Development of viscosity calculation method for mould powders

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Various physiochemical properties of mould powders, such as viscosity and break point, are found to be related to chemical composition through molar ratios, such as number of non-bridging oxygen per tetrahedrally coordinated atom and oxygen to silicon. A number of relationships have been developed between physical properties and molar ratios, and a mathematical model has been developed using the relationships to develop a quick method for analysing the suitability of the mould powder for continuous casting. The method can predict viscosity within a range of temperatures, break temperature, and the effect of inclusion pick-up on the mould powder viscosity. A Microsoft Office Excel interface has been developed to display the results, including the viscosity versus temperature curve and the effect of alumina pick-up. The model output results have been validated using a high temperature viscometer.

Keywords: Mould powder, Continuous casting, Viscosity, Mathematical model

Introduction

Recent studies using the inclined plane test (IPT) at Tata Steel's Teesside Technology Centre (TTC) show that the viscosity (at 1300°C) of mould powders is related to various molar ratios, such as number of non-bridging oxygen per tetrahedrally coordinated atom (NBO/T)\(^4,5\) and oxygen to silicon (O/Si).\(^5,7\) The NBO/T and O/Si ratios are calculated from the chemical composition of the mould powders;\(^4,6,7\) thus, a set of relationships between chemical composition and mould powder viscosities have been established from the IPT results.\(^2\) It has also been noted that the viscosity is also dependent on the excess group (either CaO or CaF\(_2\)) of the mould powder in question. Depending on the composition of the mould fluxes, they can be classified into either CaO excess or CaF\(_2\) excess groups. It is known that during solidification of a mould flux, CaO, SiO\(_2\) and CaF\(_2\) are consumed to form a crystalline phase of Cuspidine (Ca\(_2\)SiF\(_2\)O\(_{1.1.3.5}\)). In order to form the theoretical maximum amount of Cuspidine during solidification, SiO\(_2\) is always in excess and is never the limiting factor. Thus, when the reaction has gone to completion, either CaO or CaF\(_2\) will remain in the system. This will dictate how the mould powder could be classified as either CaO excess or CaF\(_2\) excess.

The IPT method measures the viscosity value for only 1300°C. However, in order to select a suitable mould powder for continuous casting, knowledge of the various physiochemical characteristics (viscosity over a large temperature range, the break point and the effect of inclusion pick-up by the top flux layer) is required.

One of the methods to obtain this information is to use a high temperature viscometer (HTV); however, HTV runs are a time, effort and cost consuming process.\(^2\) As a result, this study aims to develop a fast and validated reliable method of predicting mould powder properties using chemical composition as input. It has been observed that viscosity can be calculated from a set of relationships using the chemical composition of the mould powders. A Microsoft Office Excel (MS Excel) interface has been developed to calculate viscosity, and the method, named the TTC viscosity calculation method, is capable of predicting the following within a reasonable uncertainty level:

(i) viscosity within a range of temperatures
(ii) break temperatures
(iii) the effect of online inclusion pick-up on viscosity.

The MS Excel interface is also capable of displaying the predicted results through interactive tabular and graphical illustrations. For example:

(i) a predicted viscosity versus temperature plot
(ii) a predicted viscosity versus alumina pick-up plot.

The model output results have been validated using HTV.

Development of method

A typical viscosity versus temperature plot is shown in Fig. 1. The study aimed to develop a method that produces a similar plot through a series of mathematical relationships using the composition of the powders as an input.

Step 1: calculation of viscosity at 1300°C

Dey et al.\(^2\) reported that calculation of the excess group in mould powders is a prerequisite to select the correct set of viscosity equations. Calculations for determining mould powder excess group have been discussed in the
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1 Viscosity plot: measured with HTV

Previous literature\(^2\)\(^5\) The viscosity of CaO excess and CaF\(_2\) excess mould powders can be calculated by equations (1) and 2 respectively:

\[
\eta_{\text{CaO-excess}} = 0.2656\exp \left[ \frac{470}{140.7(O/Si)^2 - 735.23(O/Si) + 1054.8} \right] \tag{1}
\]

\[
\eta_{\text{CaF}_2\text{-excess}} = 0.2656\exp \left[ \frac{470}{175.13(O/Si) - 410.7} \right] \tag{2}
\]

where \(\eta_{\text{CaO-excess}}\) is the viscosity (dPa s) of the CaO excess group mould powder, and \(\eta_{\text{CaF}_2\text{-excess}}\) is the viscosity of a CaF\(_2\) excess group of mould flux. The (O/Si) ratio can be calculated using the equation:\(^6\)\(^7\)

\[
\frac{(O/Si)}{n} = (NBO/T) \tag{3}
\]

where \(n\) signifies the number of moles of a component in a mould flux.

