“Functional Refractory Filter Design and Processing for Advanced Large Steel Castings”

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High Temperature Materials and Applications

Porous Ceramics

Composite Materials and Processing
For the past 40 years, ceramic foam filters have helped foundries to produce metal products with superior properties.

Filter systems provide two basic functions:

- to remove impurities in the millimetre, micron and submicron size range
- to promote non-turbulent melt filling of the mould thus reducing molten metal reoxidation and mould erosion.
Feeder with integrated Filter
In Europe, filter usage per metal foundry includes

- 140 million for iron filtration,
- 20 million for aluminium casting and
- 2 millions for steel filtration applications.

Their market is forecast to expand by 3.5% per year.
Innovation in Filter Technology

RODEX
Pressed filter body

STELEX
Foam structure for steel filtration

SEDEX
SiC foam structure
The main production is based on the patent of Schwartzfeldar

- whereby a polymer foam is impregnated in a ceramic slurry (this first coating contributes as an adhesive porous layer for further coating processes),
- the ceramic slurry is squeezed out of the functional pores,
- the dried green body is coated several times up to 300 µm wall thickness.

Special efforts are required to avoid:
- shrinkage defects such as cracks,
- fissuring deformation that occurs during the burn out of the polymeric foam, and
- edge chipping or breakout due to the low strength of the hollow filter strand walls.
Fissuring

Cracks

Deformations

End chipping
Ceramic foam filters have to fulfil certain requirements like:
- thermal shock,
- creep stability and
- functional permeability.

The thermal shock properties can be achieved by “intelligent manipulation of the polymer foams” or by choice of durable material with advanced thermal shock performance.

One way is to introduce foam with some flocking, using cotton fibres on the top of the polymer foam, to get a better thermal shock resistance of the refractory.
PU - Foam untreated

PU - Foam treated
Diesel soot filters
C.G. Aneziris, W. Schärfl
German Patent DE 1020055036394.6

AZT
95% Alumina
2.5% Zirconia, Mg-PSZ
2.5% Titania, Nanoparticles

- Aluminiumtitanate formation
- Zirconiumtitanate formation
- Glass formation and recrystallization
- Spinel formation
- Zirconolite formation
- Zirconia destabilisation

Stable Micro - Crack Formation, Linear Thermal Expansion
+ 8.5 GPa Young Modulus of Elasticity!
1600°C, 180 min
1500°C
1350°C
1200°C
2 K/min

Technische Universität Bergakademie Freiberg
Non thermal stability of Al$_2$TiO$_5$
Impingement test of AZT (RT - 1530 °C, Iron): No Cracks!

For a foam macrostructure a functional optimum is achieved by a wall thickness value 300 µm.

The strength of the AZT ceramic (appx. 20 MPa) in these dimensions is not sufficient high enough to withstand the “metal weight”.
### (MgO)ZrO₂ with TiO₂ and Al₂O₃ - additions

<table>
<thead>
<tr>
<th>Mat.</th>
<th>Composition (wt%)</th>
<th>d₅₀ (µm) before firing</th>
<th>open por. (%)</th>
<th>total por. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100% MgO(3.5 wt%) partial stab. ZrO₂</td>
<td>2-4</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>B</td>
<td>100% MgO(3.5 wt%) partial stab. ZrO₂</td>
<td>7-9</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td>C</td>
<td>98% MgO(3.5 wt%) partial stab. ZrO₂ 1%Al₂O₃, 1% TiO₂</td>
<td>7-9</td>
<td>13</td>
<td>16</td>
</tr>
<tr>
<td>D</td>
<td>98% MgO(3.5 wt%) partial stab. ZrO₂ 1% MgAl₂O₄, 1% TiO₂</td>
<td>7-9</td>
<td>14</td>
<td>16</td>
</tr>
</tbody>
</table>

- slip based on 70 wt % solids with 0.3 wt% electrolyte
- slip casted discs (thickness: 4 mm, diameter: 100 mm)
- 1600°C, 2h
the destabilising additive forces and supports the spinel formation

material C contains secondary spinel and material D primary spinel
Submerged Entry Nozzle for Thin Steel Slab Casting manufactured by the slip casting technique

