Prediction of Graphite Nodule Count and Shrinkage Tendency of Spheroidal Graphite Cast Iron by One Cup Thermal Analysis

Toshitake Kanno, Yuki Iwami and Ilgoo Kang

Kimura Chuzosho Co., Ltd., Suntougun, Shizuoka 441–0905, Japan

Three cup thermal analysis is a good method for predicting chill depth, tensile strength and graphite type in gray cast iron. However, it cannot be used in ductile cast iron due to several reasons. For this reason, we have developed a method for investigating the graphite eutectic temperature (hereafter TEC) and cementite eutectic temperature (hereafter TEG) in ductile cast iron, from the chemical composition of the molten metal, as follows:

\[
\Delta T_{TE} = T_{EG} - T_{EC}
\]  

\[
\Delta T_{E} = T_{EC} - T_{TE}
\]  

EGA = \Delta T_{E} \times 100/\Delta T_{E}  

Zero EGA means to become all chill (0 point degree molten metal) and hundred EGA means to become all A type graphite (100 point degree molten metal)

Figure 1 shows the relationship between EGA and chilling depth (D)\(^{10}\). As shown in eq. (4), there is a good correlation between EGA and chilling depth (r = 0.98). It can be said that chilling tendency is predicted correctly with 3 cups thermal analysis in gray cast iron.

\[
D = -0.27 \times (\Delta T_{E} \times 100/\Delta T_{E}) + 26 (r = 0.98)  
\]  

In addition, there is also a good correlation between EGA and tensile strength\(^{11}\).

The three cups thermal analysis is very useful for predict-
ing the quality of molten metal of gray cast iron. However, it cannot be used in ductile cast iron due to the following reasons.

First, in the ductile iron, as austenite solidifies ahead of graphite, the highest eutectic temperature ($T_{\text{max}}$) does not reach to $T_{\text{EC}}$ even in the inoculated cup (A).

Secondly, as Te is at the same family with S and O on the periodic table, the added Te in the cup bonds Mg to make MgTe. That is, it cannot work for making chill and $T_{\text{EC}}$ cannot be shown.

Thirdly, it is possible to make the molten metal to gray cast iron’s melt with adding Fe-S alloy, and to measure $T_{\text{EG}}$ and $T_{\text{EC}}$. However, the influence of S on eutectic temperature is too strong. In addition, we have to prepare an extra cup every times.

Fourthly, we could not find the influence of Mg on eutectic temperature.

2. Principle of One Cup Thermal Analysis System in Ductile Iron

Figure 2 shows the influence of Si amount on $T_{\text{EG}}$ and $T_{\text{EC}}$ in gray iron\(^{12}\). $T_{\text{EG}}$ increases 4.7°C with adding 1 percent Si and $T_{\text{EC}}$ decreases 11.6°C with adding 1 percent Si.

Table 1 shows the influence of each element on $T_{\text{EG}}$ and $T_{\text{EC}}$\(^{12}\). From these data, $T_{\text{EG}}$ and $T_{\text{EC}}$ can be calculated, as shown in eqs. (5) and (6).

$$\begin{align*}
T_{\text{EG}} &= 1149.1(\degree\text{C}) + 4.7\text{Si}\% - 4.0\text{Mn}\% - 44\text{P}\% \\
&\quad + 2.7\text{Cu}\% + 1.0\text{Ni}\% + 1.8\text{Co}\% + 13.9\text{Al}\% \\
&\quad - 17.7\text{Mo}\% - 10.5\text{Cr}\% - 9.3\text{Sn}\% - 5.2\text{Sb}\% \\
&\quad - 6.1\text{W}\% - 3.7\text{Nb}\% - 14.8\text{V}\% - 80.3\text{B}\% \quad (5) \\
T_{\text{EC}} &= 1142.6(\degree\text{C}) - 11.6\text{Si}\% - 0.75\text{Mn}\% - 46.2\text{P}\% \\
&\quad - 1.4\text{Cu}\% - 1.1\text{Ni}\% - 0.7\text{Co}\% - 1.8\text{Al}\% \\
&\quad - 14.5\text{Mo}\% + 5.9\text{Cr}\% - 6.0\text{Sn}\% - 5.1\text{Sb}\% \\
&\quad - 2.8\text{W}\% + 0\text{Nb}\% + 3.3\text{V}\% - 26.0\text{B}\% \quad (6)
\end{align*}$$

In the case of gray cast iron, Mn bonds S to makes MnS. This MnS does not affect $T_{\text{EG}}$ and $T_{\text{EC}}$. Therefore, soluble Mn and soluble S should be calculated and be used. The calculation method for soluble Mn and soluble S in gray cast iron is reported by T. Kanno\(^{13}\).