A strong correlation (\(R^2=0.99\)) was observed from equation (1), but unfortunately, equation (2) shows a relatively weaker correlation (\(R^2=0.75\)) with the measured data, and therefore, the relationships for CaF\(_2\) excess powders were further improved through the following observations using regression analysis.

If the value of \((5 \times \% \text{CaO} \times \% \text{F})/(\% \text{SiO}_2 \times \% \text{Al}_2\text{O}_3 \times \% \text{Na}_2\text{O})\) is >1

\[
\eta_{\text{CaF}_2\text{-excess}} = \frac{165.69}{(NBO/T)^2} - \frac{86.9981}{(NBO/T)} + 12.227 \tag{4}
\]

Table 1 Measured values of \(E_u/R\), \(T_{\text{break}}\) and calculated \(A\) and NBO/T

<table>
<thead>
<tr>
<th>NBO/T</th>
<th>Break temperature</th>
<th>Average (E_u/R)</th>
<th>Average (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M7</td>
<td>2.62</td>
<td>1169</td>
<td>20.395</td>
</tr>
<tr>
<td>M8</td>
<td>2.55</td>
<td>1137</td>
<td>22.223</td>
</tr>
<tr>
<td>M9</td>
<td>2.52</td>
<td>NF</td>
<td>22.022</td>
</tr>
<tr>
<td>M10</td>
<td>2.32</td>
<td>1095</td>
<td>18.809</td>
</tr>
<tr>
<td>M12</td>
<td>2.72</td>
<td>1160</td>
<td>22.354</td>
</tr>
<tr>
<td>M14</td>
<td>2.90</td>
<td>1171</td>
<td>23.277</td>
</tr>
<tr>
<td>M16</td>
<td>2.22</td>
<td>NF</td>
<td>19.624</td>
</tr>
<tr>
<td>M16</td>
<td>1.75</td>
<td>1175</td>
<td>19.956</td>
</tr>
</tbody>
</table>

*NF indicates that no break point was observed until 1050°C.

2 Analysis of predictability of \(T_{\text{break}}\) for Azhari et al. and Dey’s model

However, the calculated break temperature did not show a good agreement with the measured values (Table 1), and this can be seen from Fig. 2 and Table 2, where none of the predicted \(T_{\text{break}}\) actually fall within the \(\pm 20°C\) uncertainty range.\(^9\)

Fluidity point is known as the temperature at which a flux starts to infiltrate through the mould and strand gap in a continuous casting mould and can be measured through the DIN 51730 process,\(^4\)\(^8\) in which the height of a mould flux column is measured at different temperatures, and compared against the initial room temperature height of the column. At the fluidity point, the height of the mould flux column becomes one-third of its room temperature height.\(^10\) The author has identified that the break point is related to the fluidity point of
3 Effect of excess group and various compounds on fluidity point

mould powders, and therefore, an equation for break points can be derived from the fluidity point and mould powder composition. Similar to viscosity, fluidity point is also found to have a complex relationship with the powder composition, and the relationship is greatly influenced by the excess group of mould powder. A statistical analysis in Fig. 3 shows that CaO, SiO2, Na2O and CaF2 have a strong influence over fluidity point. It can be seen from the figure that the fluidity points follow three distinct curves Y1, Y2 and Y3. The straight line Y1 is the least squared regression equation for CaO excess mould powders. Y2 and Y3 represent the least squared regression curves for CaF2 excess mould powders. For the CaO excess mould powders, Y1 in Fig. 3 has shown a high correlation coefficient ($R^2=0.91$) between the predicted and measured fluidity points. Y1 can be expressed by the following equation

$$FP_{CaO-excess} = 87.237 \times \frac{X_{CaO}}{2X_{CaF2}+1.0X_{SiO2}} + 1007.5 \quad (7)$$

Similarly, for most of the CaF2 excess mould powders, the fluidity point can be calculated using the following equation for curve Y2

$$FP_{CaF2-excess} = 89.274F_{PDS} \frac{X_{CaF2}}{X_{SiO2}} + 495.28F_{PDS} + 1748.6 \quad (8)$$

where

$$F_{PDS} = \frac{X_{CaO} + 5X_{Na2O}}{X_{SiO2}}.$$

However, it can be seen from Fig. 3 that some of the CaF2 excess mould powders obey the curve Y3. A detailed study on these powders reveals that if the value of ($2X_{CaO} + 2X_{CaF2} + 2X_{Na2O} + 6X_{Fe2O3}) < 1.2$, the mould powders follow Y2. Otherwise, for CaF2 excess powders, the fluidity point can be expressed by the equation below (Y3 curve)

$$FP_{CaF2-excess} = -3.2997F_{PDS}^2 + 48.965F_{PDS} + 990.97 \quad (9)$$

where

$$F_{PDS} = \frac{[(X_{CaO} + 5X_{Na2O})/X_{SiO2} \times X_{CaO}/(2X_{CaF2} + 0.1X_{SiO2})]}.$$ 

