NON-FIBROUS INSULATION OF SUBMERGED NOZZLES FOR CONTINUOUS CASTING

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ABSTRACT
This investigation reports on the use of a microporous insulation on the basis of calcium hexaluminate as an alternative to the fibrous insulation usually employed nowadays on submerged nozzles for continuous casting. The new insulation offers advantages in submerged nozzle production owing to its greater suitability for process automation. The new insulation has also shown good results in practice due to its good heat insulating qualities and easy handling. These positive test results have now been confirmed in an industrial trial with more than 100 submerged nozzles. Compared to the fibrous alternative, thermal insulation is improved with the new insulation even with the same thickness. Following these positive results, microporous insulation is being applied to more and more submerged nozzles.

INTRODUCTION
For continuous casting of slabs submerged entry nozzles are employed between the tundish and mold. Geometry and material properties are adjusted to the special needs of each application. For the main body, alumina / graphite materials are used, whereas for the slag-body zirconia / graphite materials are used in order to increase the resistance against aggressive mold powders. The ceramic materials for sub entry nozzles contain up to about 30% graphite (see table 1) to increase elasticity and thermal conductivity, mainly to avoid cracks caused by thermoshock during start of casting. Generally the subentry nozzles
will be preheated before start of casting to avoid any damages caused by thermal shock.

Table I: Typical data of materials for submerged nozzles

<table>
<thead>
<tr>
<th>Weight [%]*</th>
<th>Body material</th>
<th>Slag body material</th>
<th>Microporous insulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>47</td>
<td>&lt;0,5</td>
<td>89</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>3</td>
<td>76</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
<td>24</td>
<td>&lt;0,5</td>
<td>&lt;0,5</td>
</tr>
<tr>
<td>SiC</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>C_free</td>
<td>26</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>Bulk density [g/cm³]</td>
<td>2,35</td>
<td>3,48</td>
<td>0,91</td>
</tr>
<tr>
<td>Apparent porosity [%]</td>
<td>15,0</td>
<td>18,5</td>
<td>62</td>
</tr>
<tr>
<td>Thermal conductivity [W/mK]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 °C</td>
<td>23,5</td>
<td>13,1</td>
<td>0,43</td>
</tr>
<tr>
<td>500 °C</td>
<td>15,3</td>
<td>10,5</td>
<td>0,40</td>
</tr>
<tr>
<td>1000 °C</td>
<td>9,4</td>
<td>9,2</td>
<td>0,38</td>
</tr>
<tr>
<td>1400 °C</td>
<td>10,7</td>
<td>9,5</td>
<td>0,38</td>
</tr>
</tbody>
</table>

*Chemical analysis of the materials as received (sum includes carbon)

During preheating the high thermal conductivity of the materials for submerged nozzles leads to heat losses so that as a countermeasure an insulating material is applied on the outside of the nozzle. By these means heat loss will be minimized. This is especially important for the transport of the tundish to the mold. Generally this transfer time is about five minutes.

Nowadays ceramic fiber materials are usually employed as insulation of submerged nozzles for continuous casting. Recently there are efforts to replace these materials by non-fibrous materials. Goals are the improvements of the thermal insulation and also to provide advantages in submerged nozzle production owing to the greater suitability of process automation. This investigation reports about the results obtained in industrial trials with the new high-temperature insulation material at Thyssen Krupp Stahl AG in Dortmund, Germany.

MICROPOROUS MATERIALS
Perich [1] and Morikawa et al. [2] report about non-fibrous insulation materials for submerged entry nozzles. In their papers, insulation materials
based on SiO$_2$ - Al$_2$O$_3$ compounds are presented. These are sprayed on sub entry nozzles after foaming up. The process of foaming up is important in order to receive the porosities necessary for thermal insulation. In comparison to the trials reported by this investigation, a new microporous raw material was applied which directly provides the desired insulating properties at service temperatures.

The insulation raw material SLA-92 used for the trials contains 92% Al$_2$O$_3$. The other main chemical component is calcium oxide with 7 - 8 %. From the point of mineralogy the raw material consists of calcium hexaluminate (CaO$\cdot$6Al$_2$O$_3$ or CA$_6$), showing only very little impurities e.g. SiO$_2$ and Fe$_2$O$_3$ are below 0.1 %. CA$_6$ with a melting point above 1850 °C accounts for the high refractoriness of up to 1500 °C. The bulk density of the raw material is about 0.75 g/cm$^3$.

Fig 1: SEM micrograph showing the fracture area of the microporous raw Material SLA-92 [5]

An important property of SLA-92 is its structure. Fig. 1 shows the platelet-shaped structure of the CA$_6$ crystals which are interlocking. The free distance between the crystals defines the microporous structure with a typical open porosity of about 75 % and a narrow range of pore size distribution with pore diameters of 3-4 μm (see fig 2). The microporosity leads to two essential product properties in comparison to conventional insulating raw materials.
Micropores reduce the heat transfer by radiation and therefore reduce the thermal conductivity of a material, especially for temperatures above 1000 °C [3, 4]. For the new insulation material a value of 0.4 W/mK above 1000 °C is typical.

In general, insulation materials show only slight thermal shock resistance due to the strong slope of their thermal gradient. By its microporosity the progress of crack forming in SLA-92 by thermal shock will be prevented in comparison to conventional insulation materials (except fibrous materials) as shown by the studies of van Garsel et al. [5, 6].

