DENSE REFRactories TECHNOLOGY

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The wear of most products in service is due to the chemical nature of the refractory, and the corrosive agent, and also to the structure of the product; the combination of grains of different sizes and constituent crystals, the volume of pores, their dimensions, and the characteristics of the capillary system formed by them.

Chemical reaction between refractory and atmosphere is generally unavoidable. However, the kinetics of this process for the given chemical compositions of the refractory and medium and service temperatures are determined by the structure of the products, the influence of which follows from the fact that the solubility of the refractory, as demonstrated in [1], obeys Fick's law:

\[
\frac{dV}{dx} = -DF \frac{dC}{dx},
\]

where D is the diffusion coefficient, F is the reaction surface, C is the concentration of dissolved substance in the reaction zone, V is the volume of solid passing into solution, \( \tau \) is time, (min), and \( x \) is the thickness of the reaction zone.

In this expression the magnitude F is directly related to the structure of the product, and is the total (true) surface of the refractory coming into contact with the medium. It is obvious that in a real case the magnitude of F should depend not only on the volume and dimensions of the pores, but on their capacity for being filled with melts.

The final result of the product coming into contact with the medium depends on the rate of absorption and solution of it in the refractory. This result can be assessed from the following equation [2]

\[
\frac{d^2}{l^2} = \frac{2AC^2}{\sigma_{ST} \cos \theta} \frac{T}{r},
\]

where \( d \) is the thickness of the article dissolved by melt for time \( \tau \); \( l \) is the depth of penetration of melt into the product for time \( \tau \); A is a constant for the melt, C is the concentration of dissolved substance in the reaction zone, \( \sigma_{ST} \) is the surface tension of the melt, \( \theta \) is the wetting angle of the refractory by the melt, T is the process temperature, and \( r \) is the capillary radius.

In real service conditions, A, C, \( \sigma_{ST} \), \( \theta \), and T are constants, and so,

\[
\frac{d^2}{l^2} = \frac{Q}{r} \text{ or } \frac{d}{l} = \frac{Q'}{V'},
\]

Thus, the relationship between the thickness of the dissolved layer and the penetration depth is determined by the effective pore size, which is a characteristic of the equivalent capillary system of the product. It follows from the equation that when the radius of the capillaries declines, the ratio \( d/l \) increases. So the rate of solution of the refractory, determined by the value of \( d \), becomes great, and the possible rate of absorption of the melt by the refractory, determined by the value of \( l \), less. Consequently, solution of the refractory limits its impregnation by liquid-phase.

It follows from this that reducing the size of the pores, regardless of the total porosity, is a desirable factor, since this reduces the rate of impregnation by melt. This is confirmed by experiments for dinas [3] and magnesite [4].

TABLE 1

<table>
<thead>
<tr>
<th>Refractory</th>
<th>Open porosity, %</th>
<th>Bulk density, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4,5</td>
<td>3,74</td>
</tr>
<tr>
<td>B</td>
<td>3–4,5</td>
<td>3,64</td>
</tr>
<tr>
<td>Spinel:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>3,42</td>
</tr>
<tr>
<td>B</td>
<td>1–1,5</td>
<td>3,30</td>
</tr>
<tr>
<td>Spinel-magnesite:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>2,5</td>
<td>3,46</td>
</tr>
<tr>
<td>B</td>
<td>6,6</td>
<td>3,23</td>
</tr>
</tbody>
</table>

The destruction of the refractory due to its reaction with the medium depends on the process (absorption or solution) occurring at the lowest speed. Since in practice a worn refractory almost always has an impregnated working zone, then the rate of solution should determine the wear.

In practice, it is only possible to alter the magnitude of $F$ in Fick's equation, so as to reduce the solution rate. The contact surface of refractory and impregnating melt is determined (for a given thickness of impregnated layer) by the total pore volumes and their radii:

$$F = \frac{n}{q} \cdot f,$$

where $V_p$ is the total volume of pores, $n$ is the number of pores, $q$ is the volume of a single pore, and $f$ is the surface area of one pore.

Assuming for simplicity that the pores are spherical and have the same radii, we obtain

$$F = \frac{3}{16} \frac{V_p}{r}.$$

Consequently, the contact surface can be reduced by making the pores larger but reducing the total volume. Making the pores larger cannot be recommended since this would seriously reduce the time required for sucking up the melt to the maximum possible height. Changing the pore radius from 1$\mu$m to 100$\mu$m means that the possible suction height, albeit diminished by a factor of $10^3$, remains very great, and is practically unrealized owing to the high temperature gradient over the length of the brick. The time period required to suck up the melt to the maximum height diminishes under these conditions by a factor of $10^6$, and in practical conditions is of the order of only several hours.

Thus, in practice the reduction in $F$ should be made by reducing $V_p$. This measure is well known. Quantitatively its effect can be assessed from Fick's equation, according to which the rate of solution diminishes when the pore sizes remain constant, in the following manner:

<table>
<thead>
<tr>
<th>$V_p$, fractions of unit</th>
<th>0.25</th>
<th>0.20</th>
<th>0.15</th>
<th>0.10</th>
<th>0.05</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of solution with respect to rate of solution of refractory with a porosity of 25%</td>
<td>1.0</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
<td>0.04</td>
</tr>
</tbody>
</table>

In practice, with a reduction in the total porosity of the refractory there is a reduction also in the size of the pores, and the more so the greater the density of the product; this should reduce the effectiveness of reducing the total porosity. Bearing this in mind, a marked reduction in the wear of the refractory can be obtained by reducing the total porosity to 10-15%, but a decisive result should be expected only with a porosity of below 5%.

It is thus necessary to densify the products substantially in order to greatly reduce their erosion by solution in service. Industrially, greater use is being made of high pressures for semidry pressing and high-firing temperatures for green products and finished goods, but the porosity is far from optimum. The average annual porosity level of dense-ladle high-grog products varies from 12.5 to 14.5%, of dense kaolinite bricks 13.5%, and converter periclase-spinel products 12.5-17.0%.

Increasing the pressure for semidry pressing is effective only in the first stage during conversion from low specific pressures to medium pressures, and subsequent increase in the specific pressure does not greatly affect the reduction in porosity of the green products. This is because when the specific fabrication pressure is raised in geometric progression with a factor $n$, the differences in the porosity of subsequent pressings are constants, $m = b \log n$ [5]. This means that the porosity of the pressings diminishes only in arithmetic progression with a difference of $m$. The magnitude of $m$ is determined by the coefficient $b$ in the pressing equation [6].

Boosting the firing temperature cannot be considered as effective. The green products to be fired, because of their specific properties (coarse-grain sizes of the bodies and the great inertness of the materials being used with respect to sintering because of their high-temperature preparation), are not susceptible to intensive densification by sintering.

Industrially produced thin-walled articles of highly refractive oxides and other compounds that are sintered to zero or almost zero open porosity are currently being made. Their production technology is