Effect of Chemical Composition of Mold Powder on the Erosion of Submerged Nozzles for Continuous Casting of Steel*

By Yukihiro NAKAMURA,** Teiichi ANDO,** Kousuke KURATA** and Masakazu IKEDA**

Synopsis

In order to elucidate the wear mechanism of ZrO$_2$-graphite refractories used around the powder line of submerged nozzles, the authors carried out erosion tests with the variety of mold powders using an induction furnace. The mold powders with low viscosity or high [F$^-$] content were found to wear away ZrO$_2$-graphite refractories heavily. The erosion behavior of ZrO$_2$-graphite refractories can well be explained by the basicity of a mold powder which consists of ion-oxygen attraction parameters of the chemical compositions in the mold powder. Observing the microstructures of the samples after test, it is clarified that the penetration of low-viscosity components in the mold powder disintegrate carbon bonding and also granulate ZrO$_2$ grains into fine particles, consequently the erosion of ZrO$_2$-graphite refractories is aggravated.

I. Introduction

The requirements for the refractories used in the continuous casting process have become severer with the increased ratio of continuous casting, multi-sequential casting, the direct coupling of processes such as hot charging or direct rolling, and the necessity of higher quality steel. Specially, the submerged nozzle which is the last refractory to come into direct contact with molten steel plays a very important role for steel quality. The life of the submerged nozzle depends on the life of the powder line portion or the nozzle clogging with Al$_2$O$_3$ clusters. The recent high-speed casting necessitated the use of low viscosity mold powder, which has made the life of submerged nozzle shorter.

In order to elucidate the wear mechanism of ZrO$_2$-graphite refractories which are used for the powder line portion of submerged nozzles, the authors carried out some erosion tests with the variety of mold powders.

II. Experimental Methods

1. ZrO$_2$-graphite Refractories and Mold Powders Used for Experiments

Table 1 shows properties of ZrO$_2$-graphite refractories used for the experiments. They were selected from commercial nozzles with different ZrO$_2$ contents. The chemical compositions of mold powders tested are given in Table 2. Bi is not CaO/SiO$_2$, but the basicity of a mold powder which consists of ion-oxygen attraction parameters of the chemical compositions in the mold powder.

CaO/SiO$_2$ ratios of mold powders $a$, $b$ and $c$ were changed keeping Na and F contents constant so as to change their viscosities. Powder $d$ was so made to have extremely high viscosity. The mold powders, $e$~$h$ were made with the variety of Na and F contents under a constant viscosity.

2. Method of Dipping Test Using a High-frequency Induction Furnace

Dipping tests were carried out using a high-frequency induction furnace.

<table>
<thead>
<tr>
<th>Chemical composition (wt%)</th>
<th>m.p. (°C)</th>
<th>Viscosity (Poise) at 1300 °C</th>
<th>Basicity Bi (→)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>Al$_2$O$_3$</td>
<td>CaO</td>
<td>Na$_2$O</td>
</tr>
<tr>
<td>$a$</td>
<td>37.3</td>
<td>0.5</td>
<td>43.9</td>
</tr>
<tr>
<td>$b$</td>
<td>38.5</td>
<td>7.4</td>
<td>33.9</td>
</tr>
<tr>
<td>$c$</td>
<td>44.2</td>
<td>8.1</td>
<td>30.1</td>
</tr>
<tr>
<td>$d$</td>
<td>51.0</td>
<td>0.9</td>
<td>35.9</td>
</tr>
<tr>
<td>$e$</td>
<td>37.6</td>
<td>0.7</td>
<td>45.1</td>
</tr>
<tr>
<td>$f$</td>
<td>39.1</td>
<td>0.7</td>
<td>35.3</td>
</tr>
<tr>
<td>$g$</td>
<td>39.0</td>
<td>0.6</td>
<td>28.2</td>
</tr>
<tr>
<td>$h$</td>
<td>34.5</td>
<td>0.6</td>
<td>34.3</td>
</tr>
</tbody>
</table>

* Based on the papers presented to the 110th ISIJ Meeting, October 1985, S1003, at Niigata University in Niigata and to the 38th Refractories Committee, The Joint Research Society, ISIJ, December 1985, at Tokai-shiritsu Kinro Center in Tokai. Manuscript received on March 3, 1986; accepted in the final form on September 12, 1986. © 1986 ISIJ
** Hirohata Refractories Laboratory, Heat Technology Division, Plant Engineering & Technology Bureau, Nippon Steel Corporation, Fuji-cho, Hirohata, Himeji 671-11.
quency induction furnace whose capacity is 300 kg of steel. The schematic figure of the experimental apparatus is shown in Fig. 1. The steel grade used was Al-killed sheet grade steel and the test temperature was kept at 1560 ± 5°C. Square column specimens of 40 × 30 mm in size were dipped into the molten steel for 1 h (4 specimens at a time). The molten slag layer was almost the same thickness as actual operational one of about 10 mm. Specimens were preheated for 10 min above the furnace filled with molten steel.

