THE LONG-TERM HIGH-TEMPERATURE BEHAVIOR
OF REFRACTORIES PRODUCED FROM ZrO₂
STABILIZED WITH Nd₂O₃

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Equipment operating at temperatures above 2000°C is heat-insulated with refractories based on ZrO₂ stabilized with Y₂O₃. The zirconia products used for this purpose are in the form of crucibles with 5-10 mm thick walls and an internal diameter of 50-120 mm. The inside surface of the crucible is exposed constantly to high temperatures (2000-2500°C) while the outside surface is being cooled. The difference in the temperature of these surfaces is 1000-1500°C. The gaseous medium in the furnace is neutral (argon).

A temperature of 2000-2500°C must be achieved in the crucible in 1-1.5 h, and the holding time at peak temperature varies 50-150 h after which the lining is cooled rapidly (in 0.5-1 h) to room temperature. The satisfactory service life of zirconia refractories under such conditions depends primarily on the thermal stability and strength of the material. Crucibles formed of a zirconia-yttrium solid solution are not stable enough to sudden changes in the temperature, often fracture even during heating-up, and usually are unfit for further service after a single smelting cycle.

The results of an analysis of the phase composition, microstructure, and properties of materials based on the ZrO₂-Nd₂O₃ system [1] served as a basis for the development of the technological parameters for producing refractories of improved thermal strength from ZrO₂ stabilized with Nd₂O₃. The principal operations in the process are as follows:

1. Synthesis of a cubic solid solution of 88 mole % ZrO₂ + 12 mole % Nd₂O₃ in an open-flame kiln at 1700-1740°C.

2. Grinding the bricks of stabilized ZrO₂ to particles not exceeding 0.25 mm in diameter followed by magnetic separation of the powder.

3. Combined fine-grinding of 70% cubic solid solution and 30% nonstabilized ZrO₂ in a vibro-mill with rubber lining and Relit (a tungsten carbide) balls; at least 50% grains finer than 3 μ in the ground product.

4. Wetting the mix with a 5% solution of polyvinyl alcohol, moisture content of the mix prior to pressure-molding 7-8%.

**TABLE 1. The Phase Composition of the Zirconia Refractory before Service and after Service for 100 h**

<table>
<thead>
<tr>
<th>Furnace temp, °C</th>
<th>Zone</th>
<th>Content, %</th>
<th>Nd₂O₃ conc. in zone, mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cubic solid soln</td>
<td>monoclinic phase</td>
</tr>
<tr>
<td>Refractory before service</td>
<td>Least-changed Working</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>2100</td>
<td></td>
<td>59</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>Least-changed Working</td>
<td></td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td>2500</td>
<td></td>
<td>100</td>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 1. Products molded from ZrO$_2$ stabilized with Nd$_2$O$_3$.

Fig. 2. The microstructure of the zirconia products before service: The gray areas are cubic solid solution Nd$_2$Zr$_2$O$_7$ - ZrO$_2$, the white areas monoclinic phase, and the black areas pores. x340. Reflected light. Etching for 10 min.

Molding the products at a pressure of 400-500 kg/cm$^2$.

Firing the products in an open-flame kiln at 1750°C with 5-h holding in corundum saggers resting on supports of unfired granular MgO.

This technology gave rings and disks of good quality (Fig. 1) in spite of the considerable (12-13%) linear shrinkage. The apparent porosity of the products varied 5-10%. The microstructure of the fired products is characterized by the even distribution of the unstabilized ZrO$_2$ around the larger grains of the cubic solid solution (Fig. 2). Zirconia refractories with such a microstructure withstand over 20 temperature reversals from 1300°C into water.

Assembled crucibles 70 mm in height with an inside diameter of 70 mm and 6-mm thick walls were subjected to testing under production conditions. The high thermal stability and strength of these crucibles enabled them to withstand four smelting cycles in the furnace.

The phase composition of the refractory before and after service is shown in Table 1. The figures show that the content of unstabilized ZrO$_2$ in the products before service differs significantly from its content in the original mix. This change in the degree of ZrO$_2$ stabilization is the result of a redistribution at 1750°C of some of the neodymium oxide between the synthesized solid solution and the tetragonal ZrO$_2$. The result of this redistribution of Nd$_2$O$_3$ is that the amount of cubic solid solution Nd$_2$Zr$_2$O$_7$-ZrO$_2$ increases while its content of stabilized oxide decreases from 12 to 10.9 mole%.

An analysis of the crucibles after service for 100 h (one cycle) at a furnace temperature of 2100°C showed that the temperature gradient produced three zones in the zirconia refractory, viz., a working, an intermediate (less dense), and a least-changed zone. The depths of the zones were 3.0-3.5, 1.5-2.0, and 1.5-2.0 mm, resp.

The working zone is the densest (zero apparent porosity) and consists of stabilized ZrO$_2$ (see Table 1). The density of the least-changed zone is almost the same as the sintered density of the product before service. The high degree of sintering of the material in the working zone produces grain growth and the recrystallization of the cubic solid solution the crystal size of which increases from 30-40 μ to 100-150 μ.

The after-shrinkage of the working zone is a source of isolated fissures in this zone but owing to the high strength of the refractory in the least-changed zone the crucible is not destroyed.

The structure of the intermediate zone of the crucibles is distinctly microfissured. The microfissures are formed as a result of the intensive sintering of the material in the working zone and as a result of the difference in the coefficients of thermal expansion of the working (single-phase) and least-changed (two-phase) zones. In spite of the microfissured structure of the intermediate zone, the crucibles were in a satisfactory condition after one operating cycle and were fit for further service. It was only after four cycles (400 h at 2100°C) that spalling was observed to develop in the working zone of some of the rings of the built-up crucible.