As stated earlier, the break point temperature in a viscosity plot is related to the fluidity point of mould fluxes. The break temperature $T_{break}$ of the mould powders used was measured using HTV with a cooling rate of 10°C min$^{-1}$. A regression analysis on the measured break temperature values has shown that $T_{break}$ is dependent on the composition (%C, %CaF2, %Na2O) and the basicity of the mould powders in the following manner.

If basicity >0.9

$$T_{break} = 0.8871FP + 100.47 \quad (10)$$

 Else if

$$\left(\frac{(%C)}{basisitty}\right) - (%F^- + %Na2O) \times \left(\frac{(%F^-)}{(%Na2O)}\right) < 10$$

$$T_{break} = 0.8871FP + 100.47$$

Else

$$T_{break} = 0.8871FP + 10 \times \frac{(%Na2O - 1.5)}{(%F^- - 1.5)} + 30.47 \quad (11)$$

| Table 2 Model validation with HTV measurement, PDS values* |
| --- | --- | --- | --- | --- | --- | --- |
| Viscosity at 1300°C | Fluidity point | Break temperature |
| HTV measured | PDS | IPT | Model predicted | PDS | Model predicted | HTV measured | Model predicted |
| M1 | x | 2.7 | 2.0 | 2.27 | 1220 | 1194 | x | 1160 |
| M2 | x | 37.9 | 39.4 | 36.42 | 1190 | 1193 | x | 1135 |
| M3 | x | 19.5 | 20.2 | 22.34 | 1155 | 1151 | x | 1075 |
| M4 | x | 6.4 | 7.1 | 7.21 | 1165 | 1173 | x | 1141 |
| M5 | 4.3 | 4.6 | 4.1 | 4.62 | 1320 | 1314 | NF | 1266 |
| M6 | x | 4.5 | 3.6 | 3.65 | 1280 | 1277 | x | 1233 |
| M7 | 3 | 3.2 | 3.2 | 2.49 | 1180 | 1184 | 1169 | 1151 |
| M8 | 3-1 | 3.5 | 3.0 | 2.97 | 1200 | 1215 | 1137 | 1178 |
| M9 | 3-1 | 3.22 | 2.9 | 3.80 | 1205 | 1217 | NF | 1180 |
| M10 | 3-1 | 3.2 | 2.8 | 3.25 | 1130 | 1127 | 1095 | 1100 |
| M11 | x | 2 | 2.4 | 1.96 | 1170 | 1166 | x | 1135 |
| M12 | 2-6 | 2.6 | 2.2 | 2.23 | 1180 | 1183 | 1160 | 1150 |
| M13 | x | 3 | 2.1 | 2.75 | 1130 | 1125 | x | 1098 |
| M14 | 1-7 | 2.02 | 2 | 1.91 | 1150 | 1154 | 1171 | 1124 |
| M15 | 6-6 | 3.9 | 4.1 | 4.01 | 1090 | 1088 | NF | 1026 |
| M16 | 1-47 | 1.3 | 1.3 | 1.35 | 1220 | 1221 | 1175 | 1184 |
| M17 | x | 1.9 | 1.6 | 1.59 | 1190 | 1175 | x | 1143 |
| M18 | x | 10 | 8.6 | 11.10 | 1250 | 1229 | x | 1190 |

* x indicates that no HTV measurements have been carried out, and NF indicates that no break point was observed until 1050°C. PDS: product definition sheet, IPT: inclined plane test.
The break point calculations using equations (10) and (11) have shown promising results (minimum error, 5°C; maximum error, 47°C) over the equation of Azhari et al. (minimum error, 28°C; maximum error, 144°C). Figure 2 shows the comparisons with the measured values and the equation of Azhari et al. The results are further discussed in the model validation section.

**Step 3: plotting of viscosity values over large temperature range**

With having a calculated viscosity value at 1300°C and a calculated break point of a mould powder, the next task is to extend the viscosity calculation to a greater range of temperatures (e.g. Tbreak to 1500°C). The temperature dependence for the viscosity of a molten flux can be expressed by the following Arrhenius type equation $^{2,11-13}$

$$\eta_T = A \exp \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} (12)

where $A$ is a constant, $E_a$ is the activation energy for viscous flow, $R$ is the universal gas constant, $T$ is the temperature in K and $\eta_T$ is the viscosity at temperature $T$.

