REFRACTORIES AT THE USER

MgO – Al₂O₃ – Cr₂O₃ REFRactories OF INCREASED CORROSION RESISTANCE FOR NONFERROUS METALLURGICAL furnaces

I. D. Kashcheev,¹ V. P. Semyannikov,² V. E. Gel’fenbein,² V. M. Bibaev,³ T. V. Yarushina,³ and V. P. Konygin⁴


Refractories of the MgO – Al₂O₃ – Cr₂O₃ class include a wide range of compositions for the manufacture of refractories that consist of periclase, spinel, and spinellide in various proportions. Although quite a number of studies concerned with these refractories have been undertaken to date, some issues have yet to be explored from a technological point of view as concerns the advent of a fused spinel-containing material (Specs. TU 3988-025-0221841-95), which is one of the ingredients in this ternary system. In terms of durability, existing periclase-chromite (PKh) and chromite-periclase (KhP) refractories for nonferrous metallurgical furnaces fall short of metal-makers’ requirements.

Conversion of nickel matte entails severe wear of the refractory converter lining, especially in the tuyere zone. The near-tuyere and other parts of the converter operate under very adverse conditions. In addition to chemical and physical exposure, they have to stand up to sudden changes in temperature. As a result, the duration of the campaign is drastically reduced to 7–12 days, and increased quantities of refractories have to be used [1]. The maximum wear of KhP refractories in the subtuyere zone is 200 mm, and the rate of wear for KhPT and MKhVP refractories in the tuyere belt is 13.5 and 11.6 mm/day, respectively.

When the molten matte bath is blown, the metallic iron is oxidized first with formation of FeO, which passes into slag as fayalite if SiO₂ is present in the converter. The exothermic reactions that take place raise the temperature to a point significantly different from the average bath temperature. As has been found by theoretical calculations, with an air blast the temperature is 1400–1500°С for copper matte and 1650–1700°С for nickel matte.

As will be recalled, the durability of linings can be enhanced mainly by use of fused refractories. Iron oxides cause chromite-spinellide grains to swell, so, where contact with iron slags is inevitable, preference should be given to compositions containing fused aluminum-magnesium spinel (AMS). In practice, use is made of fused AMS with a 10 to 20% excess of MgO over the stoichiometric composition [2]. Industrial tests [3, 4] have confirmed the advantage of fused spinel as a constituent of periclase refractory mixes. The optimum spinel content of the mix is 20%, if its composition is 8.9 – 16.9% Al₂O₃, 73.9 – 82.3% MgO, and 1.7 – 2.5% Cr₂O₃.

Addition of chrome to spinel-containing refractories turns the system into a complex one. Chrome spinellide is wetted by the melt less, the higher its chromium oxide content [5]. An optimum proportion (from 1.5 : 1 to 2.0 : 1) has been found to exist for the spinels MgCr₂O₄ and MgAl₂O₄, at which periclase-spinellide refractories loosen least [6].

The worst impurity in spinel refractories is SiO₂ – it forms a glassy phase, and this drastically impairs the physi-

¹ Ural State Technical University, Ekaterinburg, Russia.
² Kompozit-Ural Closed Joint-Stock Company, Ekaterinburg, Russia.
³ Magnezit Joint-Stock Company, Satka, Chelyabinsk Region, Russia.
⁴ Ufaleinikel’ Joint-Stock Company, Ufa, Russia.
⁵ Here and elsewhere, wt.% is meant.
TABLE 1. Chemical Composition of the Starting Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgO</td>
</tr>
<tr>
<td>Periclase:</td>
<td></td>
</tr>
<tr>
<td>sintered¹</td>
<td>92.7</td>
</tr>
<tr>
<td>fused</td>
<td>94.0</td>
</tr>
<tr>
<td>Fused aluminum-magnesium spinel</td>
<td>35.7</td>
</tr>
<tr>
<td>Chrome-ore concentrate</td>
<td>16.0</td>
</tr>
<tr>
<td>Chrome ore</td>
<td>20.0</td>
</tr>
<tr>
<td>Fused periclase-chromite</td>
<td>81.9</td>
</tr>
</tbody>
</table>

* Grains smaller than 3 mm; the remainder, grains smaller than 0.063 mm.

The mechanical properties of the material, especially at high temperatures [7]. The strength at room temperature and the high-temperature creep of multiphase refractories depend on the size of the crystals that make up the structure. Fine-grained refractories are stronger at room temperature but are more susceptible to high-temperature creep, and vice versa. At the same time, recrystallization reduces the creep of the material [8].

In view of the foregoing, a study was undertaken that had as its objective to develop refractories of increased corrosion resistance for harsh service conditions. The starting materials were sintered and fused periclase powders, fused aluminum-magnesium spinel, fused periclase-chromite, chrome ore, and chrome-ore concentrate. The chemical composition of the starting materials is given in Table 1.

Laboratory specimens 50 mm high and 36 mm in diameter were shaped under a pressure of 150 MPa. The binder was 5–6% aqueous LST solution with a density of 1.20 g/cm³. The specimens were fired in the Magnesit Works' tunnel furnaces at 1650, 1750, and 1880°C. The mix composition was varied between wide limits. Experimental findings are given in Figs. 1–4. As can be inferred, a change in the ratio of the chrome-containing ingredient to fused AMS in the finely ground fraction affected the strength of the specimens differently (see Fig. 1). With an increase in the chrome ore and concentrate content of the mix, the strength of the specimens first decreased, and then it increased when the chrome-spinelide constituent became predominant. The fused periclase-chromite powder raised the strength of the specimens in all cases. This difference in the behavior of the mix was probably related to the purity of the chrome-containing ingredient. An increase in firing temperature from 1650 to 1750°C affected more strongly the mixes that contained chrome-ore concentrate (see Fig. 1a), with the strength of the fired specimens rising from 40 to 70 MPa. In the case of high-temperature firing (at 1750°C and higher), the MgO grains were additionally sintered and the periclase crystals grew by a factor of 1.5–2 compared with the starting periclase powder.

![Fig. 1. Strength σ of specimens fired at (1) 1650 and (2) 1750°C plotted against the ratio n of (a) chrome-ore concentrate to AMS, (b) chrome ore to AMS, and (c) periclase-chromite to AMS.](image)

According to an x-ray phase analysis and petrographic examination, all specimens had about the same phase composition, porosity in the fine-grained part, and macro- and microstructure. The rise in temperature affected most of all the reactions between the spinel and the chrome-ore concentrate. As a result, iron and chromium oxides migrated into the spinel, its refractive index rose from 1.716 to 1.950, and its composition approached that of the spinellide Mg(Al, Cr, Fe)₂O₄ due to saturation with the oxides. Concurrently, diffusion—exchange reactions took place between the periclase and the chrome-containing ingredients with formation of a periclase-based solid solution. On cooling, the latter decomposed to secondary spinel in the bulk of the residual solid-solution crystals. These inclusions measured from 1 to 3 μm across.

Thus, firing produced three kinds of spinellide, namely, ones based on fused AMS, periclase, and residual chromite, which differed in the concentration of the constituent oxides. In all probability, it is the proportion of these spinellides that determines both the strength and the corrosion resistance of the refractories in service.

Further work involved chrome-ore concentrate, which imparted the highest strength to the specimens. The manner in which the grain size of fused AMS in a mix that varied in the percentage of chrome-ore concentrate