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<th>著者</th>
<th>OHNO Reiichi</th>
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Behavior of Sulfur in Cast Iron*

Reiichi OHNO

The Research Institute for Iron, Steel and Other Metals

(Received November 8, 1962)

Synopsis

The effects of sulfur on graphite and eutectic cell formations in solidification have been studied in synthetic Fe-C, Fe-C-Si, Fe-C-P and Fe-C-Si-Mn alloys. When sulfur is added as Fe-C-S and Fe-C-Si-S alloys, in each of hyper-eutectic Fe-C and Fe-C-Si alloy systems, there is a range in which no further obstruction of graphitization occurs by the increase of sulfur. The appearance of such a range is considered to be due to the effect of sulfur which promotes graphitization in solidification. At a certain concentration sulfur makes the size of flake graphite maximum and the number of eutectic cells minimum. These effects are interpreted on the basis of the growth and the nucleation theory of crystals. The effect of sulfur on the size of flake graphite is decreased by manganese, which shows the formation of MnS in solidification.

I. Introduction

Sulfur has various effects on the structure of cast iron. Although it has long been known that sulfur promotes the formation of carbide, at low concentration it markedly increases the size of flake graphite\(^{(1)(2)(3)(4)}\) and varies the number of eutectic cells\(^{(5)}\). On the other hand, sulfur increases the activity coefficient of carbon, while manganese and chromium which promote the formation of carbide decrease it. This is the same effect as that of silicon which promotes the graphitization of cast iron\(^{(6)(7)}\), being contradictory to the carbide-stabilizing effect of sulfur. It is therefore, important both fundamentally and practically to examine precisely these various effects of sulfur on the structure of cast iron; hence, the present work was carried out.

II. Experimental procedure

Experiments were divided into three series, all of which were carried out under condition that impurities, especially gaseous components, might be excluded as far as possible by applying vacuum and argon atmosphere melting.

* The 1071st report of the Research Institute for Iron, Steel and Other Metals.

(1) A. Boyles, Trans. AIME, 125 (1937), 141.
(2) W.J. Williams, J. Iron & Steel Inst., 164 (1950), 407.
(5) H. Morrogh and W. Oldfield, Iron and Steel, 32 (1959), 479.
(7) F. Neumann, H. Schenck und W. Patterson, Giesserei, 47 (1960), 25.
1. Measurement of graphitization in solidification

Details of the chemical composition of all the alloys used in this series of experiments are shown in Table 1, in which the marks B and A relate to base alloy and addition alloy respectively.

<table>
<thead>
<tr>
<th>Mark</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Sc</th>
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<tbody>
<tr>
<td>B 3601-11</td>
<td>4.63</td>
<td>0.27</td>
<td>trace</td>
<td>0.029</td>
<td>0.019</td>
<td>1.11</td>
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<tr>
<td>A 3601-12</td>
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<td>0.25</td>
<td>trace</td>
<td>0.085</td>
<td>0.014</td>
<td>1.05</td>
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<td>0.050</td>
<td>0.011</td>
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<td>1.16</td>
<td>0.012</td>
<td>1.15</td>
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<tr>
<td>B 3605-3</td>
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<td>0.008</td>
<td>0.050</td>
<td>0.011</td>
<td>1.12</td>
</tr>
<tr>
<td>A 3605-4</td>
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<td>0.007</td>
<td>1.27</td>
<td>0.008</td>
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<td>B 3602-3</td>
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<td>0.020</td>
<td>0.017</td>
<td>0.80</td>
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<tr>
<td>A 3602-7</td>
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<td>0.004</td>
<td>1.42</td>
<td>0.012</td>
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<td>B 3601-10</td>
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<td>0.017</td>
<td>0.013</td>
<td>1.12</td>
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<tr>
<td>B 3609-13</td>
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<td>trace</td>
<td>0.020</td>
<td>0.009</td>
<td>1.19</td>
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<td>FeS 0.79</td>
<td>0.36</td>
<td>trace</td>
<td>28.1</td>
<td>0.022</td>
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</table>

(i) Preparation of base and addition alloys

Fe-C base alloys 3601-11 and 3601-10 were made by the following procedure. An Fe-C mother alloy was made from electrolytic iron and graphite, covering with a mixture of calcium oxide and graphite powders, in atmosphere by using a high frequency induction furnace. Two hundred grams of this mother alloy was melted at 1500°C in another high frequency induction furnace for 5 minutes in vacuum and then cast into a 10 mm φ iron mold in vacuum.

