-C alloy, and there is no transformation during the cooling at the solidification. Based on these aspects, it would be interesting to investigate how the formation parameters affect the graphite morphology in the Ni-C alloy. For the reasons above, Ni-C alloy was used in this study for the observation easiness of the solidified structure.

In this study, a series of experiments were carried out in order to investigate in detail the influences of the melting conditions on the graphite morphology of the Ni-C alloys. Experiment-1: Influence of the cooling rate; Experiment-2: Influence of the sulfur addition; Experiment-3: Influence of the atmosphere and holding time; Experiment-4: Further investigation of the holding time. The crystallographic orientation of the matrix around the graphite was also studied in the Ni-C alloy with different graphite morphologies by EBSD observations. Meanwhile, we used the
“One Way Nucleation” theory to explain the growth mechanism of the Ni grains on the graphite, which has some relationship with the crystallographic orientation.

4.1 Experimental setup and procedure

4.1.1 Sample preparation

Pure nickel was melted by a high-frequency induction furnace with Ar gas flowing at 1.0L/min, and different amount of NiS, 99.999%Si, high-purity graphite, spheroidizing elements of pure Ce, pure Ca or Mg$_2$Ni were added to the melt to produce different kinds of alloys. After melting, the melt was cast into ceramic tube molds of 10mm diameter. The chemical compositions of the samples, Group 1 and Group 2, are given in Table 4.1. The Group 1 samples were sulfur-free, while the Group 2 samples contained a small amount of sulfur except for the sample .

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>S</th>
<th>Ce</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-C</td>
<td>1.98</td>
<td>0.0002</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni-C-Ce</td>
<td>2.00</td>
<td>—</td>
<td>0.16</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni-C-Mg</td>
<td>1.94</td>
<td>—</td>
<td>—</td>
<td>0.23</td>
<td>—</td>
</tr>
<tr>
<td>Ni-C-Ca</td>
<td>1.80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Table 4.1 Chemical composition of the samples.
<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>S</th>
<th>Ce</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-C</td>
<td>2.08</td>
<td>0.0002</td>
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<td></td>
</tr>
<tr>
<td>Ni-C-S</td>
<td>2.10</td>
<td>0.0035</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-C-S-Ce</td>
<td>1.95</td>
<td>0.0051</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-C-S-Mg</td>
<td>2.14</td>
<td>0.0046</td>
<td></td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>

*Approximate values analyzed from cut samples.

### 4.1.2 Experimental procedure

The experimental apparatus is an infrared gold image lamp furnace with a gas-inlet and a gas-outlet system, as shown in Fig. 4.1. The image furnace was equipped with a 1kW halogen lamp, a B-type thermocouple with a 4mm×4mm×0.2mm Pt-plate, a vacuum pump and a PID temperature controller. The inside wall of the image furnace was elliptical and plated with gold to increase the reflection efficiency. Cooling air was also introduced to cool the lamp. A schematic illustration of the sample placement method is shown in Fig. 4.2.

![Fig. 4.1 Schematic of experimental apparatus.](image1)

![Fig. 4.2 Sample placement method.](image2)
The thermocouple was placed right under the sample to monitor the sample temperature throughout the experiment, which was connected to the PID controller. The temperature was calibrated using the melting point of pure Ni before the experiment. The chamber was first evacuated by the rotary pump to about $1 \times 10^{-3}$ Pa, and then an Ar or Ar+3%H$_2$ gas was introduced into the chamber. The cubic sample, weighting 0.5 g, was placed on the alumina plate and melted at 1673K within few minutes. After a specific holding time, the specimen was cooled at the different cooling rate of 20K/min or 1000K/min. The heating and cooling cycle is shown in Fig. 4.3. The solidified specimen was longitudinally sectioned and polished to observe the graphite morphology using an optical microscope and an SEM. The SEM observation was carried out using the samples etched for 10min in a corrosive liquid (HCl : H$_2$O$_2$ = 2:1) to observe the three-dimensional shape of the graphite.

Fig. 4.3 Heating and cooling cycle.

Tm: melting temperature of Ni-C eutectic alloy
4.2 Results of Graphite morphology

4.2.1 Experiment-1

In Experiment-1, the group 1 samples were melted and held for 15 min at 1673K in the Ar atmosphere and then cooled at 1000K/min or 20K/min to identify the effect of the cooling rate on the graphite morphology. However, no perfect spheroidal graphite could be recognized even at the cooling rate of 1000K/min. At the cooling rate of 1000K/min, the massive graphite formed, while the chunky graphite also existed. The morphology of the massive graphite is shown in Fig. 4.4, while at the cooling rate of 20K/min, chunky graphite formed as the only morphology, as shown in Fig. 4.5. The sulfur content of the Group 1 alloys was about 2mass ppm, and based on previous research, the spheroidal graphite could form in Fe-C alloy at the high cooling rate. Nevertheless, in this experiment, even if the cooling rate was as high as 1000K/min, the massive graphite formed instead of the spheroidal one. Based on this result, we postulate that the atmosphere contained some oxygen, which acted in the same way as the sulfur due to the very small size of the samples with a high specific surface area. On the other hand, the holding time was possibly slightly longer causing fading of the spheroidizing elements.

4.2.2 Experiment-2

Therefore, we changed the atmosphere from Ar to Ar+3%H₂ in order to decrease the oxygen potential in the atmosphere. Meanwhile, the holding
time was shortened to 10 min, while all the other experimental parameters were identical to those in Experiment-1. At the cooling rate of 1000K/min, perfect spheroidal graphite morphology was obtained in all the samples, as shown in Fig. 4.6. When the cooling rate was decreased to as low as 20K/min, the sulfur-free samples solidified with the chunky graphite morphology. While in the samples containing sulfur, the flake graphite formed, as shown in Fig. 4.7. This was attributed to the low cooling rate, at which the sulfur in the alloy had sufficient time to react with the spheroidizing element to form the sulfide and then solidified as flake graphite, instead of having the undercooled condition at the high cooling rate to form the spheroidal graphite \(^{10}\). As can be seen from Fig. 4.5 and Fig. 4.7, the difference between the chunky graphite and the flake graphite can be easily distinguished by their three-dimensional morphologies. The graphite morphologies from Experiment-2 are summarized in Table 4.2 (In the samples of the spheroidal graphite morphology, the chunky graphite coexisted. While in the samples of the chunky/flake morphology, the chunky/flake was the only graphite morphology.).
Fig. 4.4 Massive graphite of Group 1 samples cooled at 1000K/min in Ar.