III. Experimental Results

Figure 2 shows maximum erosion depths as various mold powders for four types of ZrO₂-graphite samples of Table 1. The erosion profile is a typical local erosion at a slag line and maximum erosion depth, \( d_m \) is defined in Fig. 3. The authors made the analysis of variance for the data. Here, \( S \), \( V \), \( F \), \( F(0.01) \) is sum of square, degree of freedom, variance, F-value, F-value (confidence limit, 1 %) respectively. From the analysis result shown in Table 3, both the differences of erosion among the four types of ZrO₂-graphites and those among the powders are statistically meaningful with confidence limit, 1 %.

1. Effect of the Viscosity of Mold Powders

Figure 4 shows the relationship between viscosities (at 1300°C) of the mold powders and erosion depths of ZrO₂-graphite. The mold powder in Fig. 4 has the same amount of (Na), (F⁻), but the mold powder of 10 Poise (d) has less amount than others. From the result of Fig. 4, the lower the viscosity of a mold powder is, the deeper the erosion of ZrO₂-graphite becomes. The differences of erosion depths among the refractory materials are evident for the mold powders of low viscosity.

2. Effect of Low Viscosity Components

Figure 5 shows the relationship between [F⁻] content in the mold powder and erosion of ZrO₂-graphite. The viscosities of all the mold powders in Fig. 5 were 1 Poise. The higher the [F⁻] content in the mold powder becomes, the deeper the erosion

<table>
<thead>
<tr>
<th>Factor</th>
<th>( S )</th>
<th>( V )</th>
<th>( F )</th>
<th>( F(0.01) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂-graphite</td>
<td>5.27</td>
<td>3</td>
<td>1.757</td>
<td>7.64**</td>
</tr>
<tr>
<td>Powder</td>
<td>87.12</td>
<td>7</td>
<td>12.446</td>
<td>54.11**</td>
</tr>
<tr>
<td>E</td>
<td>4.86</td>
<td>21</td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>

** Significance probability (reliability 99 %)

\[
d_{0} = \frac{d_{f} - d_{l}}{2}
\]

Fig. 3. Typical local erosion profile.

Fig. 4. Relationship between viscosity of mold powders and erosion of ZrO₂-graphite refractories.
depths of ZrO₂-graphite becomes. The differences among the erosion depths of A, B, C and D materials become evident in high [F⁻] content region. Such components as NaF, CaF₂, Li₂O, Na₂O, etc., lower the viscosity of a mold powder and it is reported that Na content in a mold powder affects the erosion of ZrO₂-graphite most.³ But our investigation showed that [F⁻] content in the mold powder affected it most as indicated in Fig. 5.

It is said that these low-viscosity components in the mold powder penetrate between the stratified planes of graphite and from the graphite lamellar compound which selectively destroys the bonding of non-graphite part with other impurities or swells graphite and leads to the disintegration of graphite.²

IV. DISCUSSION

1. Definition of Powder Basicity, Bi

There should be several factors such as viscosity, chemical composition, etc. of mold powder to affect the erosion of ZrO₂-graphite. But the authors tried to find a parameter which can explain the erosion well. The basicity conventionally defined as CaO/SiO₂ of actual operational mold powders is almost 1.0 and properties such as viscosity and melting point are controlled by such fluxes as NaF, CaF₂, Na₂CO₃, Li₂CO₃, etc. Consequently, recent mold powders consist of multi-components.

The ordinary basicity, CaO/SiO₂ did not work, so the authors examined another criterion of basicity, Bi which can take into account the ion bonding intensity of molten powder and low viscosity component as shown in Appendix in Ref. 3). In Appendix,³ basicity is normally limited to oxides, but as some mold powders contain NaF or CaF₂, the authors tried to extend the definition of basicity to include fluorides. It can be thought that [F⁻] and [O²⁻] are interchangeable as the ion radii of the both anions are quite similar (Table 4).