Fe-C-S addition alloy 3601-12 was made by the following procedure. A hundred grams of the same mother alloy was melted in vacuum, as described above, before 12 g of commercial iron sulfide was added under argon at 1 atm. After the addition of iron sulfide, the melt was kept at 1500°C for 5 minutes and then cast into the 10 mm φ iron mold.

Fe-C-Si base alloys 3605-1, 3609-13, 3605-3 and 3602-3 were made by vacuum melting of 200 g of another mother alloy at 1500°C for 5, 5, 10 and 40 minutes respectively as described above. The mother alloy was synthesized from electrolytic iron, metallic silicon and graphite in atmosphere, from which Fe-C-Si-S addition alloys 3605-2, 3605-4 and 3602-7 were made by the same procedure as described in the preparation of Fe-C-S addition alloy 3601-12 after the vacuum melting at 1500°C for 5, 10 and 5 minutes respectively.

(ii) Method of adding the addition alloys to the base alloy

In Table 1, a base alloy and an addition alloy are coupled with each other in order from the top of the rows, while the FeS in the lowest row is an addition agent to the base alloys 3601-10 and 3609-13.

A base alloy and an addition alloy were mixed in various ratios in the fixed total amount of 10 g. Using a molybdenum furnace, the two mixtures, each of which was charged in an alumina silicate crucible held in a graphite boat, were at one time, melted at 1350°C for 5 minutes under argon at 1 atm. After heating up to
900°C in vacuum and then cooled, the cooling rate from 1350 to about 1000°C being 250–300°C in 30 sec.

The graphite boat used was shaped from pure graphite rod and had two cavities drilled into it, so that two samples could be melted at one time under the same condition. The molybdenum furnace is a molybdenum wire resistance furnace which was made gas-tight.

Experiments for FeS addition were made by using only the graphite boat.

The temperature was measured by sighting a disappearing-filament optical pyrometer through the end window attached to a glass cap onto the end of the graphite boat. The system was calibrated by measuring the apparent melting temperatures of copper, manganese and nickel, which were held in the alumina silicate crucible.

The samples were cooled by pulling them out into a cold place of the furnace at a fixed rate. The cooling rate was measured by a Pt/Pt–13% Rh thermocouple, a junction of which was inserted into the graphite boat so as to touch the bottom of the alumina silicate crucible.

Commercial argon (>99.99% per cent) was passed over a series of boats containing phosphorus pentaoxide before it entered the furnace.

(iii) Methods of chemical analysis and microscopic examination

Ten grams ingots were sectioned vertically through the center, and one half was mounted for microscopic examination; the other half was used for chemical analysis. The analyses of total carbon, graphite carbon and sulfur were made by the combustion volumetric method. All specimens were etched in nital and observed at magnifications of 120 diameters.

2. Experimental methods concerning effects of phosphorus and sulfur on graphite size and number of eutectic cells

The chemical composition of alloys used is shown in Table 2.

<table>
<thead>
<tr>
<th>Mark</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>3609-9</td>
<td>4.26</td>
<td>0.21</td>
<td>0.008</td>
<td>0.013</td>
<td>1.19</td>
</tr>
<tr>
<td>3609-11</td>
<td>4.07</td>
<td>0.065</td>
<td>0.008</td>
<td>0.82</td>
<td>0.005</td>
</tr>
<tr>
<td>3609-8</td>
<td>4.74</td>
<td>0.11</td>
<td>0.004</td>
<td>0.013</td>
<td>0.005</td>
</tr>
</tbody>
</table>

(i) Experimental method concerning phosphorus

Fe-C-P 3609–9 and Fe-C 3609–8 alloys were made as follows: Fe-C-P and Fe-C alloys were synthesized in atmosphere from electrolytic iron, graphite and iron phosphide; these alloys were melted in magnesia crucible in vacuum at 1500°C for 5 minutes and then cast into the 10 mm φ iron mold. Both alloys were mixed in various ratios in the total amount of 10 g and treated as in the case of 1 (ii), by using the molybdenum furnace.