Fig. 4.5 Chunky graphite of Group 1 samples cooled at 20K/min in Ar.
Fig. 4.6 Spheroidal graphite morphology in Group 1 samples of Experiment-2 cooled at 1000K/min.

Fig. 4.7 Graphite morphology in Group 2 samples of Experiment-2 cooled at 20K/min.
Fig. 4.8 Etch pit of spheroidal graphite area observed with SEM.

Table 4.2 Graphite morphologies of Experiment-2 samples.

<table>
<thead>
<tr>
<th>Group1</th>
<th>1000K/min</th>
<th>20K/min</th>
<th>Group2</th>
<th>1000K/min</th>
<th>20K/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>①Ni-C</td>
<td>SG*</td>
<td>CHG**</td>
<td>⑤Ni-C</td>
<td>SG</td>
<td>CHG</td>
</tr>
<tr>
<td>②Ni-C-Ce</td>
<td>SG</td>
<td>CHG</td>
<td>⑥Ni-C-S</td>
<td>SG</td>
<td>Flake</td>
</tr>
<tr>
<td>③Ni-C-Mg</td>
<td>SG</td>
<td>CHG</td>
<td>⑦Ni-C-Ce-S</td>
<td>SG</td>
<td>Flake</td>
</tr>
<tr>
<td>④Ni-C-Ca</td>
<td>SG</td>
<td>CHG</td>
<td>⑧Ni-C-Mg-S</td>
<td>SG</td>
<td>Flake</td>
</tr>
</tbody>
</table>

*SG: Spheroidal graphite  **CHG: Chunky graphite

(a) Influence of graphite morphology on etch pit shape.  (b) Etch pit pattern models of (a).

Fig. 4.9 Influence of graphite morphology on etch pit pattern and the model.
Fig. 4.8 shows the hexagon etch pit of the matrix in the spheroidal graphite area, from which the spheroidal graphite fell out during the deep etching. Fig. 4.9 (a) demonstrates the massive graphite (marked with \( \alpha \), quoted from Fig. 4.4) as well as the spheroidal graphite (marked with \( \beta \)). Fig. 4.9 (b) shows the models of the graphite morphology and the etch pit shape. The etch pit of the spheroidal graphite is hexagon, while that of the massive graphite is polygon. The graphite in these two pictures shows one area in the field of view, and in the other area, the graphite morphology is identical.

### 4.2.3 Experiment-3

By changing the atmosphere and the holding time, the spheroidal graphite morphology was observed in the samples held for 10 min and cooled at the rate of 1000K/min in the Ar\(+3\%\text{H}_2\) atmosphere. In order to investigate which of the two parameters is more effective for the formation of spheroidal graphite in the Ni-C alloy, we designed Experiment-3 by independently changing the two parameters. The notations of these specimens were \( \alpha \), \( \beta \), \( \gamma \), and \( \delta \) in Table 4-1, which provided different spheroidizing elements and sulfur contents.

For the same holding time of 10 min and the cooling rate of 1000K/min, the spheroidal graphite formed in all the four samples both in the atmosphere of Ar and Ar\(+3\%\text{H}_2\), while the surface of the spheroidal graphite in Ar\(+3\%\text{H}_2\) was much smoother than that in Ar.
In the atmosphere of Ar+3%H₂ at the cooling rate of 1000K/min, these specimens were prepared at the different holding times of 10 min or 20 min. The spheroidal graphite morphology occupied most of the area fraction in the 10min-held samples. Nevertheless, in the 20min-held ones, the spheroidal graphite was the main morphology in the Ni-C and the Ni-C-Mg samples, while in the Ni-C-S and the Ni-C-Mg-S samples, the chunky graphite formed as the main morphology.

A further investigation was done to examine the fractions of the chunky graphite area in the Ni-C-S and the Ni-C-Mg-S alloys. It was observed that the chunky graphite has an area fraction up to 85.5% in the Ni-C-S sample and 74.5% in the Ni-C-Mg-S sample, as shown in Fig. 4.10.

![Fig. 4.10 Area fractions of graphite morphology of 20min-held samples.](image)

(a) Ni-C-S alloy. (b) Ni-C-Mg-S alloy.

These results show that the holding time significantly affects the graphite morphology in the alloys with sulfur. The chunky graphite formed as a result of the fading due to the long holding time.
4.2.4 Experiment-4

In order to investigate the influence of the holding time on the graphite morphology in the samples alloyed with spheroidizing element, the holding time was reduced to 0 min, in which the sample was immediately cooled by switching off the lamp just after the melting. Considering some real time delay, the holding time was defined to be 1 min. The Ni-C and Ni-C-Mg alloys were melted in the Ar+3%H₂ atmosphere and cooled at the cooling rate of 1000K/min.

These results showed that perfect spheroidal graphite and chunky graphite could form in all of the samples. We compared the chunky graphite fractions between the samples held for 1 min and 20 min. For the Ni-C alloy, the chunky fraction was 47.1% and 49.0% respectively, at the holding time of 1 min and 20 min, and they were nearly identical, as shown in Fig. 4.11. For the alloys containing the spheroidizing element of Mg, the chunky fractions dramatically changed from 6.4% in the 1 min-held sample to 20.9% in the 20 min-held one, as shown in Fig. 4.12. This should be the influence of the Mg fading due to the chemical reaction with the residual oxygen in the furnace, which led to a decrease in the spheroidal graphite fraction.
4.3 Crystallographic orientation of the matrix

4.3.1 EBSD observation results

The surface of the spheroidal graphite consists of the (0001) basal plane of the graphite, and the matrix around it is supposed to be single crystal \(^1\). As can be seen from the shape of the etch pit around the massive graphite
(shown in Figs. 4.4, 4.8 and 4.9), we suspect that the matrix around the massive graphite is polycrystalline. If this hypothesis is true, the matrix around the massive graphite is composed of many grains.

In order to confirm this hypothesis, the matrix structure was observed by EBSD. The results are shown in Fig. 4.10 for the spheroidal graphite and the massive graphite. The matrix grains could be distinguished by color, as the different colors represent different crystallographic orientations. The difference in the hardness of the graphite and the matrix has a harmful influence on the quality of the polished matrix surface and formed noise at the graphite/matrix interface. It is clear that the matrix around the spheroidal graphite is mainly single crystal and partly bi-crystals, while that around the massive graphite is poly-crystal, as expected.

4.3.2 Discussion

Based on the EBSD observations, the number of matrix grains around the spheroidal graphite and the massive graphite is quite different. The difference in the matrix grain numbers could be explained by the structural difference in the two graphite morphologies.

