Influence of fading on characteristics of thermal analysis curve of compacted graphite iron

Liu Jinhai, Yi Litao¹, Li Guolu¹, Liu Changqi², Li Yinguo² and Yang Zhaoyu¹
(1. School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300132, China; 2. Tianjin Sabulance Probe Engineering Co. Ltd., Tianjin 300402, China)

Abstract: In general, during the production of compacted graphite iron (CGI), the active residual magnesium reduces and the effect of inoculation fades after magnesium treatment. In this paper, characteristics of the thermal analysis curve of CGI are compared with those of ductile iron and grey cast iron. The fading effect on the compacted graphite percentage and thermal analysis curve were also studied. Results indicate that the undercooling of CGI is as low as that of ductile iron, but CGI shows evident recalescence. In fading process, the magnesium element acts with oxygen. For a decrease in magnesium content, both the compacted graphite percentage and the austenitic liquidus temperature increase. The temperature of eutectic undercooling ($T_{EU}$) decreases before the flake graphite appears. After that, $T_{EU}$ increases quickly, up to as high as 20°C, and then gradually decreases. The evolution of recalescence degree is opposite to that of $T_{EU}$.

Key words: compacted graphite iron; thermal analysis; fading; compacted graphite percentage; characteristic value


Compacted graphite iron (CGI) as a kind of defect was found during the production of ductile iron. The graphite morphology in CGI, known as vermicular graphite with a round head, is between flake and spherical graphite. With the help of scanning electron microscope, it was shown that the vermicular graphite is connected in three-dimension [1]. The unique shape of the graphite leads to the unique performances of CGI. Compared to flake graphite, the vermicular graphite reduces stress concentration in the matrix significantly, resulting in an improved mechanical property. Compared to nodular graphite in ductile iron, the inter-connected vermicular graphite makes the thermal conductivity of CGI higher. Meanwhile, the carbon equivalent of CGI is close to the eutectic composition, so CGI has a better castability and less shrinkage defect. Based on these characteristics, CGI has an unparalleled advantage when used in both high strength and high thermal conductivity required components [2, 3].

Despite good overall performances, the steady production of CGI is a problem for foundry workers. To ensure the overall performance of CGI, the general requirement of compacted graphite percentage is higher than 50%. For blow-fed engine block, cylinder head and other complex components, the percentage of compacted graphite in the key position of the parts should be controlled to more than 80% [4, 5]. Reference [6] shows that when the percentage of compacted graphite is higher than 80%, the residual magnesium content in the molten iron need to be controlled to a fluctuation range of ± 0.003% after the magnesium treatment. Because of fading during the holding and pouring of the treated liquid iron (residual magnesium burning at a rate of 0.001% per 5 minutes), the "operating window" of molten metal is extremely narrow. In addition, the percentage of compacted graphite is affected also by the inoculation and cooling rate [7].

In order to produce the CGI stably, it is needed to determine the compacted graphite percentage. The method is to measure the cooling curve of CGI by thermal analysis. To predict the compacted graphite percentage, the first step is to classify the vermicular iron, grey iron and ductile iron. The second is to define the percentage of compacted graphite. In this paper, the difference in thermal analysis curves was studied based on the eutectic growth pattern of three different kinds of cast iron. And the effect of magnesium content on the characteristics of the thermal analysis curve was investigated in the fading process.

1 Experimental procedure

The DX104-type data collection instrument with four-channel was used to measure the time-temperature curve. The instrument has the functions of amplification, filtering and...
A/D conversion. The sampling cup with a wall thickness of 5 mm was made of resin bonded sand. In order to ensure similar chemical compositions in each heat of molten metal, the pig iron was remelted and cast into small ingot of 8 kg. The chemical composition of different charges, such as pig iron, ferrous-silicon, inoculant and vermicularizer, are shown in Table 1.

