Variety in High Corrosion Resistance Magnesia-Chrome Bricks for Clean Steel Refining Vessels

Hisashi Tomiya*1 Koichi Igabo*2 Koyo Murakami*3

Abstract

Application of semi-rebonded magnesia-chrome bricks for clean steel refining vessels as RH degasser and AOD is extending because of its superior corrosion resistance. We have an extensive lineup of semi-rebonded magnesia-chrome bricks as; material A with general versatility, material B with high spalling resistance and material C and D with excellent erosion resistance. While chemical compositions of these four materials are almost identical, unique characteristics such as spalling resistance and erosion resistance are given by adjustments of grain size distribution and/or sinterability. Reduction of wear rate is possible by applying appropriate material corresponding to individual wear status.

1. Introduction

Magnesia-chrome bricks have been widely applied to many kinds of steel refining vessels since it exhibits good corrosion resistance to high basicity (C/S), high FeO fraction slag. Magnesia-chrome bricks are obtained by high temperature firing of pressed body consists of magnesia and chrome ore. We classify the Magnesia-chrome brick to following three types as ; direct bonded type, rebonded type and semi-rebonded type according to the bonding status and composition of raw materials. Direct bonded type is characterized by the microstructure that magnesia grain and chrome grain directly connect each other through the liquid phase in which magnesia-chrome spinel crystals that precipitated. Rebonded type consists of high purity electro fused magnesia-chrome aggregates in which bonding structure is highly evolved. During the firing process, bonding among fused magnesia-chrome grains is formed again. This brick exhibits extremely high corrosion resistance while its thermal spalling resistance is inferior. Adding to above two types, we manufacture the direct bonded bricks containing electro fused magnesia-chrome grain which we classify as semi-rebonded type. Semi-rebonded type shows intermediate features between direct bonded type and rebonded type.

Recently, in accordance with increase in demand of high cleanliness steel, intensive metallurgical treatment is required to steel refining vessels such as RH degasser and AOD. Since the intensive treatment seriously promotes the refractory wear, applications of semi-rebonded brick have been extended because of its excellent slag corrosion resistance.

According to the investigations of semi-rebonded bricks obtained from these vessels after use, two critical wear statuses were recognized. The one is thermal spalling occurred by thermal stress and the other is erosion caused by molten steel reflux or stirring. While the influences of operational condition and/or geometric dimensions of vessel on brick wear status is unclear, adjustment of brick properties sometimes effectively reduces the wear rate. In this article, four semi-rebonded bricks; high versatility A, high thermal spalling resistance B, high erosion resistance C and D, for vessels which showed specific wear status are described.
2. Features of Materials A, B, C and D

As summarized in Table 1, chemical compositions of these four materials are almost identical. Thermal spalling resistance of material B is improved by applying coarse grain size distribution. Improvement of thermal spalling resistance is achieved by adequate introduction of microcracks in the matrix. Figure 1 shows the thermal expansion curves of electro fused magnesia aggregate and electro fused magnesia-chrome aggregate. Both of which are contained in semi-rebonded magnesia-chrome bricks. The difference in thermal expansion behavior between the two aggregates causes microcracks in the bonding phase as shown in Fig.2. Introduction of microcracks improves thermal spalling resistance not only by decreasing Young's modulus but also by crack branch and detour effects. Suitable microcrack introduction is achieved by adequate arrangement of course grain size aggregates.

High erosion resistances of materials C and D were the result of sintering structure enhancement achieved by acceleration of the mass transfer rate in the matrix during firing, while, different technologies were applied

Table 1  Typical properties of semi-rebonded magnesia-chrome bricks

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition</td>
<td>MgO</td>
<td>Cr₂O₃</td>
<td>SiO₂</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>/ mass%</td>
<td>63.8</td>
<td>24.1</td>
<td>0.8</td>
<td>6.0</td>
</tr>
<tr>
<td>Apparent porosity / %</td>
<td>13.3</td>
<td>14.0</td>
<td>12.7</td>
<td>13.2</td>
</tr>
<tr>
<td>Bulk density / g·cm⁻³</td>
<td>3.34</td>
<td>3.31</td>
<td>3.36</td>
<td>3.34</td>
</tr>
<tr>
<td>Cold crushing strength / MPa</td>
<td>60</td>
<td>45</td>
<td>65</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig.1  Thermal expansion of fused magnesia and fused magnesia-chrome.

Fig.2  Microcrack observed in bonding phase of semi-rebonded magnesia-chrome bricks.

