Influence of cooling rate and antimony addition content on graphite morphology and mechanical properties of a ductile iron

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Abstract: Cooling rate and inoculation practice can greatly affect the graphite morphology of ductile irons. In the present research, the effects of the cooling rate and antimony addition on the graphite morphology and mechanical properties of ductile irons have been studied. Three ductile iron castings were prepared through solidification under cooling conditions S (slow), M (medium) and F (fast). The cooling rates around the equilibrium eutectic temperature (1,150 °C) for these cooling conditions (S, M and F) were set at 0.21 °C·min⁻¹, 0.32 °C·min⁻¹ and 0.37 °C·min⁻¹, respectively. In addition, four ductile iron castings were prepared by adding 0.01%, 0.02%, 0.03% and 0.04% (by weight) antimony, respectively under the slow cooling condition. The results show that the nodularity index, tensile strength and hardness of the ductile iron castings without antimony addition are all improved with the increase of cooling rate, while the ductile iron casting solidified under the medium cooling rate possesses the largest number of graphite nodules. Furthermore, for the four antimony containing castings, the graphite morphology and tensile strength are also improved by the antimony additions, and the effect of antimony addition is intensified when the addition increases from 0.01% to 0.03%. Moreover, the rare earth elements (REE)/antimony ratio of 2 appears to be the most effective for fine nodular graphite formation in ductile iron.

Key words: ductile iron; cooling rate; antimony; graphite morphology; mechanical properties
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The production of ductile iron has been increasing due to its excellent strength and ductility. The graphite morphology determines the mechanical properties of ductile iron. Spherical graphite in ductile iron leads to excellent properties, while chunky graphite severely reduces the properties of ductile iron castings. Melt holding time and cooling rate can greatly affect the microstructure, while the chemical composition and inoculation practice also influence the graphite morphology of ductile iron [1-3]. In general, deteriorated graphite is more likely to appear in heavy section ductile iron castings than in small section ones, for the heavy section ductile iron castings solidify under very slow cooling rate and exhibit longer eutectic plateau, but chunky graphite may also appear in small section castings [4-5].

In order to reduce the chunky graphite formation, chills and anti-spheroidizing elements such as antimony and bismuth are normally used, which sometimes lower the degenerating level of graphite. Previous studies [6-8] showed that appropriate addition of antimony is beneficial to the graphite morphology and mechanical properties of ductile iron because antimony reacts with rare earth elements (REE) to form high melting point compounds which can act as nucleus of globular graphite; moreover, the concentration of antimony around graphite can impede the graphite deterioration. At present, however, antimony addition is usually used to improve graphite morphology in heavy section ductile iron, but the appropriate content of antimony addition is still controversial, and a clear understanding on chunky graphite appearance and a safe metal preparation method to avoid chunky graphite are not yet available. Accordingly, in the present work, the combined effects of the cooling rate and different antimony addition contents on the graphite morphology and mechanical properties of ductile iron have been studied. The results were discussed, and both similarities and discrepancies were addressed.

1 Experimental procedure

The compositions of the raw materials used in this experiment
are listed in Table 1. The nominal composition of the ductile iron is 3.6%C, 2.2%Si, 0.42%Mn, 0.47%Cu, <0.02%P, <0.01%S, and Fe is the balance. The melting process was carried out in a medium frequency induction furnace of 30 kg in capacity. The melt was poured into a preheated ladle at 1,500 °C for spheroidisation and inoculation treatment by sandwich method, and the pure antimony was added at the same time. After being treated, the molten metal at 1,250 °C was poured into an insulated crucible inside the knockdown multifunctional resistance furnace, as shown in Fig. 1.