Specimens were etched in warmed Stead’s reagent and nital for microscopic
examinations. When warmed Stead’s reagent was used, the etched surfaces of all specimens were not completely coated by copper in appearance. In copper coated state in appearance, there was a difficulty in counting the number of eutectic cells in the case in which the coarsening of graphite occurred by sulfur addition. Microscopic examinations were made on several parts of a longitudinal section through the center of an ingot, and the eutectic cell numbers in these parts were averaged.

(ii) Experimental method concerning sulfur

Fe-C-P alloy 3609-9 and Fe-C-S alloy 3609-11 shown in Table 2 were used. The latter was prepared in vacuum by the same method as that for the addition alloy mentioned in 1 (i). Both alloys were treated as in the case of 1 (ii).

Microscopic examinations were made at magnifications of 400 diameters without etching, and the lengths of several comparatively large graphite flakes were averaged. The number of eutectic cells was measured as in the case of 2 (i). Analytical method for sulfur is the same as that in 1 (iii).

3. Experimental method concerning effects of manganese and sulfur on the size of flake graphite

The chemical composition of alloys used is shown in Table 3. The base alloys were made by the vacuum melting of an Fe-C-Si mother alloy at 1500°C for 30 minutes. The addition of manganese was carried out under argon at 1 atm. An addition alloy 3511-9 was made by adding iron sulfide to the same mother alloy under argon at 1 atm.

Under the same condition as described in 1 (ii), each of the base alloys and the the addition alloy were melted and cooled. The measurement of graphite size was carried out in the same way as in 2 (ii).

### Table 3. Chemical composition of alloys used.

<table>
<thead>
<tr>
<th>Mark</th>
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<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>3501-1</td>
<td>3.62</td>
<td>1.54</td>
<td>0.002</td>
<td>0.018</td>
<td>0.002</td>
</tr>
<tr>
<td>B 3510-7</td>
<td>3.58</td>
<td>1.55</td>
<td>0.002</td>
<td>0.009</td>
<td>—</td>
</tr>
<tr>
<td>B 3510-8</td>
<td>3.39</td>
<td>1.55</td>
<td>0.10</td>
<td>0.015</td>
<td>—</td>
</tr>
<tr>
<td>B 3510-9</td>
<td>3.52</td>
<td>1.56</td>
<td>0.21</td>
<td>0.012</td>
<td>—</td>
</tr>
<tr>
<td>B 3510-11</td>
<td>3.41</td>
<td>1.57</td>
<td>0.40</td>
<td>0.009</td>
<td>—</td>
</tr>
<tr>
<td>B 3510-12</td>
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<td>1.53</td>
<td>0.51</td>
<td>0.005</td>
<td>—</td>
</tr>
<tr>
<td>A 3511-9</td>
<td>3.24</td>
<td>1.34</td>
<td>0.021</td>
<td>1.81</td>
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III. Experimental results and considerations

1. Relation between graphitization and sulfur concentration in solidification

The experimental results in II 1 are shown in Fig. 1. In the case of sulfur addition to the hyper-eutectic Fe-C and Fe-C-Si alloys, in which sulfur was added as alloys having a composition similar to that of each base alloy except sulfur concentration, although the interruption of graphitization proceeds until about 0.15 per cent sulfur, a further increase of sulfur concentration shows a range
Fig. 1. Relation between graphitization and sulfur concentration.

in which graphitization is no longer interrupted in each addition series. These ranges extend to 0.9 per cent and 0.6 per cent in Fe-C-S and Fe-C-Si-S systems respectively. On the other hand, when sulfur is added as commercial iron sulfide, in spite of similar Sc, such a range does not appear and the formation of carbide rapidly proceeds with the increase of sulfur concentration.

The calculated amount of sulfur could be added to the Fe-C alloy and the hypo-eutectic Fe-C-Si alloy. However, in the hyper-eutectic Fe-C-Si alloys, the analytical values of sulfur were always lower than the values calculated from the amount of sulfur added.

In the most of sulfur additions, a sooty substance was found on the surface of the ingots, the amount of which increased with increasing sulfur additions.