Fig 2: Micro pore size distribution of SLA-92 (Hg-intrusion method) [5]

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PREPARATION OF THE NON-FIBROUS INSULATION
To prepare a sub entry nozzle SLA-92 and calcium aluminate cement are mixed with water (see table 1) where the mixing water (70-90%) controls the consistency and workability of the insulation mix. With regard to an automated production process spray-coating was well suited. This procedure allows taking the geometry and special operating conditions into account e.g. application of insulating layers of different thickness depending on position. Furthermore the spray coating procedure allows applying the insulation material in the port-holes of the sub entry nozzles in order to avoid thermal stress (see Fig. 3).

During preheating up to temperatures of 400 °C water from the cement
bonding will be released. This water may cause oxidation of the carbon in the sub entry nozzle materials. So for a better protection against oxidation a separate glass-building layer is prepared between sub entry nozzle and insulation, also by means of spray coating. Another property of this intermediate layer is providing the bonding at temperatures above 700 °C.

Fig. 3 Submerged nozzle with sprayed on microporous insulation

INDUSTRIAL TRIAL
Fig. 4 shows the geometry of the long stopper and sub entry nozzle arrangement at the Thyssen Krupp Stahl AG in Dortmund. In the area of the bath level the sub entry nozzles are equipped with zirconia / graphite as slag body material. During casting the tundish is moved in cycles towards certain positions so that the erosion caused by the mold powder is distributed over this range (see Fig. 4). By these means the sub entry nozzles achieve durabilities of up to ten hours.

Fig. 5 shows the preheating equipment in Dortmund. Preheating time is about 120 minutes. Then the tundish car will transfer the tundish into casting position. During this time period of about four to five minutes until start of casting the sub entry nozzle is not being preheated.
This period is of special importance as the ZrO₂ of the slag-body material will show a modification of the crystal structure from tetragonal to monoclinic in the temperature range from 900 to 1100 °C, if the sub entry nozzle would cool down too much. This modification of the crystal structure will result in an
increase of volume by about 9% [7] and can cause cracks in the sub entry nozzle. Therefore especially for this short period of time before start of casting an optimum of thermal insulation is required. Morikawa et al. [2] could find strong differences in the speed of cooling down of submerged nozzle with and without insulation by measuring the temperatures 10 mm below the surface. Without insulation, a starting temperature level of 1000 °C cools down to below 800 °C within 3 minutes. In the case of using a 6 mm thick fibrous insulation this same cooling down temperature range requires 12 minutes.

Fig. 5 Submerged nozzle preheating device, with microporous insulation (right hand side)

Two trials with the microporous insulation were made. On the two strand caster, one strand was equipped with the trial material and the other strand with the standard fibrous insulation. The wall thickness of the sub entry nozzles was about 22 mm for the main body and 27 mm for the slag body. The thickness of the spray coating was in the range of 1-3 mm, the thickness of the fibrous insulation 3 mm for the first test and 6 mm for the second test. In the first trial the outside temperature of the submerged nozzles was measured
during preheating and casting with a contact thermometer. The position of the measuring points are shown in Fig. 4. In the second test thermoscans were made with a scanner of Flir Systems type Agema System 470.

The results of both trials are shown in table II. When comparing the same thickness of the insulation layers, the outside temperatures of the sub entry nozzle with microporous insulation are about 30 - 50 °C lower during preheating and about 220 °C lower during casting in comparison to the fibrous material. The results during casting show clearly a gain in insulation properties of the microporous materials at higher temperatures. When comparing a double thickness (6 mm) for the fibrous material the preheating and casting measurements show very similar temperatures for both types of insulation.

Table II: Temperatures [°C] at the outer side - Results with microporous and with fibrous insulation

<table>
<thead>
<tr>
<th>Test I: (Measuring points, Fig. 4)</th>
<th>Time [min] after start of preheat</th>
<th>Microporous 1-3 mm</th>
<th>Fibrous 3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Main body)</td>
<td>120</td>
<td>480</td>
<td>530</td>
</tr>
<tr>
<td>2 (Slag body)</td>
<td>120</td>
<td>550</td>
<td>580</td>
</tr>
<tr>
<td>1 (Main body) (during casting)</td>
<td>190</td>
<td>750</td>
<td>970</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test II: (Thermoscan, Fig. 6 &amp; 7)</th>
<th>Microporous 1-3 mm</th>
<th>Fibrous 6 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>115</td>
<td>349 – 496*</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>496 – 765*</td>
</tr>
<tr>
<td></td>
<td>(during casting)</td>
<td>264 – 466*</td>
</tr>
<tr>
<td></td>
<td>(during casting)</td>
<td>496 – 773*</td>
</tr>
</tbody>
</table>

* measured along the measuring line (see Fig. 6 & 7)

The temperature distribution during preheating is more homogeneous in the case of microporous spray coating.

The trials showed that the new microporous spray coating achieves a better thermal insulation in comparison to fibrous materials. Using fibrous materials a double thickness is necessary to achieve similar insulating results.

OUTLOOK
Because of these positive results sub entry nozzles equipped with the microporous insulation are used now in larger quantities. The handling of the nozzles with spray coating applied showed no problems in the steel plant, but it is recommended that in case the submerged nozzles are put down horizontally for tundish preparation to use a soft material underneath to avoid
damage to the insulation layer. Currently there are developments to increase the strength of the spray coating by modification of the bonding.

The high refractoriness and insulating ability of this microporous material makes it an interesting material also for other applications in the steelmaking process.

Fig 6: Thermoscan of submerged nozzles with (left) microporous insulation (1-3 mm) and fibrous insulation (6 mm) during preheating

Fig 7: Thermoscan of submerged nozzles with (left) microporous insulation (1-3 mm) and fibrous insulation (6 mm) during casting

REFERENCES


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