### Table 1: Chemical compositions of raw materials (wt.%)

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Mg</th>
<th>Ca</th>
<th>Ba</th>
<th>Al</th>
<th>REE*</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pig iron</td>
<td>0.04</td>
<td>0.02</td>
<td>0.019</td>
<td>0.019</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Scrap steel</td>
<td>0.16</td>
<td>0.15</td>
<td>0.38</td>
<td>0.01</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Carburant</td>
<td>97.6</td>
<td></td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Ferromanganese</td>
<td>6.15</td>
<td>0.80</td>
<td>65.04</td>
<td>0.150</td>
<td></td>
<td>7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.62</td>
<td>Bal.</td>
</tr>
<tr>
<td>Nodulizer</td>
<td>42.6</td>
<td></td>
<td></td>
<td>1.84</td>
<td>4.22</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Inoculant</td>
<td>70.2</td>
<td></td>
<td></td>
<td>1.84</td>
<td>4.22</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Silicoferrite</td>
<td>72.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
</tbody>
</table>

* - REE contains 50% Y and 50% Ce.

![Fig. 1: Experimental apparatus for simulative solidification](image)

When the melt is held in the resistance furnace, its cooling condition can be accurately controlled by the ENVADA-programme controlling instrument. Firstly, set the cooling curve through the controlling instrument, then the controlling instrument will control the heating current in the U-shape silicone molybdenum rods to make the cooling rate of the iron melt matches the programmed cooling curve. In the present study, cooling curves S (slow), M (medium) and F (fast) have been taken into account as shown in Fig. 2. The cooling rates around the equilibrium eutectic temperature (1,150 °C) for these cooling conditions (S, M and F) were set at 0.21 °C·min⁻¹, 0.32 °C·min⁻¹ and 0.37 °C·min⁻¹, respectively.

To investigate the effects of cooling rate and antimony addition on the graphite and matrix microstructure of ductile iron, three ductile iron castings (S0, M0 and F0, Φ110 mm × 120 mm) were prepared through solidification under cooling conditions S (slow), M (medium) and F (fast), respectively. In addition, four ductile iron castings (S1 to S4, Φ110 mm × 120 mm) were prepared by adding 0.01%, 0.02%, 0.03% and 0.04% (by weight) antimony, respectively under the slow cooling condition, as shown in Table 2. The blocks for microstructural observation and tensile test were taken from the center of the cylindrical castings. Microstructural observation was performed by a LEICA DM1500M intelligent optical microscope. Tensile test was conducted with a universal testing apparatus (CMT5105, SANS Co. Ltd., China). Brinell hardness measurement was carried out using a Brinell Hardness Tester (HB-3000B, HUAYIN Co. Ltd, China). After tensile test, all the fractured blocks were used to detect the compositions of the castings by chemical analysis method, excluding the Mg, Y, Ce and Sb contents, which were detected using the ICP-MS (Inductively coupled plasma mass spectrometry) technique.

In addition, to study the graphite morphology evolution above the equilibrium eutectic temperature, the melts without antimony addition were sucked into a Φ5 mm quartz tube at the temperature of 1,240 °C and 1,170 °C, and then they were taken out and quenched in cold water as soon as possible. Melt in the tube solidified within 3 to 5 s, thus graphite morphology in the melt was obtained.
2 Results

Chemical analysis and mechanical performance testing for seven groups of blocks were carried out. The evaluated graphite morphology and the residual contents of spheroidizing elements REE and Mg are listed in Table 3, and the graphite morphology and matrix structure of seven castings are shown in Figs. 3 and 4. By combining with the relative values in Table 3, it is clear that the smaller the globular graphite average diameter, the larger the number of graphite nodules, and the higher the volume fraction of the ferrite phase.

As for the former three castings, the graphite morphology becomes better as the cooling rate increases. An increased nodularity from 30.5% to 61.6% and then 85.2% can be seen as the cooling rate increases, and a similar tendency can also be observed from the values of tensile strength and hardness. In addition, the casting solidified under the medium cooling rate possesses the smallest graphite nodules and presents the highest value of elongation (Table 3).