Fig. 4.11 2) (a) is one of the models of the spheroidal graphite surface. The surface of the spheroidal graphite is like a cabbage. Fig. 4.11 2) (b) shows the circumferential growth model of a graphite spheroid. The graphite prism plane (1010) proceeds forward with the growth of the graphite, and acts as a substrate for the Ni-austenite due to the one-way
nucleation, which requires the lowest formation energy for the austenite to grow. There are many sites on the graphite surface which act as the nucleus site for the growth of austenite, and the grain number of the matrix is determined by the number of dominant nucleus sites. When only one nucleus site exists, the austenite grows from there, and the matrix is of only one grain. Nevertheless, when the nucleus sites exceed two, the matrix is polycrystalline, which could also be confirmed by the EBSD results. In our experiments, the matrix grain number around one spheroidal graphite is only one or two. In fact, the situation that the grain number exceeds two also exists.

In the samples with the massive graphite morphology, the graphite surface is not smooth, which provides more nucleation sites for the Ni matrix to grow from. From the “the number of nucleus sites determines the grain number” theory, it is easy to understand why the matrix around the massive graphite is poly-crystal.

The matrix grain number around the graphite was confirmed for the first time in the Ni-C alloy, while it could not be confirmed in the study using the Fe-C alloys due to the transformation during the cooling from austenite to ferrite. Therefore, we cannot observe the solidified structure when employing the Fe-C alloys.
(a) Single crystal matrix around spheroidal graphite.

(b) Bi-crystal matrix around spheroidal graphite.

(c) Poly-crystal matrix around massive graphite.

(d) Poly-crystal matrix around massive graphite.

Fig. 4.10 Observation of matrix grain around graphite by EBSD.

(a) Model of spheroidal graphite surface.

(b) Circumferential growth model of a graphite spheroid.

Fig. 4.11 Model of spheroidal graphite surface and circumferential growth.
4.4 Conclusions

The influences of the cooling rate, atmosphere and holding time on the graphite morphology were studied by comparing the graphite morphologies under different experimental conditions using the 0.5 g Ni-C alloy samples. The grain number of the matrix around the spheroidal graphite and the massive graphite was investigated based on EBSD observations. The following points have been established in this study.

1. The atmosphere and holding time are important parameters that affect the fading and the oxidation.
2. Based on the results of which the atmosphere changed from Ar to Ar+3%H2 in Experiment-2, oxygen in the atmosphere has a similar effect as that of sulfur on the graphite morphology in the Fe-C alloy and the Ni-C alloy.
3. The grain number of the matrix around the graphite is determined by the number of dominate nucleus sites on the spheroidal graphite surface.
4. The grain number of the matrix is fewer in the alloy with the spheroidal graphite than that with the massive graphite.

References

Chapter 5

Influence of Copper on Matrix Structure of Cast Iron

In the past, there have been a significant number of studies \(^1\text{-}^9\) on the influence of Cu on the matrix of cast iron showing that Cu was a pearlite-forming element both in the flake and spheroidal graphite cast irons. However, in the book of ‘Cu Addition in Cast Iron’ \(^1\), Fig. 22 on p. 42 was misquoted for the flake graphite cast iron, while in fact, it is the data for the spheroidal graphite cast iron \(^10\). Therefore, the actual influence of Cu on the matrix of the flake graphite cast iron was not clear.

There have been few recent reports about the influence of Cu on the flake graphite cast iron and the influence is considered to be very weak. In this study, the cast iron with almost the same C and Si contents was used, and the influence of Cu on the spheroidal graphite cast iron and the flake graphite cast iron was discussed. In the flake graphite cast iron, because the pearlite-stabilizing effect of S is very strong \(^11\), then the same effect of Cu is difficult to detect. Therefore, the effects of S and Cu on the flake graphite cast iron are separately discussed.

5.1 Experimental procedure and the observation method

5.1.1 Sample preparation

In an Ar atmosphere, electrolytic iron (11ppmC, <10ppmP, 8ppmS, <5ppmSi, 1ppmMn, 1ppmCu, 8ppmN), 99.999%Si, electrode graphite,
ferro-phosphorus (25%P), iron sulfide (35%S), pure copper and electrolytic manganese were melted at 1500°C in a 7kg-high-frequency furnace with an alumina lining. An inoculant (Fe-75%Si-3%Ca) and a spheroidizer (Fe-45.4%Si-1.54%Ca-3.67%Mg-1.71%RE) were added to a ladle, and then the melt was cast into 25mm diameter knock-off type keel blocks. The chemical composition of the base alloys was 3.7%C-2.0%Si, and for the flake graphite cast iron (abbreviated as FC), 0.5-1.0%Mn, 0.03-0.1%P, 0.5-1.0%Cu and 0.01-0.02%S were added. For the spheroidal graphite cast iron (abbreviated as FCD), the contents of Mn, P and Cu were in the identical range as that in the FC, while free of S.

The chemical compositions of the samples are shown in Table 5.1, and the notation of the sample represents both the content type of the added element. For example, FC-0.5Mn denotes that 0.5%Mn was added to the FC base alloy, while the base alloys are marked as FC-Base or FCD-Base.

Table 5.1 Chemical composition of samples. (mass%)