The matrices of the hyper-eutectic Fe-C-Si base alloys which were melted as described in II I (ii) without sulfur addition were the mixtures of ferrite and
pearlite, becoming completely pearlite with the addition of 0.15 per cent sulfur. From this observation, it can be inferred that the initial interruption of graphitization is due to the interruption of graphitization in austenite by sulfur.

In the Fe-C base alloy melted as described in II 1(iii) without sulfur addition, the whole matrix was originally pearlite, being the same as matrices in the case of sulfur addition. In this case, the initial interruption of graphitization is considered to be due to the interruption of graphitization of austenite along E'S' line in the Fe-C phase diagram by sulfur.

In both the Fe-C and the Fe-C-Si system, the refinement of pearlite lamellae by the sulfur addition was observed. According to Zener\(^{(8)}\), the interlamellar spacing Sp of pearlite lamellae is expressed by the following equation:

\[
S_p = 4\sigma T_e/Q \rho (T_e - T)
\]  

(1)

where \(Q\) is the heat of transformation per gram, \(T_e\) the eutectic temperature, \(T\) the actual transformation temperature, \(\rho\) the density of austenite, and \(\sigma\) the ferrite-cementite interfacial tension. According to this equation, the refinement of pearlite lamellae can be attributed to the decrease of \(\sigma\) or of \(T\) by sulfur.

The following consideration is made on the above-described results of graphitization. In the sulfur addition to each of the Fe-C and the Fe-C-Si alloy, the cause of the difference in graphitization between the case in which sulfur was added as Fe-C-S or as Fe-C-Si-S alloy and the case in which it was added as iron sulfide, is not clear. However, the oxygen which is contained in iron sulfide and which promotes the formation of carbide\(^{(9)}\)\(^{(10)}\)\(^{(11)}\) is pointed out to be a cause. It can be considered that the oxygen concentration in the addition alloys is low compared with that of the iron sulfide if carbon or silicon is in equilibrium with oxygen in the addition alloys during their preparation. Therefore, it may be considered that the appearance of the ranges in which the interruption of graphitization no longer proceeds with the increase in sulfur concentration is due to the effect of sulfur which promotes graphitization in addition to the carbide-stabilizing effect.

Next, factors promoting graphitization are discussed in the following sections (i) (ii) and (iii) and those promoting the formation of carbide in (iv) and (v). (i) Increase of diffusion coefficient of carbon

Under the consideration that it is more reasonable to use activity gradient \(\partial a/\partial x\) instead of the concentration gradient \(\partial c/\partial x\) in Fick's law, Iwase and Kachi\(^{(12)}\) have derived the following equation:

\[
\frac{D_e}{D_0} = \frac{\partial a_e}{\partial c},
\]

(2)

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\(^{(9)}\) K. Iwase and M. Homma, J. Japan Inst. Metals, 16 (1952), 111.

\(^{(10)}\) M. Homma et al., ibid., 16 (1952), 280.

\(^{(11)}\) M. Homma and Y. Hashimoto, ibid., 16 (1952), 169.

where $D_c$ is the diffusion coefficient of carbon in a dilute solution, $a_c$ the activity of carbon, and $C$ the concentration of carbon. The following appreciation is made on the effect of sulfur on $\partial a_c/\partial c$. According to Neumann and Schenck(6), the interaction parameter $\varepsilon_c^{(v)}$ in carbon saturated liquid iron at 1550°C is

$$\varepsilon_c^{(v)} = \frac{1}{\partial} \frac{1}{N_i} r_c = + 5$$

(3)

where $\gamma_c$ is the activity coefficient of carbon when graphite is taken as standard state, and $N_i$ the mole fraction of sulfur. As $\varepsilon_c^{(Si)}$ is $+3.5$ (6), sulfur increases the activity of carbon $a_c$ more strongly than silicon. If the relation (3) can further be applied to carbon unsaturated solution (13), $\partial a_c/\partial c$ should be increased by the increase of sulfur concentration. Therefore, $D_c$ should also be increased by the increase in sulfur concentration.

The rate of transformation will be controlled by the nucleation rate and the growth rate of a new phase. If the growth rate of graphite is controlled by the diffusivity of carbon, the increase of the growth rate of graphite by sulfur can be expected.