Ion-oxygen attraction parameters of main oxides and fluorides are shown in Table 5. In the calculation of the mold powder basicity, Bi the authors defined neutrality as the midpoint between SiO₂ and CaO which are typical acid and base respectively. And deviations from neutrality which is calculated to be 1.72 are derived. It can be shown on thermodynamic grounds that Na₂O and CaF₂ react to form NaF by Eq. (1) in molten slag, thus the authors can represent Na₂O and CaF₂ by NaF.

\[ \text{Na}_2\text{O} + \text{CaF}_2 \rightarrow \text{CaO} + 2\text{NaF} \quad \text{(1)} \]

Thus the mold powder basicity, Bi can be defined as follows,

\[ Bi = \frac{\sum (\text{Basic component})}{\sum (\text{Acid component})} = \frac{\sum ai[Xi]}{\sum a_j[Xj]} \quad \text{(2)} \]

\[ \sum ai[Xi] = 0.28[\text{Fe}_2\text{O}_3] + 0.78[\text{MgO}] + 1.02[\text{CaO}] + 1.22[\text{Li}_2\text{O}] + 1.37[\text{Na}_2\text{O}] + 1.46[\text{K}_2\text{O}] + 1.54[\text{NaF}] + 1.48[\text{LiF}] + 1.39[\text{CaF}_2] \quad \text{(3)} \]

Table 4. Ion radius of F⁻, O²⁻.

<table>
<thead>
<tr>
<th>Anion</th>
<th>F⁻</th>
<th>O²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion radius [Å]</td>
<td>1.36</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Table 5. Ion-oxygen attraction parameter of oxides and fluorides.

<table>
<thead>
<tr>
<th>Oxide or fluoride</th>
<th>Coordination number</th>
<th>M²⁺</th>
<th>O²⁻ or F⁻</th>
<th>Interionic length a [Å]</th>
<th>I</th>
<th>Deviation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>4</td>
<td>0.40</td>
<td>1.31</td>
<td>1.71</td>
<td>♦ 2.74</td>
<td>+1.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4</td>
<td>0.49</td>
<td>1.51</td>
<td>1.80</td>
<td>1.85</td>
<td>+0.13</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6</td>
<td>0.64</td>
<td>1.40</td>
<td>2.04</td>
<td>1.44</td>
<td>-0.28</td>
</tr>
<tr>
<td>MgO</td>
<td>6</td>
<td>0.66</td>
<td>1.40</td>
<td>2.06</td>
<td>0.94</td>
<td>-0.78</td>
</tr>
<tr>
<td>CaO</td>
<td>6</td>
<td>0.99</td>
<td>1.40</td>
<td>2.39</td>
<td>♦ 0.70</td>
<td>-1.02</td>
</tr>
<tr>
<td>Li₂O</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>2.00</td>
<td>0.50</td>
<td>-1.22</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>2.40</td>
<td>0.35</td>
<td>-1.37</td>
</tr>
<tr>
<td>K₂O</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>2.79</td>
<td>0.26</td>
<td>-1.46</td>
</tr>
<tr>
<td>NaF</td>
<td>6</td>
<td>0.97</td>
<td>1.36</td>
<td>2.33</td>
<td>0.184</td>
<td>-1.54</td>
</tr>
<tr>
<td>LiF</td>
<td>6</td>
<td>0.68</td>
<td>1.36</td>
<td>2.04</td>
<td>0.240</td>
<td>-1.48</td>
</tr>
<tr>
<td>CaF₂</td>
<td>8</td>
<td>1.03</td>
<td>1.43</td>
<td>2.46</td>
<td>0.330</td>
<td>-1.39</td>
</tr>
</tbody>
</table>

* A = \frac{2.74 + 0.70}{2} = 1.72 \quad \text{Deviation} = I - A

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\[ \sum a_j x_j = 1.02[\text{SiO}_2] + 0.13[\text{Al}_2\text{O}_3] \] where \([\ ]\) indicates mold fraction of each element and each coefficients are shown as deviation in Table 5.

Bi's of the mold powder used for dipping tests are calculated and indicated in Table 2. It can be noticed from the table that Bi becomes higher as the viscosity of mold powder becomes smaller and that Bi differs much with the kind of low viscosity components in a mold powder even if the viscosity is the same.

2. Relationship between Basicity Bi of a Mold Powder and Erosion of ZrO2-graphite

Figure 6 shows the relationship between Bi's of mold powders and maximum erosion depths of ZrO2-graphite refractories for the dipping tests and for some actual operations. It is understandable from Fig. 6 that ZrO2-graphite refractories erode much with the increment of the basicity Bi and their relationship is a good correlation. It can be observed that the erosion depth in actual operations are deeper than those in the dipping tests, which is probably due to the differences of mold powder consumption and heat capacity.

3. Relationship between Basicity Bi and Viscosity of a Mold Powder

Figure 7 indicates the relationship between Bi's and viscosities of some commercial mold powders. Although this relationship is a pretty good correlation, there is much difference of Bi's for the same viscosity mold powders because of the different contents of low viscosity elements such as Na, F, Li, etc.