This equation can be applied to ductile cast iron. In ductile cast iron, all S bonds Mg to makes MgS, so we do not consider S effect. Mg amount is small enough to be ignored. All Mn should be treated as soluble one, because Mn does not bond S and remains as soluble Mn.

Figure 3 shows the EGA measuring method with one cup thermal analysis. With the cooling curve of one cup (no addition cup), the minimum eutectic temperature at recalescence ($T_{\text{SC}}$) can be searched. As explained above, we can calculate $T_{\text{EG}}$ and $T_{\text{EC}}$ from the influence of each elements on $T_{\text{EG}}$ and $T_{\text{EC}}$. From these results, EGA can be calculated as follow: $\text{EGA} = \Delta T_1 \times 100/\Delta T_E$.

Mg forms MgS, MgO and Mg$_3$N$_2$ in the molten metal of ductile iron. If the amount of S, O and N are 0.01%, 0.20 ppm and 0.52 ppm, 0.024% Mg might be used for making these compounds. If the residual Mg amount is 0.045% after spheroidizing treatment, the soluble Mg amount decreases to 0.021%. Therefore, compared with the influence of Si on $T_{\text{EG}}$ and $T_{\text{EC}}$, that of Mg on $T_{\text{EG}}$ and $T_{\text{EC}}$ is very

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_{\text{EG}}$, °C</th>
<th>$T_{\text{EC}}$, °C</th>
<th>Range, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4.7</td>
<td>-11.6</td>
<td>0.28–2.44</td>
</tr>
<tr>
<td>Al</td>
<td>13.9</td>
<td>-1.8</td>
<td>0.49</td>
</tr>
<tr>
<td>(C)</td>
<td>10.2</td>
<td>5.7</td>
<td>CE &lt; 3.5</td>
</tr>
<tr>
<td>Cu</td>
<td>2.7</td>
<td>-1.4</td>
<td>0.08–2.63</td>
</tr>
<tr>
<td>Co</td>
<td>1.8</td>
<td>-0.7</td>
<td>0.3–3.18</td>
</tr>
<tr>
<td>P</td>
<td>-44.0</td>
<td>-46.2</td>
<td>0.07–0.35</td>
</tr>
<tr>
<td>Ni</td>
<td>1.0</td>
<td>-1.1</td>
<td>0.15–2.57</td>
</tr>
<tr>
<td>C</td>
<td>0.0</td>
<td>0.0</td>
<td>CE &lt; 3.5</td>
</tr>
<tr>
<td>Sb</td>
<td>-5.2</td>
<td>-5.1</td>
<td>0.2–4.0</td>
</tr>
<tr>
<td>Mo</td>
<td>-17.7</td>
<td>-14.5</td>
<td>0.06–1.87</td>
</tr>
<tr>
<td>Mn</td>
<td>-4.0</td>
<td>-0.75</td>
<td>0.44–2.69</td>
</tr>
<tr>
<td>W</td>
<td>-6.1</td>
<td>-2.8</td>
<td>0.22–2.11</td>
</tr>
<tr>
<td>Sn</td>
<td>-9.3</td>
<td>-6.0</td>
<td>0.2–2.86</td>
</tr>
<tr>
<td>Nb</td>
<td>-3.7</td>
<td>0.0</td>
<td>0.38–1.37</td>
</tr>
<tr>
<td>(S)</td>
<td>-20.5</td>
<td>-10.3</td>
<td>0.16–0.44</td>
</tr>
<tr>
<td>Cr</td>
<td>-10.5</td>
<td>5.9</td>
<td>0.11–1.69</td>
</tr>
<tr>
<td>V</td>
<td>-14.8</td>
<td>3.3</td>
<td>0–1.29</td>
</tr>
<tr>
<td>S</td>
<td>-50.0</td>
<td>-18.0</td>
<td>0.45–0.65</td>
</tr>
<tr>
<td>B</td>
<td>-80.3</td>
<td>-26.0</td>
<td>0–0.50</td>
</tr>
</tbody>
</table>
3. Experimental Method, Its Result and Consideration for One Cup Thermal Analysis in Ductile Cast Iron

3.1 Predicting graphite nodule count with one cup thermal analysis

Melting was carried out in a silica lined high frequency induction furnace of 60 kg, 3000 Hz. The basic composition was as follows: 3.7 mass%C, 2.15%Si, 0.3%Mn, 0.02%P, 0.01%S, Sb0.040% and Mg0.06%. After graphite spheroidizing treatment with sandwich method, the molten metal was returned to the furnace and was held at 1350°C. We added various kinds of inoculants (Graphite type, Ba type, Ce type, Ca-Si type and Bi type) into the molten metals, and then cast them at various fading time (0, 1, 2.5, 5.0, 7.5, 10, 15 and 20 min) into one cup (ϕ30 × H50 mm, 250 g).