[Aneziris C.G., Maier H.R., Pfaff E., German Patent 199 38 752, April 2002]
<table>
<thead>
<tr>
<th>Properties</th>
<th>material A</th>
<th>material B</th>
<th>material C</th>
<th>material D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{RT}$ MPa</td>
<td>177</td>
<td>164</td>
<td>138</td>
<td>163</td>
</tr>
<tr>
<td>$\sigma_{1400^\circ C}$ MPa</td>
<td>55</td>
<td>35</td>
<td>54</td>
<td>55</td>
</tr>
<tr>
<td>$K_{IC}$ MPam$^{1/2}$</td>
<td>4.5</td>
<td>4.0</td>
<td>6.5</td>
<td>5.5</td>
</tr>
<tr>
<td>$\sigma_{600}$ rem. MPa</td>
<td>24</td>
<td>28</td>
<td>72</td>
<td>49</td>
</tr>
<tr>
<td>$\sigma_{1000}$ rem. MPa</td>
<td>13</td>
<td>16</td>
<td>46</td>
<td>42</td>
</tr>
<tr>
<td>$E_{RT}$ GPa</td>
<td>105</td>
<td>100</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>$E_{1000^\circ C}$ GPa</td>
<td>90</td>
<td>75</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>$E_{1450^\circ C}$ GPa</td>
<td>85</td>
<td>70</td>
<td>58</td>
<td>64</td>
</tr>
<tr>
<td>$\alpha_{RT-1000^\circ C}$ $10^{-6}$/K</td>
<td>10.7</td>
<td>10.5</td>
<td>6.6</td>
<td>8.5</td>
</tr>
<tr>
<td>$\alpha_{RT-1450^\circ C}$ $10^{-6}$/K</td>
<td>10.5</td>
<td>10.4</td>
<td>5.5</td>
<td>8.3</td>
</tr>
<tr>
<td>$\lambda_{1000^\circ C}$ W/mK</td>
<td>2.5</td>
<td>2.3</td>
<td>2.1</td>
<td>2.2</td>
</tr>
<tr>
<td>$\lambda_{1450^\circ C}$ W/mK</td>
<td>2.4</td>
<td>2.2</td>
<td>2.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>
For this reason glass bonded zirconia is used. Due to insufficient creep stability the size of the filters is limited up to 200 mm.
Reference: Unitec 7-9µm, bulk sample

Production slurry, filter sample
Cylinder

PSZT

PSZMg

Norton
The solutions for this problem are foamless filters, so called spaghetti-filters.

Strands, based on ceramic powder, are extruded with the addition of only inorganic binders/plasticizers; the strands with a diameter of appx. 2 mm can be structured into unordered filter components by a piston extruder.

Filters based on SiC, zirconia/mullite and zirconia can be produced.
[Essock, D., Jaunich, H., Aneziris, C.G., Hubalkova, J.,
“Novel foamless ceramic filters for advanced metal casting
technologies”, UNITECR’05, Nov.8-11, 2005 Orlando, Florida, U.S.A,
printed on behalf of the “Amer. Cer. Soc.”]
Thermal shock due to oxyacetylene torch
Spaghetti

Impingementstest - Stahl
Fa. Bischoff - Lüdinghausen
- 1625°C
- Fallhöhe 450 mm
- ca. 55 kg

Kein Ergebnis - Stopfen gebrochen
Spaghetti Filter
dia. 200 x 40mm
632 g
recipe: 97% SiC
3% bentonite
firing temperature:
7 k/min -> 1400 °C (17 h)

pouring basin with
sleeve TAE 23/50
and filter

GGG 70
pouring temperature: 1370 °C
casting weight: 1200 kg
pouring time: 16 s

P J M
Spaghetti Filter
pouring trial

Hulvershom
(30.08.2004)
edition: 07.09.04

FOSECO
Woven filter approaches
New Technics
Spaghetti Filter
Woven Filters

D.I. Test
Filter print “1”
Iron (app. 1530 °C)
Problems: Due to the thixotropy of the mass the high weight of the filter generates inhomogeneous macrostructure and so the height is limited.
In order to reduce shrinkage defects,
improve thermal shock resistance,
increase the creep resistance and also
achieve higher filtration capacities by
reducing total filter costs,

the carbon bonded ceramic technology

has been successfully applied for steel filtration!
Comparing a carbon bonded alumina ceramic filter and a glass bonded zirconia filter, in spite the fact that the same porous polymer macrostructure of 200 mm has been used, with the CBC filter 1500 kg steel melt have been filtered at 1620°C against 1000 kg by the zirconia filter, after filtration.

These results show that a higher specific surface and a higher creep resistance (no deformation during casting) lead to improved capacities as well as to improved filtration efficiencies.
Further out of the lower specific weight of the carbon mix a better processing control during spray coating has been achieved that leads to more homogeneous wall thicknesses and as a result to more open structures.

As a result of these superior properties the market for large casting is going to change. Carbon steel is becoming the main market, but also the manganese steel is now no longer a problem. The very liquid manganese oxide silica slag attacks even the zirconia filter leading to erosion of the filter, but erosion will not happen with the alumina / carbon filter. Low and high alloy steel market will be covered by both, zirconia and alumina / carbon filters.

The very small filters for investment castings are still remaining out of mainly zirconia.
Coal-tar Pitch

Resin + Carbores T10 + Carbores P

Resin + Carbores P

Resin + Carbores P

Resin

isotropic

anisotropic
The coke structure of CBC filters give to the customer a high creep resistance and good priming properties, but friability and bending strength are not in the level of i.e. zirconia filters, well known by the foundrymen.