<table>
<thead>
<tr>
<th></th>
<th>C, %</th>
<th>Si, %</th>
<th>Mn, %</th>
<th>P, %</th>
<th>S, %</th>
<th>Cu, %</th>
<th>Mg, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC-Base</td>
<td>3.70</td>
<td>2.02</td>
<td>&lt;0.01</td>
<td>0.0048</td>
<td>0.0022</td>
<td>&lt;0.002</td>
<td>---</td>
</tr>
<tr>
<td>-0.5Mn</td>
<td>3.65</td>
<td>1.97</td>
<td>0.493</td>
<td>0.0046</td>
<td>0.0023</td>
<td>&lt;0.002</td>
<td>---</td>
</tr>
<tr>
<td>-1.0Mn</td>
<td>3.55</td>
<td>1.97</td>
<td>0.927</td>
<td>0.0045</td>
<td>0.0022</td>
<td>&lt;0.002</td>
<td>---</td>
</tr>
<tr>
<td>-0.03P</td>
<td>3.64</td>
<td>1.99</td>
<td>&lt;0.01</td>
<td>0.0315</td>
<td>0.0013</td>
<td>&lt;0.002</td>
<td>---</td>
</tr>
<tr>
<td>-0.1P</td>
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<td>1.97</td>
<td>&lt;0.01</td>
<td>0.0973</td>
<td>0.0025</td>
<td>&lt;0.002</td>
<td>---</td>
</tr>
<tr>
<td>-0.5Cu</td>
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<td>1.95</td>
<td>&lt;0.01</td>
<td>0.0043</td>
<td>0.0034</td>
<td>0.461</td>
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<td>0.0025</td>
<td>1.003</td>
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<tr>
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<td>1.99</td>
<td>&lt;0.01</td>
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<td>0.0083</td>
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<td>0.0047</td>
<td>0.0185</td>
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</tr>
<tr>
<td>FCD-Base</td>
<td>3.78</td>
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<td>0.0424</td>
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</tr>
<tr>
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<td>3.87</td>
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<td>0.0472</td>
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<td>-0.03P</td>
<td>3.94</td>
<td>1.95</td>
<td>&lt;0.01</td>
<td>0.0312</td>
<td>0.0036</td>
<td>&lt;0.002</td>
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</tr>
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<td>-0.5Cu</td>
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<td>0.0054</td>
<td>0.0030</td>
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</tr>
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<td>-1.0Cu</td>
<td>3.78</td>
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<td>&lt;0.01</td>
<td>0.0050</td>
<td>0.0024</td>
<td>0.933</td>
<td>0.0463</td>
</tr>
</tbody>
</table>
5.1.2 Observation method

The samples (cooled in air to room temperature) were polished and then the microstructures were observed using an optical microscope and an SEM. For the optical microscope observations, the samples were etched with 1% natal. Thirty different sites were observed at a 50x magnification under the optical microscope, and the images were analyzed by image-processing software. The average pearlite volume fraction value was calculated and was used as the pearlite volume fraction for this sample. The segregation of the alloying elements was investigated by color-mapping of the WDX-EPMA results.

To observe the Cu film around the spheroidal graphite, we etched off the matrix in the cast iron without etching the Cu, which was realized using the degassed 7% HCl aqua solution for 2 hours. As the ionization tendency of O is after Fe and Cu \(^{12}\), and hydrogen is between Fe and Cu, therefore, when oxygen is present, Fe and Cu will be simultaneously etched. Therefore, we degassed the HCl aqua solution before etching so that Fe could be etched off while the Cu remained for the SEM observation of the Cu film.

5.2 Results

5.2.1 Influence of Cu and S on the matrix of flake graphite cast iron

The influence of Cu and S on the matrix of the flake graphite cast iron is
shown in Fig. 5.1. The microstructure of the FC-Base was chosen as the standard for comparing those of FC-0.5Cu, FC-0.01S-0.5Cu and FC-0.02S-0.5Cu. The result shows that a small amount of S, even 0.01%, could pearlitize the matrix at 100%, which is in agreement with our previous research ¹¹, while the addition of Cu promotes the ferrite (the pearlite volume fraction decreased from 31.4% to 14.7%) and D-type graphite formation. It is already acknowledged that the matrix around the D-type graphite is easy to ferritize. Therefore, we supplemented another measurement here, which was done by calculating the pearlite volume fraction of the A-type graphite area in the FC-1.0Cu alloy. The results were FC-1.0Cu of 32.8%, while that of FC-0.5Cu was 11.3%. Based on these results, it is clear that for the high-purity Fe-C-Si cast iron, the Cu addition has a ferritization effect on the matrix.

Therefore, in the following experiments, the influence of the alloying elements was investigated in the FC and the FCD without sulfur addition.

![Fig. 5.1 Influence of S and Cu on matrix structure in flake graphite cast iron.](image)

a) FC-Base; b) FC-0.5Cu; c) FC-0.01S-0.5Cu; d) FC-0.02S-0.5Cu.
5.2.2 Influence of Mn, Cu and P on the matrix of cast iron

The influence of Mn on the matrix is demonstrated in Fig. 5.2. The pearlite volume fraction is shown at the left bottom of the figure. It can be seen that the addition of Mn promotes pearlite in each sample. Meanwhile, the chilling tendency increases with the Mn addition to the FCD. These results agree well with previous research reports 1-4). Furthermore, the pearlization effect of Mn in the FC is much more obvious than in the FCD. However, when the addition of Mn exceeds 0.5%, ledeburite could be observed in the matrix of the FCD. This is probably because the Si content in the sample is low.

Fig. 5.3 shows the influence of Cu on the matrix, and it is clear that in the FCD, Cu promotes pearlite, while in the FC, Cu has an adverse effect such that it promotes ferrite. In this experiment, the amount of S was very small, and therefore, the different results for the FC and the FCD could not be attributed to the S content.

The effect of P on the matrix is demonstrated in Fig. 5.4. Like Mn, the pearlization effect of P in the FC is much more obvious than in the FCD. In the FC, only 0.1% P could fully pearlitize the matrix.
Fig. 5.2 Influence of Mn on matrix structure in flake and spheroidal graphite cast iron.

(The numbers denote pearlite fractions.)

Fig. 5.3 Influence of Cu on matrix structure in flake and spheroidal graphite cast iron.
5.3 Discussion

5.3.1 Influence of alloying elements on the matrix

The influence of alloying elements on the pearlite volume fraction is summarized in Fig. 5.5. In the FC and the FCD, the influence of Mn and P is nearly identical to that in a previous report. However, the influence of Cu is quite different between the FC and the FCD, and completely disagrees with the previous reports 1-4) which described Cu as a pearlite-stabilizing element for the FC. Why was Cu regarded as a pearlite-forming element in the FC? Based on the experimental results of this study that the ferritization effect of Cu was detected in the high-purity FC, we then consider that in the past research, the S level in the FC was high, and thus the pearlitization...
effect of S was so strong that the ferritization effect of Cu could not be detected. Si is a strong ferritization element although it also has the cementite-prevention effect. Cu could also prevent the formation of chill, while its ferritization effect is weak compared to that of Si. Therefore, instead of Si, Cu is often used together with Cr, Mo and V for preventing the chill formation of these alloying elements.

P promotes the graphitization during the solidification process and the pearlitization in the eutectoid process. Cu demonstrates the identical graphitization for the solidification, while in the eutectoid process, it has a pearlite-forming effect in the FCD, but a ferrite-forming effect in the FC. The different behavior of Cu in the FC and the FCD is a unique phenomenon.