(ii) Decrease of solubility of carbon

It has experimentally been known in connection with the increase of $\gamma_c$ that the solubility of carbon is decreased by the presence of sulfur (14). Eq. (3) is also expressed as follows (6):

$$\varepsilon_c^{(v)} = - \frac{1}{\partial} \frac{1}{N_i} N_{e\text{max}} = + 5$$

(4)

where $N_{e\text{max}}$ is the mole fraction of carbon in saturation. Since $\varepsilon_c^{(Si)}$ is $+3.5$ as described above, sulfur decreases the solubility of carbon more strongly than silicon.

As the solubility of sulfur in $\gamma$-Fe is of order of $10^{-2}$ in weight percentage (15), sulfur concentrates in liquid phase with the proceeding of eutectic reaction. Therefore, in addition to the graphitization in eutectic reaction, another graphitization proceeds with the decrease of solubility of carbon which is caused by the concentration of sulfur in liquid.

(iii) Increase of nucleation rate of graphite

According to Becker-Döring theory (16), Turnbull and Fischer (17), and Turnbull (18) have derived the following equations respectively for the rate of homogeneous and heterogeneous nucleation in solidification of one component system.

---

(18) D. Turnbull, ibid., 20 (1952), 411.
$$I_v = K_v \exp \left[ -a \sigma^3 / (\Delta F_v)^2 k T \right]$$  \hspace{1cm} (5)

and

$$I_s = K_s \exp \left[ -a \sigma^3 f(\theta) / (\Delta F_s)^2 k T \right],$$  \hspace{1cm} (6)

where $\sigma$ is the interfacial free energy per unit area between crystal nucleus and liquid, $\Delta F_v$ the free energy change per unit volume for the transition liquid $\rightarrow$ crystal, $a$ a constant determined by the nucleus shape, $f(\theta)$ a function of equilibrium contact angle $\theta$ between the crystal nucleus and the catalyst, and $K_v$ and $K_s$ are, though their detailed explanations are omitted, determined by nucleus shape, the surface area of critical nucleus, free energy of activation per atom for transport across the liquid-crystal interface, temperature of system, etc.

Now, if it is assumed that these types of relation can be applied to the graphite formation in eutectic reaction, $\sigma$ and $\Delta F_v$ correspond to the interfacial free energy between graphite and liquid, and the free energy of formation of graphite per unit volume respectively.

On the other hand, the interfacial tension $\sigma_{gi}$ between graphite and liquid is expressed as follows:

$$\sigma_{gi} = \sigma_g - \sigma_l \cos \theta,$$  \hspace{1cm} (7)

where $\sigma_g$ is the surface tension of graphite, $\sigma_l$ the surface tension of liquid and $\theta$ the contact angle between graphite and liquid.

By sulfur the surface tension of liquid cast iron is strongly decreased \(^{(19)}(20)(21)\) and $\theta$ is also decreased\(^{(22)}(23)\). Since the angle $\theta$ is obtuse, $\sigma_{gi}$ is also decreased by the decrease of $\sigma_l$ and $\theta$ so long as $\sigma_g$ remains constant. Because $\sigma_{gi}$ is numerically equal to $\sigma$ in Eqs. (5) and (6) \(^{(24)}\), $\sigma$ is strongly decreased by sulfur addition.

Therefore, if the above assumption is reasonable, $I_v$ as well as $I_s$ for the graphitization of cast iron is strongly increased by sulfur addition as long as $K_v$, $K_s$ and $\Delta F_v$ remain approximately constant. Such a connection between the increase of nucleation rate of graphite and the decrease of surface tension of liquid cast iron by sulfur has been already pointed out by Morrogh and Oldifield\(^{(9)}\).

(iv) Increase of supercooling

It has experimentally been confirmed that sulfur supercools cast iron\(^{(9)}(25)\) which can be expressed by the following equation\(^{(26)}\):

$$\frac{dR}{dt} \times A \times N \times L = \frac{dQ}{dt},$$  \hspace{1cm} (8)

where $dR/dt$ is the radial growth rate of a eutectic cell, $A$ the surface area of a
eutectic cell, \( N \) the number of nucleus, \( L \) the latent heat of fusion per unit volume and \( \frac{dQ}{dt} \) the rate of heat extraction. Supercooling proceeds as long as the left hand side is smaller than the right hand side. Considering from Bunin and others’ theory(27) for the growth process of eutectic cell which was supported by Morrogh and Oldfield(26), it is probable that sulfur is concentrated on the interface between liquid and eutectic cell according as eutectic reaction proceeds, being adsorbed on the interface as can be inferred from its effect on surface tension of liquid cast iron. Therefore, according to Eq. (8) it may be considered that by the sulfur addition \( \frac{dR}{dt} \) is decreased and so the supercooling is increased.