Fig.3  Microstructure of material A and D.
for materials C and D. Figure 3 compares the microstructures of A and D. Obviously, considerable neck growth and increase in pore diameter can be recognized in material D. These are the evidence of a high evolution degree of sintering structure. A highly evolved firm sintering structure, as observed in material D, inhibits bonding structure destruction induced by abrasion.

3. Evaluation of Thermal Spalling Resistance and Erosion Resistance

In this section, experimental evaluation of thermal spalling resistance and erosion resistance are described.

A thermal spalling test was carried out by utilizing an electric furnace as follows. 40mm cubic specimens were heated in an electric furnace at 1200°C for 15 minutes subsequent to 3 minutes water quenching followed by 12 minutes natural cooling. This cycle was repeated until fracture. Figure 4 shows the numbers of thermal cycles until fracture normalized by material A. As is obvious, material B shows excellent thermal spalling resistance.

For accurate evaluation of the erosion resistance of these materials, a new method was created by taking the structural deterioration that had occurred in actual vessels into consideration. As is widely accepted, erosion is the abrasion loss of the specific area of which the microstructure had been deteriorated. Since microstructure deteriorations are caused by repetition of moderate thermal shock and/or chemical alteration\(^{1,2}\), suppression of microstructure deterioration is an effective measure against erosion wear.

As for high corrosion resistance semi-rebonded brick, it was assumed that thermal shock is the dominant factor of microstructure deterioration. Refractories installed on steel refining vessels suffer from thermal cycles according to the steel treatment procedure. While the largest thermal shock, which sometime causes spalling wear, occurs at the working surface, moderate thermal shock
repeatedly affects the internal part of the refractories and it promotes microstructure deterioration. In other words, the microstructure of the working surface was previously deteriorated by repetitions of moderate thermal shock.

Based on the above discussion, the erosion resistance was evaluated by the hot modulus of rupture (HMOR) of the post-cyclic heated specimen.

The cyclic heating was performed with the cyclic heating apparatus shown in Fig.5. This apparatus consists of two vertically connected electric furnaces of which the internal temperature can be controlled independently. The hearth, on which the specimens were set, shuttles between two rooms instantly. In this case, the temperatures of the upper and lower room were controlled at 1400°C and 600°C, respectively, and 10 thermal cycles, that is, 10 minutes in the upper room and 10 minutes in the lower room were imposed to rectangular specimens of 40×40×160mm followed by evaluation of the HMOR at 1400°C.

Figure 6 shows the HMOR index after cyclic heating. Sintering structure enhanced materials C and D showed high HMOR after cyclic heating which ensures high erosion resistance. Figure 7 shows the microstructure of materials A, B and C after the cyclic heating. The smaller size of the inter-particle voids observed in material C suggests inhibition of sintering structure deterioration, which was induced by cyclic thermal shock.

4. Commercial Application

Material A, with general versatility, is being widely used in several furnaces including lower vessels of RH
degassers of steel mills X and Y. In steel mill X, post use
investigation results of material A showed that the lower
vessel of the RH degasser was obviously worn by thermal
spalling. Hence, material B, with high spalling resistance
was applied to this vessel. As a result, the wear rate was
decreased by 10% as shown in Fig.8.

On the basis of this result, material B was applied to the
RH lower vessel of steel mill Y. Unfortunately, the wear
rate was increased. According to the investigation of the
bricks after use, it was concluded that erosion wear was
dominant in the case of steel mill Y. Therefore, material
C was selected. As a result, the wear rate became smaller
as shown in Fig.9. Although material D hasn’t been used
for commercial vessels at this moment, good results are
expected for the vessels seriously damaged by abrasion.

As mentioned in the introduction, the influence of
operating conditions and lining design on the difference
in damage status is unclear. However, reduction in the
wear rate is possible by optimizing brick characteristics
on the basis of careful investigation of the used brick.
We have an extensive lineup of high corrosion resistance
semi-rebonded magnesia-chrome bricks as described
in this article. In addition, on the basis of our material
design technology, further optimization is possible.

Fig.9 Wear rate index at lower vessel of RH
degasser of Y mill.

5. Conclusion

Applications of semi-rebonded magnesia-chrome bricks
for clean steel refining facilities such as the RH degasser
or AOD are broadening because of their superior cor-
rosion resistance. We have an extensive lineup of high
corrosion resistance semi-rebonded magnesia-chrome
bricks such as; material A with general versatility, mate-
rial B with high spalling resistance and material C and
D with excellent erosion resistance. In addition, further
optimization is possible.

References
1 ) Naoyoshi Nameishi, Tanezo Ishibashi, Tatsuo Matsumura, Hideo Adachi, Hirosuke Osaki : Taikabutsu 33