Fig. 5.5 Correlation between alloying elements and pearlite fractions in cast irons.
5.3.2 Segregation of Mn, Cu and Si

The color mappings of Mn, Cu and Si in the FCD-0.5Mn and FC-0.5Mn samples were analyzed and the results are shown in Fig. 5.6 and Fig. 5.7, respectively. In the SEM image of the matrix, the brightly-observed part is pearlite, while the darkly-observed part is ferrite due to the etching. This is due to the edge effect, which is caused by the difference in the surface roughness of pearlite and ferrite. The pearlite surface is much rougher that that of ferrite. In the SEM image, the darkest part is the graphite, which is the characteristic phenomenon of the atomic number effect of the element 13) (the lower the atomic number, the darker the observed element). The atomic number of C is the lowest among the elements in the sample, and this is the reason why the graphite is the darkest part observed in the SEM image.

Fig. 5.6 Color mapping images of Mn, Si and C in FCD-0.5Mn sample.
In the color mapping, the red part shows the highest concentration of the investigated elements, and the blue part means the concentration is the lowest. Based on this principle, Mn segregates at the boundary of the eutectic cells both in the FC and the FCD. On the contrary, Si segregates at the center part of the eutectic cells or at the dendrite part, while at very low concentrations in ledeburite, as shown in Fig. 5.6 and Fig. 5.7.

The same analysis was carried out for the FCD-0.5Cu and the FC-0.5Cu samples, and the results are shown in Fig. 5.8 and Fig. 5.9 respectively. In the FCD sample, Cu is different with Mn in the segregation such that the Cu concentration is higher around the graphite. Nevertheless, as the concentration distribution in the FC sample, Cu could not be well distinguished with the same magnification, and the higher magnification was then chosen, the result of which is shown in Fig. 5.9. From Fig. 5.9, Cu and Si segregate at the dendrite part. These results indicate that Mn segregates in the final solidified part, while Cu and Si segregate in the phase generated at the beginning of the solidification process, for instance, in the austenite dendrite in the FC sample and in the austenite near the spheroidal graphite in the FCD sample.
Fig. 5.7 Color mapping images of Mn, Si and C in FC-0.5Mn sample.

Fig. 5.8 Color mapping images of Cu, Si and C in FCD-0.5Cu sample.
5.3.3 Pearlite-stabilizing effect of Cu

From the results already described, it is clear that the pearlite-stabilizing effect of Cu is totally opposite in the FC and the FCD samples. There are some reports which estimate that Cu could segregate at the graphite/matrix phase boundary and form a thin film around the spheroidal graphite, thus acting as a barrier to the carbon diffusion \(^{14,15}\). However, except for Ishiguro \(^{15}\), nobody could find the film, and Tsujikawa \(^{16}\) also reported that the Cu film could not be detected by TEM-EPMA.

In our past research, we also tried to find the existence of the Cu film based on an Auger electronic spectral analysis of the electric field radiation type. The experimental conditions are as follows. The accelerating voltage was 10KV, and the ion gun accelerating voltage was 3KV with the beam...
diameter of 30nm. Nevertheless, we could not find the Cu film and also, we could not find the film using the FIB-processed FCD sample by FE-SEM.

Therefore, a special corrosion method was introduced into this research using a degassed HCl aqueous solution. Firstly, pure water was degassed for 1 hour by vacuum treatment. After that, HCl was added into the water at 7% and degassed for another 1 hour. Because of the difference in ionization tendency of Fe and Cu without oxygen in the solution, the Fe in the matrix was corroded, while the Cu film on the graphite surface remained with this etching method 17).

The SEM observed image is shown in Fig. 5.10 at a low magnification and in Fig. 5.11 at high magnification. In Fig. 5.10, there is some bright phase around the spheroidal graphite as denoted by the arrows. The graphite at is magnified in Fig. 5.11. In Fig. 5.11, (a) is the top view, (b) is oblique view at $60^\circ$, and (c) is the magnified one of (b). The area indicated by the arrows was analyzed by EPMA. The results are shown in Fig. 5.12, which are in agreement with the research of Ishiguro 15), that the spheroidal graphite is surrounded by a thin Cu film.

However, as stated before, the Cu film could not be found neither with the Auger electronic spectral analysis nor with the FIB analysis, which was the identical result of Tusjikawa’s research 16). This may be because the Cu film is too thin to be found, or the Cu film was lost during the FIB processing. This problem should be further discussed in the future.

The reason why the Cu film is clearly observed in this study could be explained by Fig. 5.13. As can be seen, since more than half of the
spheroidal graphite is buried in the matrix, it is very easy to find the Cu film around it.

Fig. 5.10 SEM image of deeply etched FCD-1.0Cu samples.

Arrows show the bright area on the spheroidal graphites.

Fig. 5.11 SEM images of deeply etched spheroidal graphite surface.

a) Top view, b) Oblique view, c) The high magnification image.
Fig. 5.12 EPMA line analysis of spheroidal graphite edges.

Fig. 5.13 Schematic illustration of Cu-film on spheroidal graphite.
It is well known that Cu-plating is a useful method to prevent carburization in steel \(^{18}\). Therefore, it is considered to be of the identical mechanism that the Cu film around the spheroidal graphite prevents the carbon diffusion and thus promotes the pearlitization. However, in the FC, Cu promotes ferritization instead of pearlitization. This may be the actual effect of Cu on the matrix of the cast iron, and the pearlite-stabilizing effect in the FCD is a unique phenomenon. As shown in Fig. 5.3, the ferrite fraction increases with the Cu content in the FC samples.

For this unique phenomenon, two mechanisms should be considered. The first one is that the interfacial area between the graphite and austenite in the FC sample is much greater than that in the FCD sample, and as a result, Cu could not form a complete film around the graphite in the FC. The pearlitization must be promoted by the increase in the Cu addition, while the fact is quite the opposite, as shown in Fig. 5.3. Therefore, this mechanism could not well explain the ferritization effect of Cu in the FC, and another mechanism is taken into account. For the cast iron, Cu is a ferrite-forming element, while in the FCD, it forms a film around the spheroidal graphite and thus prevents the carbon diffusion and stabilizes pearlite in the matrix as a result. This mechanism provides a good explanation for the different effects of Cu in the FC and the FCD samples.

5.3.4 Precipitation of Cu

For the confirmation of the Cu film formation, a ternary phase diagram of Fe-C-Cu was calculated \(^{19,20}\) and is shown in Fig. 5.14. The solubility
limit of Cu decreases with the temperature and the dissolved Cu is precipitated at 750°C if the iron contains 1%Cu and at 710°C for the 0.5%Cu sample, as can be estimated in the figure. It is well known that the growth of the spheroidal graphite is controlled by the diffusion of carbon through the austenite shell. If the spheroidal graphite is covered with a Cu film, the diffusion rate is significantly low, and the carbon is enriched in the austenite to form the pearlite. This is believed to be the reason why Cu promotes the pearlite formation in the spheroidal graphite iron in the eutectoid transformation.