The test alloys were melted in a 30 kg medium frequency induction furnace, and the tapping temperature of the molten metal was about 1,530°C. Sandwiches method was adopted for producing the compacted graphite cast iron. After vermicularized treatment, the molten iron was put back into the furnace for holding. Then samples were taken for thermal analysis after different holding times. Based on wavelet filter and support vector machine [8], the characteristic values were determined from the thermal analysis curve. Some of the characteristic values are named and shown in Table 2 and Fig. 1.

### Table 1: Chemical composition of different charges (mass%)

<table>
<thead>
<tr>
<th>Charge</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Mg</th>
<th>Ba</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pig iron</td>
<td>3.75</td>
<td>1.68</td>
<td>0.277</td>
<td>0.039</td>
<td>0.027</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Si-Fe</td>
<td>...</td>
<td>72.96</td>
<td>...</td>
<td>0.04</td>
<td>0.02</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Inoculant</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>1.0–2.0</td>
<td>...</td>
</tr>
<tr>
<td>Vermicularizer</td>
<td>...</td>
<td>43.96</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>4.26</td>
<td>...</td>
<td>8.62</td>
</tr>
</tbody>
</table>

### Table 2: The significance of characteristic values of thermal analysis curve

<table>
<thead>
<tr>
<th>Characteristic value</th>
<th>Significance</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{es})</td>
<td>Stable (graphite) eutectic equilibrium temperature</td>
<td>Theoretical temperature for C to precipitate as graphite</td>
</tr>
<tr>
<td>(T_{mst})</td>
<td>Metastable (white) eutectic equilibrium temperature</td>
<td>Temperature when C is chemically combined with iron (Fe(_3)C)</td>
</tr>
<tr>
<td>(\Delta T_e)</td>
<td>Range of equilibrium eutectic temperature</td>
<td>(\Delta T_e) should be as large as possible</td>
</tr>
<tr>
<td>(T_{al})</td>
<td>Liquid temperature of commencement of pro-eutectic austenite precipitation</td>
<td>The first arrest temperature</td>
</tr>
<tr>
<td>(T_{ser})</td>
<td>Temperature of the start of eutectic freezing (nucleation)</td>
<td>Derivative has a minimum between (T_{al}) and (T_{eu})</td>
</tr>
<tr>
<td>(T_{eu})</td>
<td>The lowest eutectic temperature</td>
<td>The minimal point from which the temperature is increasing and the first derivative is zero</td>
</tr>
<tr>
<td>(T_{er})</td>
<td>The highest eutectic temperature</td>
<td>The maximum temperature after increase in temperature and first derivative is zero</td>
</tr>
<tr>
<td>(T_{es})</td>
<td>Temperature of the end of solidification</td>
<td>All metal has solidified and the lowest value of the negative peak on the first derivative</td>
</tr>
<tr>
<td>(\Delta T_r)</td>
<td>Recalecense degree</td>
<td>It reflects the amounts of austenite and graphite that are precipitated in the first part of eutectic freezing</td>
</tr>
</tbody>
</table>

### 2 Results and discussion

#### 2.1 Comparison of thermal analysis curves of CGI, grey iron and ductile iron

For the same chemical composition, the thermal analysis curves of grey iron, compacted graphite iron and ductile iron were measured, as shown in Fig. 2. The characteristic values are listed in Table 3.
From Table 3, it can be seen that for the same composition, the lowest eutectic temperature \( T_{EU} \), the highest eutectic temperature \( T_{ER} \) and recalescence degree \( \Delta T_r \) of the three tested cast irons are significantly different. The reasons for these phenomena can be explained in the following aspects.

During eutectic growth of grey iron, the graphite tip always grows and extends into the liquid ahead of the austenite crystal frontier. Since the carbon diffusion rate in liquid phase is about 20 times faster than that in solid austenite, the graphite grows quickly and results in poor carbon distribution in area surrounding the growing graphite tip. This contributes to the growth of austenite also. Therefore, the eutectic growth requires less driving force and the eutectic undercooling is small. It shows on the curve that \( T_{EU} \) is higher compared to those in ductile iron and CGI. Also, because of the higher \( T_{EU} \), which is closed to \( T_{ER} \), recalescence degree \( \Delta T_r \) is also smaller.

