CERTAIN PROPERTIES OF MgO-Cr₂O₃-TiO₂ COMPOSITIONS

A. I. Gudilina, N. V. Pitak, and A. V. Kushchenko

Rigid demands are placed on refractories intended for design elements in steel ladles, especially in terms of density, strength, slag and metal resistance, and thermal-shock resistance.

Periclase refractories are distinguished by a high resistance to the chemical action of molten steel and slag, but they have low thermal-shock resistance and mechanical strength and a high porosity.

This paper gives the results of a study into the influence of compositional additions of Cr₂O₃ and TiO₂ on the physical-ceramic and thermomechanical properties of specimens based on electrofused periclase with the aim of using the newly developed material in plant working at high temperatures and under melt conditions and thermal stress.

The starting materials consisted of electrofused periclase of the following chemical composition, %: MgO 94.66, SiO₂ 1.88, Al₂O₃ 0.60, Fe₂O₃ 0.39, CaO 2.44, Mn 0.44; chromium oxide OKhM grade as specified by GOST 2912-79; and titanium dioxide of chemical purity grade as specified by TU 6-09-2166-77.

Specimens were pressed at 150 MPa from batches of the following grain-size composition: 45% electrofused periclase fractions 2-0.5 mm, 20% fractions 0.5-0.063 mm, and 35% fractions minus 0.063 mm. The compositional additives were incorporated in the finely milled form (minus 0.063 mm) as a result of reducing the amount of finely grained constituent of the batch. The bond consisted of an aqueous solution of sulfite lye with a density of 1.16 g/cm³. The firing temperature of the periclase specimens containing the additives was 1780°C, with a soak at this temperature of 6 h.

The results of the study of the effect of the additives on the main properties of the specimens are shown in Table 1.

<table>
<thead>
<tr>
<th>Additive Composition</th>
<th>Apparent Density (g/cm³)</th>
<th>Open Porosity (%)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>3.05</td>
<td>10.2</td>
<td>73.2</td>
</tr>
<tr>
<td>No. 2</td>
<td>3.13</td>
<td>9.8</td>
<td>75.3</td>
</tr>
<tr>
<td>No. 3</td>
<td>3.29</td>
<td>9.0</td>
<td>77.4</td>
</tr>
</tbody>
</table>

Uniformly with a reduction in the open porosity there is an increase in the mechanical strength to maximum values of 106 and 100.7 MPa, which correspond to specimens prepared from batches Nos. 8 and 10 (see Table 1).

The specimens' resistance to the thermal loading is in reverse relationship to the mechanical strength of the refractories. The highest thermal-shock values (3-4 heat cycles) are noted in specimens whose compressive strength is 28.2-66.3 MPa, which agrees with [2].

The refractoriness under load of 0.2 MPa is reduced with increase in the content of titania, especially with a reduction in the amount of chromium oxide (batches Nos. 4, 5, and 7).

The resistance of periclase specimens with the compositional additives in regard to converter slag, obtained during the melting of steel grade 08kp, was determined by the crucible
TABLE 1. Influence of Additions of Cr₂O₃ and TiO₂ on the Properties of Periclase Specimens

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>Batch composition, %</th>
<th>Properties of fired specimens</th>
<th>Refractoriness under load of 0.2 MPa, °C</th>
<th>Slag resistance (area of penetration), mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>electro-fused periclase</td>
<td>Cr₂O₃</td>
<td>TiO₂</td>
<td>apparent density, g/cm³</td>
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<tr>
<td>1</td>
<td>100</td>
<td>6.5</td>
<td>6.5</td>
<td>3.05</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>13.5</td>
<td>3.5</td>
<td>3.17</td>
</tr>
<tr>
<td>3</td>
<td>83</td>
<td>13.5</td>
<td>3.5</td>
<td>3.19</td>
</tr>
<tr>
<td>4</td>
<td>87</td>
<td>6.5</td>
<td>6.5</td>
<td>3.25</td>
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<tr>
<td>5</td>
<td>90</td>
<td>6.5</td>
<td>6.5</td>
<td>3.13</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>13.5</td>
<td>3.5</td>
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<td>7</td>
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<td>8</td>
<td>83</td>
<td>10.0</td>
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<td>9</td>
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<td>10.0</td>
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<td>3.17</td>
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<tr>
<td>10</td>
<td>83</td>
<td>10.0</td>
<td>7.0</td>
<td>3.29</td>
</tr>
</tbody>
</table>

TABLE 2. Approximate Content of Mineral Phases in Specimens Based on Electrofused Periclase with Additions of Cr₂O₃ and TiO₂

<table>
<thead>
<tr>
<th>Specimen No. (Table 1)</th>
<th>Mineral composition, %</th>
<th>Perovskite</th>
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<tr>
<td></td>
<td>periclase</td>
<td>magnesiochromite</td>
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<tr>
<td></td>
<td>93-95</td>
<td>93-85</td>
</tr>
<tr>
<td></td>
<td>80-85</td>
<td>80-85</td>
</tr>
<tr>
<td></td>
<td>75-78</td>
<td>75-78</td>
</tr>
</tbody>
</table>

*According to petrographic analytical data.

The resistance of periclase specimens containing additives to molten slag attack, although it increases in certain cases, is very slight (not more than 20% increase). The area of penetration of purely periclase specimens is 725 mm², and for specimens containing 6.5-10.0% Cr₂O₃ and 3.5-7.0% TiO₂ it is located in the limits of 600-655 mm². The slag resistance of periclase specimens containing 13.5% Cr₂O₃ regardless of the concentration of titania is impaired (batches Nos. 2 and 3).

As a comparison we determined the slag resistance of periclase–chromite articles grade PKhV produced by the Magnezit combine, and used to line ladles for outside-furnace working of steel. The area of penetration of these articles was 948 mm² which is about 45% greater than for specimens of electrofused periclase with additions of 10% Cr₂O₃ and 5% TiO₂.

The properties of the refractories largely depend on the microstructure which is determined by the composition, the quantity and mutual arrangement of the phases, and the presence of microcracks [3].

In this connection, we studied the microstructure of the specimens containing Cr₂O₃ and TiO₂ additives and determined the optimum property factors.

As shown by petrographic studies, the purely periclase specimen has a clearly expressed brecciated structure as a result of the presence of grains and aggregates of fused periclase measuring 1-2 mm and fine-grained bonding mass. The periclase is the main component, and is present in the form of separate, large (up to 2 mm) groupings of single crystals and aggregates measuring 0.1-1.5 mm, consisting of yellowish and colorless grains with a predominant size of 0.08-0.15 mm. The refractive index of periclase is normal. Separate grains in the groups of single crystals contain fine (0.02-0.03 mm) pores of isometric forms frequently half filled with silicates.