The addition of fibres to filter materials, especially fibrils like described in the patent of Nixdorf, will overcome this problem, but fibrils are very expensive.
TWO MAIN ISSUES ACCORDING TO ADDITIVES
- Graphite at lower Temperatures
- Crystalline Phases remaining at high temperatures
Formation of Dumbbell-shaped $\text{Al}_4\text{C}_3$, $\text{Al}_2\text{OC}$, $\text{Al}_4\text{O}_4\text{C}$ crystalline whiskers and TiC and TiCN carbides and carbonitrides

Tab. 4: Results of thermal shock experiments

<table>
<thead>
<tr>
<th></th>
<th>CMOR / MPa</th>
<th>CMOR Lost / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 TS</td>
<td>1\textsuperscript{st} TS</td>
</tr>
<tr>
<td>1</td>
<td>3.6</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>4.9</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>4.4</td>
</tr>
<tr>
<td>3*</td>
<td>6.2</td>
<td>6.3</td>
</tr>
</tbody>
</table>

1: MgO – C, 2: MgO – C + Al, 3: MgO – C + Al + TiO\textsubscript{2} all coked at 1000 °C

3\* : MgO – C + Al + TiO\textsubscript{2} coked at 1500 °C

Dumbbell-shaped SiC - Fibers
Feitlike Ti(C,N) structure

Thesis of Volker Stein during his practical semester at WUST

Further development was targeting to produce fibres inside the surface of the filter matrix. Carbonitrides were the most desired reinforcement and could be produced in situ due to sugar and/or urea based coatings on the surface of the $\text{Al}_2\text{O}_3/\text{C}$ - filters before heat treatment.

The heat treatment has to be very much balanced between oxidising and neutral time / temperature profiles, best to be realized in continuous kilns with buffered heat zones, that offer specific gas atmospheres.
urea surface coating

sugar based surface coating

urea and sugar surface coating
"Real flexibility“
<table>
<thead>
<tr>
<th>Composition in [Mass%]</th>
<th>Recipe 1</th>
<th>Recipe 2</th>
<th>Recipe 3</th>
<th>Recipe 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
</tr>
<tr>
<td>Alumina</td>
<td>44.6</td>
<td>44.6</td>
<td>44.6</td>
<td>44.6</td>
</tr>
<tr>
<td>Graphite</td>
<td>16.5</td>
<td>16.5</td>
<td>16.5</td>
<td>16.5</td>
</tr>
<tr>
<td>Processing additives</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Coating</td>
<td>None</td>
<td>urea</td>
<td>Sugar</td>
<td>Urea and sugar</td>
</tr>
<tr>
<td>Properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOR in [MPa]</td>
<td>0.25±0.03</td>
<td>0.12±0.02</td>
<td>0.52±0.03</td>
<td>0.32±0.03</td>
</tr>
<tr>
<td>Bending line in [μm]</td>
<td>555±177</td>
<td>430±209</td>
<td>549±168</td>
<td>399±119</td>
</tr>
<tr>
<td>Failures due to cyclic applied stress at 40% and 80% of MOR</td>
<td>5 out of 8</td>
<td>5 out of 8</td>
<td>2 out of 8</td>
<td>1 out of 8</td>
</tr>
<tr>
<td>Impingement test survived</td>
<td>100 out of 100</td>
<td>100 out of 100</td>
<td>100 out of 100</td>
<td>100 out of 100</td>
</tr>
</tbody>
</table>
Principles of Electro-wetting

- The solid-liquid interfacial tension ($\gamma_{sl}$) can be controlled by electric potential across the interface.

**Young equation:**

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$$

- Droplet on normal hydrophobic surface

**Lippmann equation**

$$\gamma_{sl}(V) = \gamma_{sl}(V = 0) - \frac{CV^2}{2}$$

- Applying $V$ → Reducing $\gamma_{sl}$ → reducing $\theta$ → more wetting and vice versa
FUNCTIONAL FILTER COMPONENTS

Electrical assisted filtration
<table>
<thead>
<tr>
<th>Reference filter without applied voltage</th>
<th>Filter with an applied voltage of 35 V; + on filter, - grounded</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image 1" /></td>
<td><img src="image2.png" alt="Image 2" /></td>
</tr>
<tr>
<td><strong>1 - on surface of filter with transition to the inside</strong></td>
<td><strong>2 - in the middle of the filter</strong></td>
</tr>
</tbody>
</table>
Intensity of Brightness

<table>
<thead>
<tr>
<th></th>
<th>Sample 5 foam</th>
<th>Sample 6 foam + Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt above filter</td>
<td>37108.1</td>
<td>17522.5</td>
</tr>
<tr>
<td>Component after filter</td>
<td>48934.4</td>
<td>23903.1</td>
</tr>
<tr>
<td>ratio</td>
<td>1.32</td>
<td>1.36</td>
</tr>
</tbody>
</table>
### Intensity of Brightness

<table>
<thead>
<tr>
<th></th>
<th>Sample 7 Spaghetti + Voltage</th>
<th>Sample 8 Spaghetti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt above filter</td>
<td>15594.3</td>
<td>39900.7</td>
</tr>
<tr>
<td>Component after filter</td>
<td>19772.3</td>
<td>50363.7</td>
</tr>
<tr>
<td>ratio</td>
<td>1.27</td>
<td>1.26</td>
</tr>
</tbody>
</table>
Foam - structure

Spaghetti - structure

Deep-filter functionality

Surface- and deep-filter functionality
September 18 – 21, 2007
D R E S D E N