The measured values of $E_a/R$ and $T_{break}$ from viscosity measurement with an HTV and the corresponding calculated values of $A$ and NBO/T for some of the Tata Steel mould powders are given in Table 1.

A plot of measured $E_a/R$ versus NBO/T is shown in Fig. 4, and it can be seen from the figure that the excess group of powders has influenced the $E_a/R$ values. The regression equation between $E_a/R$ and NBO/T for both excess groups are developed and given below.

For CaO excess powders

$$\left( \frac{E_a}{R} \right)_{\text{CaO-excess}} = 9602(\text{NBO}/T)^2 - 44732(\text{NBO}/T) + 72865$$ \hspace{1cm} (13)

For CaF$_2$ excess powders

$$\left( \frac{E_a}{R} \right)_{\text{CaF}_2\text{-excess}} = 1593-4(\text{NBO}/T) + 16357$$ \hspace{1cm} (14)

A plot for actual $E_a/R$ versus calculated $E_a/R$ is shown in Fig. 5. It can be seen that equations (13) and (14) calculate the $E_a/R$ values with a correlation coefficient $R^2$ of 0.68. Now, as the value of $E_a/R$ is known, the constant $A$ can be calculated by rearranging equation (12) as

$$A = \frac{\eta_T}{T \exp(\frac{E_a}{RT})}$$

where $A$ is a constant in equation (12), and $\eta_T$ values can be obtained using the appropriate equations for viscosity (equation (1), (4) or (5)) at $T=1300$°C (1573 K).

If $E_a/R$ and $A$ values of a mould powder are known, the viscosity values can now be calculated over a large range of temperature by changing ‘$T$’ in equation (12).

**Step 4: calculation of viscosity increase below $T_{break}$**

As seen in Fig. 1, the viscosity of a mould flux drastically increases during cooling at temperatures below $T_{break}$. The viscosity value at a temperature below $T_{break}$ can be expressed by the following equation

$$\eta_T = \eta_{T+1} + 0.15\eta_{T+2}$$ \hspace{1cm} (15)

where $\eta_T$ signifies viscosity at temperature $T$ below $T_{break}$.

**Step 5: flowchart development**

The various mathematical relationships from equations (1)–(15) are combined to develop a method for mould powder viscosity calculation. The flowchart of the viscosity calculation method is shown in Fig. 6.

**Model validation**

The model has been compared with the product definition data and the measurements with HTV. Comparison with the predicted versus actual viscosity (at 1300°C) for both CaO and CaF$_2$ excess mould powders was previously reported elsewhere. The predictions for two slab casting powders (one CaO excess and one CaF$_2$ excess powders) are shown in Figs. 7 and 8 respectively.

The predicted results for all the 18 mould powders in this study are given in Table 2. It is to be noted that a table for the powder compositions was published in the previous report and is not repeated here. In Table 2, the model predictions on viscosity (at 1300°C) are compared with the HTV measurements, product definition sheet data, and IPT results. Fluidity point data that are given in the product definition sheet were measured through the DIN 51730 process and used for validating the model prediction. Good results were obtained using
equations (7)–(9). For most of the powders, the difference between the measured and predicted fluidity points was less than 10°C. There were not enough data for validating the break temperatures; however, M7, M12, M14 and M16 powders have shown promising results. Further research is needed to obtain more understanding on the relationships between break temperature and mould powder chemistry.

Development of user interface

The author has identified a need in both the steel and mould flux industries for a simple tool that would be capable of analysing the mould powder properties using mould flux composition as input. By having this aim, a user interface using MS Excel has been developed by the author at Tata Steel’s TTC. The user interface is shown in Fig. 9.

Application and benefit

The method is found to be a useful tool for analysing current and new mould powders and fluxes. A good understanding can be obtained on the effect of various compounds, such as alumina on the mould powder properties. For example, the effect of alumina pick-up can be calculated by changing the alumina content in the input composition. Figure 9 shows the effect of alumina pick-up on the viscosity of powder M16. Similar to alumina, the influence of other compounds can also be calculated from the model. A report will later be published on this study.

Further work

The method will be improved further by the following.

1. Developing a method for mould powder selection criteria in which input of chemical composition of the powders would provide a hint of the usability range of the powder
2. Developing a method to consider the thermal gravimetric changes and thermal changes of the flux during heating and cooling cycle. This study will aim to develop a method to represent the
9 User interface of viscosity calculation method for mould powders

3. Improvement of the equations for break temperature
4. Application of the viscosity method for different mould powders of steel plants and powder manufacturers.

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