(v) Increase of nucleation rate of cementite

The interfacial free energies not only of graphite-liquid but also of cementite-liquid are considered to be lowered by sulfur. Therefore, it is inferred that when supercooling proceeds below a metastable eutectic temperature at which an equilibrium is established among liquid, cementite and austenite, the nucleation rate of cementite increases for the same reason as described in (iii).

Although the effectiveness of the above-described factors on the solidification varies respectively according to sulfur concentration, the above-mentioned experimental results are considered to be a co-operative effect of the five factors at least.

In the hypo-eutectic cast iron, marked increase in the amount of carbide occurs as shown in Fig. 1, which is considered to be due to the following possibilities:

(a) Sulfur is concentrated in liquid phase by the separation of primary austenite.

(b) Compared with a hyper-eutectic alloy, a hypo-eutectic alloy has a small quantity of graphite nucleus.

2. Effects of phosphorus and sulfur on the size of flake graphite and the number of eutectic cells

(i) Effect of phosphorus

The effect of phosphorus on graphite structure could hardly be observed. The effect of phosphorus on the number of eutectic cells is shown in Fig. 2. The concentration of phosphorus was calculated from the amount of the Fe-C-P alloy 3609–9 added. Although the number of eutectic cells increases with increasing phosphorus until 0.6 per cent of P, in a range from 0.6 to 1.19 per cent P, there is no considerable change in the number of eutectic cells.

(ii) Effect of sulfur

Considering from the results shown in (i), experiments were carried out in a range 0.6~1.19 per cent of P so that the effect of phosphorus did not appear. The results are shown in Figs. 3 and 4. Graphite and eutectic cell structures in 0.013, 0.13 and 0.44 per cent S are shown in Photos. 1~6. The relation between graphite size and sulfur concentration is qualitatively in agreement with Garber’s results(9).

Fig. 2. Relation between phosphorus concentration and number of cells.

Fig. 3. Relation between sulfur concentration and graphite size.

Fig. 4. Relation between sulfur concentration and number of cells.
The increase of the number of eutectic cells by sulfur addition has been observed by Morrogh and Oldfield\(^{(5)}\). However, in the present experiments the minimum number of eutectic cells was observed at a certain sulfur concentration.

The reason why the growth of graphite and eutectic cell occurs with sulfur addition may be explained as follows:

First, on the basis of theories and experimental results concerning the nucleation and the growth rate of crystals in one component system\(^{(28)}\)\(^{(29)}\), it may be assumed that the nucleation and the growth rate of eutectic cell are controlled by the nucleation and the linear growth rate of graphite flakes respectively, and that the relationship of the nucleation and the growth rate to supercooling is such as depicted qualitatively in Fig. 5. The direction of the growth of graphite is perpendicular to the axis c.

Fig. 5. Schematic diagram showing growth rate and nucleation rate vs supercooling.

In the solidification of one component system, the free energy change $\Delta G^*$ for the formation of a critical nucleus in heterogeneous nucleation is \(^{(29)}\)\(^{(30)}\)

$$\Delta G^* = \alpha \sigma^3 : \dot{f} (\theta) \left( \frac{1}{\Delta T \cdot \Delta S} \right)^2,$$

where $\alpha$ is a factor concerning the shape of a nucleus, $\sigma$ the interfacial free energy.


between the nucleus and the liquid, \( f(\theta) \) a function of contact angle \( \theta \), \( \Delta T \) the degree of supercooling and \( \Delta S \) the entropy change per unit volume in phase change. In homogeneous nucleation, \( f(\theta) \) is unity.