![Fig. 5.14 Influence of temperature on solubility limit of Cu in Fe-C-Cu ternary phase diagram.](image)

### 5.4 Conclusions

In this study, the influence of copper on the matrix of the high-purity flake graphite cast iron and spheroidal graphite cast iron was discussed.
Firstly, as sulfur is a strong pearlite-promoting element in the cast iron, its influence on the matrix of the flake graphite cast iron was investigated. The result shows that when the sulfur content is more than 0.01%, the matrix of the flake graphite cast iron is completely pearlite, regardless of the presence of copper.

Manganese and phosphorus are both pearlite-stabilizing elements in the flake graphite cast iron and the spheroidal graphite cast iron. Nevertheless, copper is the pearlite-stabilizing element in the spheroidal graphite cast iron, which is in agreement with a previous study, while in the flake graphite cast iron, it is a ferrite-stabilizing element. The influence of copper on the flake graphite cast iron is clarified for the first time because the high-purity alloys were used in this study.

The pearlite-stabilizing effect of copper in the spheroidal graphite cast iron is a unique phenomenon as a result of the formation of the copper film around the spheroidal graphite.

References

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High strength steel, which often contains a few tens of ppm B, has been used in the automobile industry due to weight reduction for energy savings. If this steel scrap is recycled for producing high strength spheroidal graphite iron castings, the alloying element, B, changes the matrix from pearlite to ferrite. In this chapter, the influence of B on the matrix of the high strength spheroidal graphite iron castings and the means of counteracting its ferritization effect were investigated.

6.1 Experimental procedure and the alloy compositions

In an Ar atmosphere, carbon steel rods (Fe-0.25%C-0.14%Si-0.18%Mn-0.017%P-0.021%S), graphite electrode and ferro-manganese were melted in a high-frequency induction furnace. After that, metallic silicon and pure copper were added to the melt. High purity ferro-boron (14.6%B) was added to the melt to study the influence of B on the matrix. Ferro-manganese nitride (4.66%N) and sponge titanium (98%Ti) were also added to the melt to study the effect of N and Ti, respectively. Thermal analysis was done during the melting using a CE-cup, and the carbon equivalent was adjusted to 4.4%. An inoculant (22%Fe-75%Si-3%Ca) and a spheroidizer (48%Fe-45.4%Si-1.54%Ca-3.67%Mg-1.71%RE) were
added in a ladle, and the melt was then cast into knock-off type keel blocks of 25mm diameter. The chemical compositions of B-added, B-N-added, and B-Ti-added alloys used in this study are shown in Table 6.1, Table 6.2 and Table 6.3, respectively.

The samples were polished and then etched with 3% nital for about ten seconds until the metallic luster was lost. The macro- and microstructures of the samples were then observed by an optical microscope and a SEM. In order to observe the graphite surface morphology with the SEM, the samples were deeply etched in 10% nital for about 25 minutes.

Table 6.1 Chemical composition of B-added samples (mass%)

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>C</th>
<th>Si</th>
<th>Cu</th>
<th>B</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.62</td>
<td>2.52</td>
<td>1.09</td>
<td>&lt;5ppm</td>
<td>0.44</td>
</tr>
<tr>
<td>2</td>
<td>3.65</td>
<td>2.64</td>
<td>0.95</td>
<td>5ppm</td>
<td>0.43</td>
</tr>
<tr>
<td>3</td>
<td>3.61</td>
<td>2.53</td>
<td>1.08</td>
<td>10ppm</td>
<td>0.41</td>
</tr>
<tr>
<td>4</td>
<td>3.57</td>
<td>2.50</td>
<td>1.07</td>
<td>15ppm</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>3.66</td>
<td>2.56</td>
<td>1.14</td>
<td>31ppm</td>
<td>0.44</td>
</tr>
</tbody>
</table>

*: 5ppm B is the lower limit of this chemical analysis.

Table 6.2 Chemical composition of N-added samples (mass%)

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>C</th>
<th>Si</th>
<th>Cu</th>
<th>B</th>
<th>N</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3.62</td>
<td>2.52</td>
<td>1.09</td>
<td>&lt;5ppm*</td>
<td>84ppm</td>
<td>0.62</td>
</tr>
<tr>
<td>7</td>
<td>3.65</td>
<td>2.64</td>
<td>0.95</td>
<td>4ppm</td>
<td>81ppm</td>
<td>0.66</td>
</tr>
<tr>
<td>8</td>
<td>3.61</td>
<td>2.53</td>
<td>1.08</td>
<td>10ppm</td>
<td>95ppm</td>
<td>0.66</td>
</tr>
<tr>
<td>9</td>
<td>3.57</td>
<td>2.50</td>
<td>1.07</td>
<td>15ppm</td>
<td>85ppm</td>
<td>0.67</td>
</tr>
<tr>
<td>10</td>
<td>3.66</td>
<td>2.56</td>
<td>1.14</td>
<td>38ppm</td>
<td>89ppm</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Table 6.3 Chemical composition of Ti-added samples (mass%)

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>C</th>
<th>Si</th>
<th>Cu</th>
<th>B</th>
<th>Ti</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>3.62</td>
<td>2.52</td>
<td>1.09</td>
<td>&lt;5ppm</td>
<td>588ppm</td>
<td>0.63</td>
</tr>
<tr>
<td>12</td>
<td>3.65</td>
<td>2.64</td>
<td>0.95</td>
<td>8ppm</td>
<td>516ppm</td>
<td>0.65</td>
</tr>
<tr>
<td>13</td>
<td>3.61</td>
<td>2.53</td>
<td>1.08</td>
<td>11ppm</td>
<td>613ppm</td>
<td>0.67</td>
</tr>
<tr>
<td>14</td>
<td>3.57</td>
<td>2.50</td>
<td>1.07</td>
<td>21ppm</td>
<td>486ppm</td>
<td>0.67</td>
</tr>
<tr>
<td>15</td>
<td>3.66</td>
<td>2.56</td>
<td>1.14</td>
<td>37ppm</td>
<td>601ppm</td>
<td>0.61</td>
</tr>
</tbody>
</table>

For the observation of the Cu film on the graphite surface, the Fe in the matrix should be etched without the dissolution of Cu as already mentioned in 5.3.3. The ferrite volume fraction was measured using the 3% natal-etched samples with a microcomputer equipped with an optical microscope.