Table 2 shows the chemical composition of inoculants used in the pouring test. Table 3 shows the chemical composition of spheroidizer used in the pouring test. We analyzed graphite nodule count for one cup T.P. In order to prevent dust’s mixing into graphite nodule count, we cut down particles smaller than 10 micrometer. Using the cooling curve of one cup (TSC) and above equations ((5) and (6)), we calculated EGA and investigated the relationship between EGA and the graphite nodule count of ductile cast iron.

Figure 4 shows the relationship between supercooling degree (ΔT) and the graphite nodule count (N) of CE cup. T.P. Here, Tmax means the highest eutectic temperature, and ΔT means the difference between Tmax and TSC, as shown in Fig. 3. In general, it is considered that N decreases with increasing ΔT. However, as for Ba type and Ca type inoculant, they show reverse tendency; graphite nodule count increases with increasing ΔT. As for the Bi type inoculant, it shows the same tendency with the general consideration. That is, graphite nodule count increases with decreasing ΔT.

Figure 5 shows the examples of cooling curves after fading. TSC, Tmax and the difference between them decrease with fading. As like this figure, there are two problems in ductile iron molten metal as follows; (a) Tmax does not reach to TEG, (b) TEG does not show the parallel line during the eutectic solidification.

Figure 6 shows the relationship between EGA and the graphite nodule count (N) of CE cup. T.P. As shown in eq. (7), the correlation between EGA and N is very high. Therefore, it can be said that the graphite nodule count is predicted correctly with one cup thermal analysis.

\[
N = 6.13 \times (\Delta T_1 \times 100) / (\Delta T_E) - 126 \quad (r = 0.97)
\]  

---

Table 2 Chemical composition of inoculants used in pouring test (mass%).

<table>
<thead>
<tr>
<th>Kinds</th>
<th>C</th>
<th>Si</th>
<th>Ca</th>
<th>Ce</th>
<th>Ba</th>
<th>Bi</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca type</td>
<td>74.5</td>
<td>1.22</td>
<td>-</td>
<td>0.71</td>
<td>-</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>Ba type</td>
<td>73.6</td>
<td>1.85</td>
<td>-</td>
<td>2.74</td>
<td>-</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>Graphite type</td>
<td>99.9</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ce type</td>
<td>72.5</td>
<td>1.40</td>
<td>1.87</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Bi type</td>
<td>71.1</td>
<td>1.37</td>
<td>-</td>
<td>-</td>
<td>1.80</td>
<td>0.80</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Chemical composition of spheroidizer used in the pouring test (mass%).

<table>
<thead>
<tr>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>RE</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>4.0</td>
<td>0.25</td>
<td>0.25</td>
<td>bal.</td>
</tr>
</tbody>
</table>
3.2 Predicting shrinkage tendency ($\theta$) with one cup thermal analysis

3.2.1 Principle of predicting shrinkage tendency with one cup thermal analysis

Figure 7 shows the principle of investigating shrinkage tendency ($\theta$), with one cup thermal analysis. With differentiating one cup temperature cooling curve, a cooling rate curve is obtained. We can explain the relationship between the cooling rate curve and solidification process in one cup as follows.

At the initial stage of the eutectic solidification (1), there is an exothermic reaction due to the eutectic reaction in which graphite and austenite form from the molten metal. As this exothermic heat exceeds the radiation heat of CE cup, the cooling rate turns from minus to plus value.

The crystallized spheroidized graphite is engulfed with austenite just after the eutectic reaction. As carbon should diffuse through the solid phase, the cooling rate becomes slow. Therefore, at the middle stage (2), the exothermic heat becomes less than the radiation heat of CE cup, the cooling rate turns to minus value.

At the final stage (3), the eutectic cells contact each other, the remained molten metal between cells is crystallized to eutectic solid, and the eutectic solidification finishes. In this stage, as the crystallized eutectic volume is very small, the cooling rate becomes large suddenly.

At the post eutectic solidification stage (4), as sand mold has been heated during eutectic solidification, the cooling rate becomes slow. Therefore, $\theta$ shape is shown on the differentiated cooling rate curve.

When shrinkage cavity forms inside the CE cup T.P. (CE cup shown in Fig. 3, $\phi$30 x H50 mm, 250 g), thermal conductivity of T.P. becomes small, because the thermal conductivity of gas is smaller than that of solid. Then, cooling speed becomes slower and the tendency ($\theta$) becomes larger. That is, the larger the shrinkage is, the larger the $\theta$ is.