The eutectic growth of ductile iron is different from those in grey iron and compacted graphite iron. It is called the divorced eutectic growth model. When the eutectic solidification happens, the graphite nodules are surrounded by austenite. So the graphite nodules grow by carbon diffusion through the austenite shell. Because of the low diffusion speed of carbon atom in austenite, the rate of eutectic solidification is slow and the latent heat released per unit time is small. Therefore, the lowest eutectic temperature \( T_{EU} \) is lower compared to that of grey iron, and the recalescence degree \( \Delta T_r \) is small. The eutectic growth pattern of compacted cast iron is between those in grey iron and ductile iron. The compacted graphite grows with characteristics of flakes in some extent, but also has rounded edges. The test results are in good agreement with those in the reference [9]. It could be explained by the alternating growth patterns of compacted graphite. Since the presence of residual magnesium and rare earth, the eutectic transformation grows difficulty in the early stage of solidification, resulting in a large undercooling and \( T_{EU} \) as low as those in ductile iron. In the subsequent growth process, there is no enough magnesium and rare earth to support the nodule growth of graphite and it shows some signs of flake growth. The eutectic of compacted graphite and austenite grows rapidly, releasing more latent heat per unit time than those in ductile iron, and the recalescence degree \( \Delta T_r \) significantly increases.

### 2.2 Effect of fading on the compacted graphite percentage

The residual amount of active magnesium will decrease as the holding process proceeds. Figure 3 shows the variation of residual Mg content with holding time.

![Fig. 3: Residual Mg content at different holding times](image)

The graphite morphologies obtained after different fading processes were shown in Fig. 4. The compacted graphite percentage was measured based on 8 different optical field-of-views obtained from metallographic sample. Figure 5
illustrated the evolution of compacted graphite percentage in the fading process. Experimental result shows that the molten iron with magnesium treatment fades completely into grey cast iron in about 5 minutes. The speed of fading is related to the holding process. Because small furnace was used in this study, the molten iron rolls severely in the furnace and accelerating the fading of CGI. In 5 minutes after magnesium treatment, the compacted graphite percentage rises as time increases. This results from burning loss of residual magnesium as well as the reduction of inoculating nuclei. Part of the active magnesium vaporizes from molten iron under high temperature, and part of the magnesium combined with oxygen forming a stable oxide. So there is not enough active magnesium to make the eutectic graphite crystallize in vermicular shape. At the same time, the constituent fluctuation of silicon, which results from inoculation process, fades away and the number of graphite nuclei reduces [10]. The two aspects’ work together lead to the increase in compacted graphite percentage. When the amount of active magnesium is below a certain value, the molten iron fades into grey iron.

Fig. 5: Effect of magnesium content on compacted graphite percentage

2.3 Effect of fading on the characteristics of thermal analysis curve

In fading process, the characteristic changes in magnesium-treated molten iron reflect in the thermal analysis curve. The precipitating temperature ($T_{\text{AL}}$) of primary austenite, the lowest eutectic temperature ($T_{\text{EU}}$) and the highest eutectic temperature ($T_{\text{ER}}$) change with fading process remarkably, as shown in Fig. 6, Fig. 7 and Fig. 8, respectively.

Figure 6 shows the evolution of $T_{\text{AL}}$ during the fading process. The carbon equivalents of the three tested heats are 4.07, 4.02, 4.05, respectively. According to the phase diagram, with increasing in carbon equivalent, the liquidus becomes lower. This difference is reflected on the thermal analysis curve. The first heat has a lower $T_{\text{AL}}$, while, the second has a higher $T_{\text{AL}}$. In each experiment, $T_{\text{AL}}$ (liquidus temperature) increases gradually with the holding time. Reference [11] indicates that the liquidus temperature of austenite in Fe-G diagram is related to the oxygen content in the molten iron. During holding, the molten iron is in contact with the atmosphere and oxygen dissolves into the liquid iron, leading to an increase in oxygen content. It promotes the nucleation and growth of austenite.