6.2 Results and Discussion

6.2.1 Influence of B, N and Ti on the FCD matrix

6.2.1.1 Influence of B

The microstructures of the matrix of the 1%Cu spheroidal graphite cast iron at different B contents are shown in Fig. 6.1. The figure reveals that the pearlite volume fraction decreases with the increase in the B content. Where is the precipitated carbon with the ferrite formation? To study this problem, the three-dimensional shape of the spheroidal graphite surface was observed using the SEM, and the result was the same as that in Fig. 6.2
The spheroidal graphite surface was covered with a special kind of graphite, like the D-type graphite in flake graphite. Since there was no Cu film, the precipitated secondary graphite could form a layer around the crystallized spheroidal graphite, as pointed out by the arrows in Fig. 6.3. We can easily confirm the secondary graphite in all-ferrite-matrix spheroidal graphite iron due to its significant volume.

![Image](image1.png)

**Fig. 6.1** Influence of B on the matrix structure of 1%Cu spheroidal graphite cast iron.

![Image](image2.png)

**Fig. 6.2** 1) Spheroidal graphite surface of 31ppm-B sample observed by SEM.
6.2.1.2 Ferrite-preventing mechanism of N and Ti

To investigate the counteraction to the damaging effect of B on the matrix, the addition of N or Ti was studied. Approximately 85ppm N or 550ppm Ti was added to the alloys for controlling the ferrite volume fraction. The ferrite volume fraction decreased in the N-treated and the Ti-treated samples as shown in Fig. 6.4. As for the effect of the pearlite formation, Ti is much more effective than N in restraining the ferrite formation and retaining the smoothness of the spheroidal graphite surface.

6.2.1.3 Mechanism of influence of N and Ti

As indicated above, the precipitated graphite from the austenite matrix during the cooling forms the D-type-like graphite at the spheroidal graphite surface of the B-added samples. If N or Ti is added to the samples, B reacts with N or Ti to form BN or TiB₂, thus decreasing the dissolved B
concentration in the austenite and weakening the ferrite formation tendency. The reason why Ti is much more effective than N could be explained by the chemical reaction and the free energy change shown in equations (6-1) and (6-2)\(^2\).

\[
\begin{align*}
N + B &= BN \quad \Delta G_0 = -126840+94.5T \text{ (J/mol of B)} \quad (6-1) \\
Ti + 2B &= TiB_2 \quad \Delta G_0 = -160230+2.94T \text{ (J/mol of B)} \quad (6-2)
\end{align*}
\]

A thermodynamic calculation was done using these two equations; the results are shown in Fig. 6.5, via the influence of temperature on the boride formation energy \(\Delta G_0\). From Fig. 6.5, it is clear that at the eutectoid temperature, the formation energy of \(TiB_2\) is much lower than that of BN. The difference in the formation energy of BN and \(TiB_2\) demonstrates that it
is easier to form TiB₂ than BN at the eutectoid temperature. Accordingly, Ti is much more effective than N in reducing the dissolved B concentration in the matrix and neutralizing the ferrite-forming effect of B.

6.2.2 Interaction of B with Mn and Cu

To investigate the interaction of B with Mn, 1.8%Mn was added to the Fe-3.58%C-2.54%Si parent alloy at different contents of B. The effects of Mn and Cu on the ferrite formation are compared in Fig. 6.6. It shows that there is little ferritization effect of B on the Mn-added samples, and the secondary graphite was not found on the spheroidal graphite surface, and Mn segregation at the grain boundary of the eutectic cell was confirmed with the Mn mapping in the matrix by the WDX, as shown in Fig. 6.7.

When 1.0%Cu was added to the same parent alloy, the ferrite fraction increased dramatically with the increase in B, as already shown in Fig. 6.1. Nevertheless, the ferrite fraction hardly changed in the Mn-added samples. Therefore, it could be concluded that the interaction between B and Cu is a peculiar phenomenon.
Fig. 6.5 Formation energy of BN and TiB$_2$ at different temperatures.

Fig. 6.6 Changes in ferrite fraction with B content in the samples alloyed with Cu or Mn.
6.2.3 Cu film observation

The spheroidal graphite surface was observed both in the B-free sample and B-added sample by the SEM. The results are shown in Fig. 6.8 and Fig. 6.9 respectively.

We could not find any Cu film in the B-added sample, and the precipitated D-type-like graphite (secondary graphite) on the spheroidal graphite surface and the ferrite matrix around were confirmed, as shown in Fig. 6.8. Meanwhile, the graphite surface was quite coarse, which was of the identical phenomenon with that in Igarashi’s report 1).

In the B-free sample, a very thin Cu film was successfully detected, and the spheroidal graphite surface was smooth, as is shown in Fig. 6.9.
Fig. 6.8 Secondary graphite and ferrite in B-added sample by SEM.

Fig. 6.9 Thin Cu film on smooth spheroidal graphite surface in B-free sample by SEM.

6.2.4 Distribution of B

If the idea that B reacts with Cu is correct, B should exist within the area of the Cu film. In order to confirm the distribution of B, a mapping analysis was done using the WDX to detect B near the spheroidal graphite in the
31ppm-B sample (polished, not etched), and the result is shown in Fig. 6.10. B was detected near the surface area of the spheroidal graphite, and there was no Cu film, as the interaction of B with Cu destroyed the continuity of the Cu film. Therefore, it is possible for the carbon to diffuse from the matrix to the spheroidal graphite. When the carbon concentration in the matrix near the spheroidal graphite becomes low enough, the matrix will change from pearlite to ferrite.

![Fig. 6.10 EPMA mapping of 31ppm B sample (WDX).](image)

**6.3 Conclusions**

The influence of B on the matrix, the counteraction method using N and Ti to reduce the damaging effect of B, the comparison of the interaction of B with Cu and B with Mn, and the distribution of B were investigated in this research. The following points have been established in this study.

1. B could increase the ferrite fraction in the matrix, coarsen the spheroidal graphite surface, and promote the formation of the secondary graphite on the spheroidal graphite iron alloyed with Cu.
2. The addition of N and Ti could neutralize the ferritization effect of B, while Ti is much more effective.