With investigating the shrinkage tendency ($\theta$), we can predict the quality of molten metal of ductile iron. We call the angle ($\theta$) as the shrinkage tendency parameter from the above reason (hereafter $\theta$).

As shown in Fig. 8 (a) and (b), the shrinkage tendency parameter ($\theta$) changes depending on the printed grape size. In order to prevent this problem, we introduced a ratio coefficient (L) between X axis and Y axis. With introducing (L), the inside value of $\tan^{-1}(\ )$ becomes non-dimensional value. Therefore, the calculated ($\theta$) of Fig. 8 (a) graph 1 shows the same value (56°) with that of Fig. 8 (b) graph 2, even though their graph sizes are different.

\[
\theta = 180^\circ - \theta_1 - \theta_2 = 180^\circ - \tan^{-1}[L \times (\Delta R_1/\Delta t_1)]
- \tan^{-1}[L \times (\Delta R_2/\Delta t_2)]
\]
\[
L = \frac{\text{total X}}{\text{total Y}}
\]
\[
\frac{s^2}{K} = \frac{200s}{4^\circ C/s} = 50(s^2/K)
\]
\[
\theta = 180^\circ - \tan^{-1}[L \times (\Delta R_1/\Delta t_1)]
- \tan^{-1}[L \times (\Delta R_2/\Delta t_2)]
= 180^\circ - \tan^{-1}[50 \times (4/50)] - \tan^{-1}[50 \times (1.1/50)]
= 180^\circ - 76^\circ - 48^\circ = 56^\circ
\]
3.2.2 Experimental method, its result and consideration for predicting shrinkage tendency in ductile cast iron

With investigating $\theta$, we predicted the quality of molten metal of ductile cast iron. We poured spheroidized molten metal into a cone type mold (Fig. 9(a)) and the above one cup T.P., at the same time. The cone type T.P. has been being used as the shrinkage investigating T.P. However, halving the T.P. and measuring the volume of shrinkage with filling water is not easy and shows large scattering. It is desirable that we quit shrinkage T.P. and use one cup thermal analysis. As mentioned later, in one cup thermal analysis, halving the T.P. is simple and its shrinkage size can be evaluated with measuring shrinkage formed area.

The composition of molten metal, inoculants and spheroidizer are the same with that of the graphite nodule count test.

We measured shrinkage volume from the cone T.P., and measured $\theta$ and EGA with one cup thermal analysis, and investigated the correlation between them.

Figure 10 shows the relationship between shrinkage volume of cone type T.P. and $\theta$ of one cup T.P. in ductile cast iron. A good correlation is shown. For the reference, $\theta$ in gray cast iron is also plotted in the graph. In the gray cast iron, shrinkage does not form and $\theta$ is $55 \pm 10^\circ$. It is considered that shrinkage does not form even in the ductile cast iron, if $\theta$ is as small as $55 \pm 10^\circ$.

Figure 11 shows the relationship between nodule count, EGA and $\theta$ in one cup. Figure 12 shows the relationship between EGA, $\theta$, nodule count and shrinkage shape, when investigating the vertical section of CE cup ($\phi30 \times H50$ mm, 250 g). It is possible to predict the shrinkage with using CE cup, not with large cone type T.P. That is, the shrinkage does not form in the CE cup on the following conditions; (a) more than 90% EGA, (b) smaller than $55^\circ \theta$ and (c) more than 450/$mm^2$ graphite nodule count.

It is possible to measure EGA, graphite nodule count and shrinkage tendency parameter ($\theta$) with one cup thermal analysis. Therefore it can be said that one cup thermal analysis is...
a good method to predict the quality of molten metal (graphite nodule count and shrinkage tendency parameter ($\theta$)) correctly before pouring.

4. Conclusion

We have developed one cup thermal analysis and investigated if we can predict the quality of molten metal in ductile cast iron. The results are as follows.

(1) With calculating $T_{EG}$ and $T_{EC}$ from chemical composition, and with measuring $T_{SC}$ from one cup cooling curve, it is possible to measure EGA even in ductile cast iron.

(2) A good correlation is shown between EGA and graphite nodule count (N).

(3) There is a good correlation between EGA and shrinkage tendency parameter ($\theta$) in cone type shrinkage T.P.

(4) As for CE cup T.P., if EGA exceeds 70%, $\theta$ begins to decreases suddenly. And if EGA exceeds 90%, it becomes low near 55° which is that of gray cast iron.

(5) As for CE cup, there is also a good correlation between actual shrinkage volume and $\theta$.

(6) One cup thermal analysis a good method for predicting the quality of molten metal (graphite nodule count and shrinkage tendency ($\theta$)) even in ductile cast iron before pouring.

REFERENCES

4) K. Abe: Sougoimono (1975) 25