If it is assumed that this type of relation can be applied to the eutectic reaction, the decrease of supercooling should occur with the decrease of \( \sigma \) due to sulfur so long as \( \Delta G^* \), \( \sigma \), \( f(\theta) \) and \( \Delta S \) remain constant. From the relations (5), (6) and (9) it can be considered that by sulfur addition the curve (N.R.) of nucleation rate in Fig. 5 shifts to the dotted curve which is qualitatively depicted in Fig. 5. Then, according to Eq. (8), it may be expected that there is a possibility that the supercooling decreases from \( t \) to \( t' \) and further growth of flake graphite and hence eutectic cell occur with sulfur addition at a fixed cooling rate. Of course, the effect reverse to the above-described i.e., the interruption of growth of eutectic cell by sulfur must also be considered.

According to the present consideration, in the case of the graphite growth by sulfur addition the decrease of supercooling should be observed. However, such a case has not yet been reported.

The curves obtained by Garber(30) showed that with an addition of 0.025 per cent of sulfur, the temperature range of the solidification of the eutectic hardly changed, whereas the time over which solidification occurred was slightly increased. The latter fact corresponds to an effect of slow cooling.

According to Sidorenko and Tsarevskii(31), the increase of flake graphite size as well as the decrease of surface tension of the Ni-C melt was observed also in the case of sulfur addition to Ni-C alloy. They attributed the cause of the increase of flake graphite size to the selective adsorption of sulfur on the basal plane of graphite (0001), which was postulated by Kozakevitch et al.(32) According to this explanation, although it is not necessary to consider the decrease of supercooling, a difficulty in explaining the refinement of flake graphite by the further increase of sulfur will arise.

The increase of the number of eutectic cells in further increase of sulfur is considered to be due to the increase of the nucleation rate which should occur for the following reasons: (a) the lowering of interfacial tension between graphite and liquid by sulfur as was pointed out by Morrogh and Oldfield(9) and (b) the increase of \( \Delta F_a \) due to the increase of supercooling by sulfur.

Selenium and tellurium also have the same effect as sulfur on the size of flake graphite(30) and decrease the surface tension of copper melt as in the case of sulfur(31).

3. Effect of sulfur and manganese on the size of flake graphite

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(31) R.A. Sidorenko and B.V. Tsarevskii, The Physics of Metals and Metallography, 10 (1960), 73.
(32) R. Kozakevitch, S. Chatel, G. Urbain et M. Sage, Rev. Met., 52 (1955), 139.
Experimental results are shown in Fig. 6. The concentration of sulfur was calculated from the amount of the addition alloy 3511-9 added. The size of flake graphite decreases with the addition of manganese so that the effect of sulfur is cancelled. Examination of the solubility product of MnS in carbon saturated solution shows the formation of MnS during solidification. The experimental results is explained by the possibility that the concentration of sulfur is decreased by the formation of MnS during solidification.

If MnS promoted the nucleation of graphite, the coarsening of graphite might occur by the addition of manganese as was actually observed in inoculation. Because such an effect could not be observed, it seems that MnS does not act as a catalyst in the nucleation of graphite under the experimental condition.

Summary

(1) When sulfur was added as Fe-C-S and Fe-C-Si-S alloys to hyper-eutectic Fe-C and Fe-C-Si alloy systems, a range appeared in which the graphitization was not furthermore obstructed by the increase of sulfur. The appearance of such a range is considered to be due to the effects of sulfur which promote graphitization in solidification, in addition to its carbide-stabilizing effect.

(2) With initial increasing sulfur, fine eutectic graphite (undercooled graphite)

Eutectic cell structures

Photo 1. 0.013% S
Etched in Stead's reagent

Graphite structures

Photo 2. 0.013% S
Unetched

Photo 3. 0.13% S
Etched in Stead's reagent

Photo 4. 0.13% S
Unetched

Photo 5. 0.44% S
Etched in Stead's reagent

Photo 6. 0.44% S
Unetched
became almost coarse flake graphite, and with further sulfur increases, the coarse flake graphite was refined.

The same tendency was obtained also in the size of eutectic cell. These experimental results were qualitatively explained according to the theories of crystal growth and nucleation under some assumptions.

(3) Manganese decreased the size of flake graphite so as to cancel the effect of sulfur. This is considered to be due to the formation of MnS during solidification.

The effect of MnS as a nucleation catalyst for graphite formation was not observed.

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