The effect of magnesium content on $T_{\text{EU}}$ in fading process is shown in Fig. 7. It can be seen that $T_{\text{EU}}$ of compacted graphite iron is lower than that of grey iron. When the graphite is vermicularized, the presence of residual magnesium makes the eutectic grow under a large undercooling, and with decreasing of magnesium content, $T_{\text{EU}}$ reduces gradually, and the tendency of liquid undercooling increases. The data reported in reference [12] show that as to compacted graphite iron, the $T_{\text{EU}}$ decreases correspondingly with decreasing of residual magnesium content. The reason for this phenomenon is believed to be related to the solidification kinetic. When the magnesium content is lower than about 0.008%, $T_{\text{EU}}$ increases by about 20°C abruptly. This is because the oxygen in air dissolves into the liquid iron and consumes the active magnesium to form oxide. Meanwhile the dissolved excess oxygen adsorbs on
the growing graphite crystal face, blocks the spiral dislocation on (0001) crystal face of graphite. It is difficult for carbon atoms to pile up, and this promotes the growth of graphite in [1010] direction. The growing pattern of graphite changes suddenly from worm-like into D-type graphite. According to the growth relations of graphite and austenite in eutectic stage, D-type graphite grows in normal eutectic way, i.e. graphite and austenite grow forward at approximately the same rate. However, during eutectic solidification of compacted graphite iron, the growing speed of austenite is faster than that of graphite, and the growing graphite is limited to the liquid channel surrounded by austenite. Carbon that diffuses along liquid channels is the main supplying source to keep the growth of graphite \[13\]. Because of the two different kinds of microscopic growth patterns, compared to compacted graphite iron, the growth of D-type graphite requires smaller driving force and the eutectic undercooling becomes small. Furthermore, the silicon-rich micro-phase in inoculated liquid iron dissolves gradually. The active silicon content in molten iron increases, which makes the equilibrium temperature of eutectic increase \[14\]. Both actions make \(T_{EU}\) rises rapidly. When the magnesium contents reduce further and the fading effect is more severe after inoculation, the eutectic graphite grows from the D-type to A-type, and the growing graphite is limited to the product of graphite grows from compact to flake.

2.4 Effect of fading on the recalescence degree

Figure 8 shows the effect of magnesium content on the highest eutectic temperature \(T_{ER}\). With decreasing in magnesium content, \(T_{ER}\) increases. After it reaches the highest value, \(T_{ER}\) declines again. Experimental results showed that during the fading process of CGI, \(T_{ER}\) reaches the maximum at the same time the morphology of graphite grows from compact to flake.

![Fig. 9: Effect of magnesium content on \(\Delta T\)](image)

**Fig. 9**: Effect of magnesium content on \(\Delta T\),

the eutectic transformation process. The heat energy that the molten iron released per unit time increases, so the recalescence degree rises. When the magnesium content decreases to a certain value, it can not make eutectic graphite grow into the worm-like pattern, but in the form of D-type or A-type graphite. This kind of cast iron requires a smaller eutectic undercooling, that is higher \(T_{EU}\). Therefore, the heat released per unit time reduces, resulting in lower recalescence degree, i.e. smaller \(\Delta T_r\).

3 Conclusions

1. Thermal analysis curve of CGI differs significantly from those of grey iron and ductile iron; eutectic undercooling of CGI is lower than that of grey iron, but similar to that of ductile iron; while recalescence degree \(\Delta T_r\) is lower than those of ductile iron and grey cast iron.

2. The compacted graphite percentage rises in fading process, and in about 5 minutes, the morphology of graphite changes to D-type and then A-type.

3. In fading process, \(T_{AE} \) rises, \(T_{EU} \) decreases and \(\Delta T_r \) increases gradually; when it changes into grey cast iron, \(T_{EU} \) increases suddenly, while the recalescence degree \(\Delta T_r \) decreases.

References