Table 3: Graphite morphology and mechanical properties of different test blocks

<table>
<thead>
<tr>
<th>No.</th>
<th>REEres. (%)</th>
<th>Mgres. (%)</th>
<th>Globular graphite count (mm^-2)</th>
<th>Nodularity (%)</th>
<th>Globular graphite average diameter (μm)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Hardness (HBW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.025</td>
<td>0.05</td>
<td>—</td>
<td>30.5</td>
<td>84.6</td>
<td>406</td>
<td>2.4</td>
<td>182</td>
</tr>
<tr>
<td>M0</td>
<td>0.035</td>
<td>0.076</td>
<td>—</td>
<td>61.6</td>
<td>56.8</td>
<td>417</td>
<td>4.28</td>
<td>183</td>
</tr>
<tr>
<td>F0</td>
<td>0.026</td>
<td>0.045</td>
<td>—</td>
<td>85.2</td>
<td>90.8</td>
<td>517</td>
<td>4.0</td>
<td>220</td>
</tr>
<tr>
<td>S1</td>
<td>0.027</td>
<td>0.057</td>
<td>10.4</td>
<td>49.4</td>
<td>78.5</td>
<td>573</td>
<td>3.3</td>
<td>225</td>
</tr>
<tr>
<td>S2</td>
<td>0.029</td>
<td>0.060</td>
<td>24.5</td>
<td>64.2</td>
<td>63.4</td>
<td>628</td>
<td>3.07</td>
<td>234</td>
</tr>
<tr>
<td>S3</td>
<td>0.026</td>
<td>0.059</td>
<td>54.5</td>
<td>89.6</td>
<td>43.4</td>
<td>708</td>
<td>2.96</td>
<td>234</td>
</tr>
<tr>
<td>S4</td>
<td>0.028</td>
<td>0.056</td>
<td>39.8</td>
<td>70.2</td>
<td>50.5</td>
<td>569</td>
<td>1.78</td>
<td>244</td>
</tr>
</tbody>
</table>

Fig. 3: Microstructures of ductile irons without Sb addition (etched) solidified under (a) Slow cooling rate, (b) Medium cooling rate and (c) Fast cooling rate

Fig. 4: Graphite morphologies in ductile irons with various contents of Sb addition solidified under the slow cooling rate (unetched): (a) 0.01% Sb, (b) 0.02% Sb, (c) 0.03% Sb, (d) 0.04% Sb

Compared with the antimony free casting solidified under slow cooling rate, the four castings with various contents of antimony addition under the slow cooling rate possess better graphite morphology as shown in Table 3, Fig. 3 and Fig. 4. This is because the addition of antimony is an effective means of eliminating graphite degeneration in heavy section ductile iron. It can be seen from Fig. 4 that the iron with 0.03% antimony addition possesses the finest graphite nodules under the slow cooling rate. Figure 5 shows the relationship between antimony addition and properties for ductile iron castings. It appears that the tensile strength value of the casting reaches the maximum when 0.03% antimony is added, and the elongation values of castings with 0.01%, 0.02% and 0.03% antimony addition are in about the same high level, while that of the casting with 0.04% antimony addition is significantly lower. In addition, the hardness values increase slightly as the antimony content increases from 0.01% to 0.02%, and from 0.03% to 0.04%.
3 Discussion

3.1 Graphite morphology evolution above the equilibrium eutectic temperature

G. S. Cole [9] reported that the graphite nodule firstly precipitates from molten iron directly at 1,300 °C, which is far higher than the equilibrium eutectic transforming temperature (1,150 °C). In general, 1,080 °C is regarded as the final temperature of liquid-solid transformation of ductile iron [10], thus the graphite morphology in the casting should not change below 1,080 °C.

Figure 6 shows the graphite morphology in the ductile iron casting without antimony addition (quenched blocks mentioned above) at the temperatures of 1,240 °C and 1,170 °C. Apparently, the graphite morphologies at 1,240 °C and 1,170 °C are all globular graphite, indicating that the globular graphite does not begin to deteriorate above 1,170 °C. Besides, it is the initial stage of eutectic reaction above 1,170 °C, which can also be seen from the solid fraction calculated by Scheil equation [11], shown as following equation:

\[
e_s' = 1 - \left( \frac{T_m - T_i}{T_m - T_c} \right)^{\frac{1}{k}}
\]

where \(T_m\), \(T_i\), and \(k\) represents the melting temperature, liquidus temperature of the pure metal, and the distribution coefficient, respectively. Considering the deteriorated graphite in the three blocks without antimony addition (Fig. 3), it can be concluded that the graphite deteriorates between 1,170 °C to 1,080 °C during the process of solidification.