4. Wear Mechanism of ZrO2-graphite Refractories

Figure 8 shows the relationship between ZrO2 content and erosion of ZrO2-graphite refractories for dipping tests and Fig. 9 shows the case for actual operations. From the two figures, it is clear that the erosion depths of ZrO2-graphite refractories become deeper and differ much with Bi's of mold powders as ZrO2 content in the refractory decreases, namely the graphite content increases.

The microstructures around the hot faces of ZrO2-graphite refractories after dipping tests using mold powder c (5 Poise at 1,300 °C) and e (1 Poise at 1,300 °C) are shown in Photos. 1 and 2, respectively. For the case of high viscosity mold powder (Photo. 1), ZrO2 grains emerge at the hot face because of oxidation of matrix graphite and fall into molten steel or slag with the same grain size as original. For the case of the low viscosity mold powder (Photo. 2), ZrO2 grains emerge at the hot face with the same
mechanism as above. The comparison of the said two photos shows that $\text{ZrO}_2$ grains are broken into finer particles near the hat face for the case of low viscosity mold powder.

The SEM images of $\text{ZrO}_2$-graphite near the hot face are shown in Photos. 3 and 4, where only Si, Zr and Ca are detected in EDAX. For the high viscosity mold powder (Photo. 3), a little amount of Si and Ca is detected in the pores of the electrically fused $\text{ZrO}_2$ grains which have been partially stabilized with CaO and the grain boundaries cannot be found distinctly in initial large $\text{ZrO}_2$ grains. For the low
viscosity mold powder (Photo. 4), more amount of Si and Ca are detected in the grain boundaries of ZrO₂ grains and the grain boundaries can clearly be found in ZrO₂ grains near the hot face. It suggests that c-ZrO₂ transforms into m-ZrO₂ by the penetration of slag and it causes granulation of ZrO₂ grains⁴⁵ as is clearly seen in Photo. 4. Such granulation of ZrO₂ grains proceeds more and thus the erosion of ZrO₂-graphite refractories proceeds more in inverse proportion to the viscosity of mold powders. These low-viscosity components penetrate into graphite layers and lead to the disintegration of C-bonding. The wear mechanism of ZrO₂-graphite refractories in Fig. 10.

V. Conclusions

In order to elucidate the wear mechanism of ZrO₂-graphite refractories used powder line portion of submerged nozzles, the authors carried out some dipping tests with various mold powders. And the following became clear.

(1) The lower the viscosity and the higher the [F⁻] content of a mold powder is, the deeper the erosion depth of it becomes.

(2) The mold powder basicity Bi including the effect of viscosity components can explain well the erosion of ZrO₂-graphite refractories and also the viscosity of mold powders.

(3) The mold powder with high basicity, Bi erodes ZrO₂-graphite refractories much, that is, the penetration of low-viscosity slag disintegrates carbon bonding and also granulates ZrO₂ grains into fine particles.
REFERENCES

Appendix

The acidity or basicity of an oxide depends upon the intensity of interactive electrostatic attractive force. If the polarization of anion or cation can be neglected and these ions can be considered to be point charges, the interactive electrostatic attractive force, \( P \) is given by Eq. (A-1).

\[
P = \frac{z^+ \cdot z^-}{a^2} \cdot e^2 \tag{A-1}
\]

where,
- \( a \): Interionic length
- \( e \): Electronic charge

\( z^+ \): Valence of cation
\( z^- \): Valence of anion.

As the electronic charge, \( e \) in Eq. (A-1) is constant, ion-oxygen attraction parameter, \( I \) can substitute the electrostatic attractive force, \( P \).

\[
I = \frac{z^+ \cdot z^-}{a^2} \tag{A-2}
\]

Now the interionic length, \( a \) is the sum of radii of anion and cation for coordination compounds. The ion-oxygen attraction parameter, \( I \) can be calculated. For the case of oxide, the value of the ion-oxygen attraction parameter can be considered to be the criterion of the interactive intensity acted on a cation \( M^{z^+} \) and \( O^{z^-} \) around it. The greater the valence of cation, \( z^+ \) and the smaller interionic length, \( a \) of an oxide are, the greater ion-oxygen attraction parameter becomes.

Oxide with large \( I \) (ex., SiO\(_2\), Al\(_2\)O\(_3\), TiO\(_2\))

……………… Network former

Oxide with small \( I \) (ex., Na\(_2\)O, CaO, MnO)

……………… Network modifier

Oxide with small \( I \) are basic and ones with large \( I \) are acid, namely the order of the ion-oxygen attraction parameter \( I \) corresponds to the order of the basicity or acidity.