3. The ferrite-forming effect of B only exists in the spheroidal graphite iron alloyed with Cu.

4. The Cu film could form around the spheroidal graphite in the B-free sample, while is absent in the B-added sample.

5. In the samples alloyed with Cu, B is distributed on the spheroidal graphite surface.

References


Chapter 7 Conclusions

It is already known that both the graphite morphology and the matrix are critical factors for the comprehensive mechanical property of the cast iron, especially in the case of the spheroidal graphite cast iron. However, the formation sequence of the spheroidal graphite and the chunky graphite in the Fe-C was not yet clarified. Meanwhile, as there is the phase transformation from austenite to ferrite in the matrix of the cast iron, therefore, the investigation of the relationship between the graphite morphology and the matrix is difficult. Furthermore, for the ferritization effect of B in the Cu-alloyed spheroidal graphite cast iron, the research on the mechanism and its counteraction method was not sufficient. And also, the effect of Cu on the matrix of the flake graphite cast iron was not clear. Based on these problems, a series of investigation were carried out in this study, and the following conclusions were achieved.

7.1 Formation sequence of graphite in eutectic solidification

According to the previous researches, the chunky graphite often appears simultaneously with the spheroidal graphite both in the Fe-C and the Ni-C alloy, while the formation sequence of them was not clear. In this study, the formation mechanism was investigated by studying on the cooling curves via thermal analysis and calculating their differential curves to confirm the onset and end points of the solidification, and then comparing these curves
with the observed graphite morphology. Findings of this study are as follows.

1. The thermal analysis curves of the eutectic solidification decrease continuously both in the Ni-C alloy and the Fe-C alloy.
2. The crystallization sequences of the graphite in the Ni-C alloy and the Fe-C alloy are different.
3. In the Ni-C alloy, the chunky graphite crystallizes before the spheroidal graphite, while the opposite in the Fe-C alloy.
4. The increase of the cooling rate decreases the area fraction of the spheroidal graphite in the Ni-C alloy.
5. The addition of Si between 3.5%-4% in the Fe-C alloy doesn’t change the chunky graphite fraction significantly, while the addition of Ce increases the chunky graphite fraction.

7.2 Influence of melting conditions on graphite morphology and grain number of matrix

In past research, a number of researches were carried out on the influence of the melting conditions on the graphite morphology in the cast iron, while there were quite few reports of the Ni-C alloy. Meanwhile, as there is phase transformation after the eutectic solidification process in the matrix of the cast iron, it is difficult to precisely study on the relationship of the graphite morphology and the matrix. However, in the Ni-C alloy, there is no such phase transformation. Therefore, it is much easier to study on the
relationship based on the room-temperature structure. In this study, the influences of the cooling rate, atmosphere and holding time on the graphite morphology were studied by comparing the graphite morphologies under different experimental conditions using the 0.5 g Ni-C alloy samples in the Ar or Ar+3%H₂ atmosphere. The etch pit patterns of the spheroidal graphite and the massive graphite were observed by SEM and the grain numbers of the matrix around the graphite were investigated based on EBSD. The following points have been established in this study.

1. The atmosphere and holding time are important parameters that affect the fading and the change in the graphite morphology.
2. Base on the result of influence of the atmosphere change from Ar to Ar+3%H₂ in Experiment-2 on the graphite morphology, it is clear that the oxygen partial pressure in the atmosphere has an identical effect as that of sulfur in the Fe-C alloy and the Ni-C alloy.
3. The grain number of the matrix around the graphite is determined by the number of dominate nucleus sites on the spheroidal graphite surface.
4. The grain number of the matrix is fewer in the alloy with the spheroidal graphite than that with the massive graphite.

7.3 Influence of copper on matrix structure of cast iron

In the past, there have been a significant number of studies on the influence of Cu on the matrix of cast iron, because Cu is an indispensable element for the production of the high-strength spheroidal graphite cast iron. However, its influence in the flake and spheroidal graphite cast irons
were still not clear. In this study, the influence of Cu on the matrix of the high-purity flake graphite cast iron and spheroidal graphite cast iron was discussed. Firstly, as already reported, S is a strong pearlitization element in the flake graphite cast iron. Therefore, in order to exclude the pearlitization effect of S, the influence of Cu on the matrix was investigated using high-purity (very low S content) flake graphite cast iron. The result shows that when the S content is more than 0.01%, the matrix of the flake graphite cast iron is completely pearlite, regardless of the presence of Cu.

Mn and P are both pearlitization elements in the flake and the spheroidal graphite cast iron. Nevertheless, Cu is the pearlitization element in the spheroidal graphite cast iron, which is in agreement with the previous studies, while in the high-purity flake graphite cast iron, it is a ferritization element. Therefore, the influence of Cu on the flake graphite cast iron matrix is clarified for the first time because the high-purity alloys were used in this study.

The pearlitization effect of Cu in the spheroidal graphite cast iron is a unique phenomenon as a result of the formation of the thin Cu film around the spheroidal graphite, which is confirmed by a special etching method.

7.4 Interaction of boron with copper and its influence on matrix of spheroidal graphite cast iron

High strength steel, which often contains a few tens of ppm B for reducing the production price, has been used in the automobile industry due
to weight reduction for energy savings. If this steel scrap is recycled for producing high-strength spheroidal graphite iron castings, the alloying element, B, changes the matrix from pearlite to ferrite. In this chapter, the ferritization effect of B on the matrix and its counteraction method were discussed using N and Ti to reduce the amount of soluble B in the melt. Moreover, the comparison of the interaction of B with Cu and B with Mn, and the influence of B on the segregation of Cu were investigated. The following points have been established in this study.

1. B could promote the formation of the secondary graphite on spheroidal graphite surface and increase the ferrite fraction in the matrix in the Cu-alloyed spheroidal graphite cast iron.

2. The addition of N and Ti could counteract the ferritization effect of B, while Ti is much more effective.

3. The ferritization effect of B only exists in the Cu-alloyed spheroidal graphite iron.

4. The Cu film could form around the spheroidal graphite in the B-free samples, while is absent in the B-added samples.

5. In the Cu-alloyed samples, B distributes on the spheroidal graphite surface.
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## List of Publications

### 1. Papers

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<td>1</td>
<td>Influence of Si, Ce, Sb and Sn on Chunky Graphite Formation</td>
<td>China Foundry 8 (2011) 96-100</td>
<td>H. Nakae, M. Fukami, T. Kitazawa</td>
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<td>5</td>
<td>Influence of Melting Conditions on Graphite Morphology in Ni-C Alloy and Grain Number of Matrix</td>
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<td>6</td>
<td>Interaction of Boron with Copper and Its Influence on Matrix of Spheroidal Graphite Cast Iron</td>
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<td>7</td>
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## 2. Presentations

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<td>1</td>
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