3.2 Influence of cooling rate without antimony addition

In the present study, the casting which solidified under slow cooling rate owning a long eutectic plateau represents the heavy section ductile iron casting, and the casting solidified under fast cooling rate represents the small section ductile iron casting. For the three castings without addition of antimony, the nodularity index value increases as the cooling rate increases. But the casting solidified under medium cooling rate possesses the smallest size and largest number of graphite nodules (Fig. 3), because it contains higher level of residual spheroidizing elements REE and Mg than the other two castings (Table 3). Thus, the sufficient REE reacts with oxygen and sulfur to form high melting point compounds, serving as effective nucleus of the nodular graphite [12]. In addition, it can be seen from Fig. 3 that a higher content of ferrite exists around the chunky graphite due to that the chunky graphite causes the existence of carbon depletion region around itself.

It was calculated that the percentage of ferrite content in the castings solidified under the cooling rate S, M and F is 30%, 20% and 5%, respectively. Therefore, both the tensile strength and hardness increase as the cooling rate increases, because the percentage of pearlite content is the critical factor for the tensile strength and hardness values. Although the casting solidified under medium cooling rate has relatively low value of nodularity index compared with the one under fast cooling rate, it has the smallest size of globular graphite, still leading to the highest elongation value.

3.3 Influence of various contents of antimony addition

Many researchers reported that the rare earth elements (REE) in excessive concentrations may lead to chunky graphite formation in large section irons, with subsequent
degradation in the mechanical properties. However, anti-spheroidizing elements such as antimony and bismuth are normally used to dilute the negative influence of excessive REE concentrations. It should be noted that the REE/antimony ratio of 2 seems to be the most effective for fine graphite nodules (i.e. the S3 casting with 0.03% Sb addition in this study), in which case complete neutralization of antimony by REE was achieved. When 0.04% antimony was added, a little spiky graphite appears as a result of excessive antimony addition, as shown in Fig. 4(d). Furthermore, antimony can promote the formation of pearlite phase intensively. From Fig. 5, the hardness increases as the antimony addition increases from 0.01% to 0.04% owing to the increase of pearlite phase, while the tensile strength and elongation reach relatively high level when 0.03% antimony is added, owing to the refinement of graphite nodules.

All the results show that appropriate content of antimony addition plays a significant role in increasing the nucleation rate and inhibiting the deterioration of graphite nodules in heavy section ductile iron castings.

4 Conclusions

Three ductile iron castings were prepared by solidifying under three different cooling rates S (slow), M (medium) and F (fast). The cooling rates around the equilibrium eutectic temperature (1,150 °C) for the cooling conditions S, M and F are 0.21 °C·min⁻¹, 0.32°C·min⁻¹ and 0.37 °C·min⁻¹, respectively. In addition, four ductile iron castings were prepared by adding 0.01%, 0.02%, 0.03% and 0.04% (by weight) antimony, respectively under the slow cooling rate. Based on the experimental results, the following conclusions were obtained.

For the three ductile iron castings without antimony addition, an increased nodularity index from 30.5% to 61.6% and 85.2% can be seen as the cooling rate increases, and a similar tendency can also be noticed from the values of tensile strength and hardness. But the casting solidified under the medium cooling rate possesses a larger number of graphite nodules than those under fast and slow cooling rates.

The results of the other four castings with variable antimony addition indicate that the graphite morphology and mechanical properties can be improved by adding antimony, and when 0.03% antimony is added, the optimal complex mechanical properties can be obtained. Appropriate content of antimony addition plays a significant role in increasing their nucleation rate and inhibiting their deterioration of graphite nodules in heavy section ductile iron castings as well as in small section ones. REE/antimony ratio of 2 appears to be the most effective for fine nodular graphite formation in ductile iron castings with a relatively long eutectic plateau during their solidification.

References