Improvement of porous refractory material in contact with glass

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1 Motivation

Why improvement of refractories?

- reduction in energy consumption in the past
- corrosion of refractory reduces glass quality
  → increasing of energy consumption per glass product
- development of a treatment technology for all available porous refractories
  → reduce the interaction with glass melt
  → independent from refractory producer

<table>
<thead>
<tr>
<th>sector</th>
<th>energy consumption [GJ/t]</th>
</tr>
</thead>
<tbody>
<tr>
<td>container glass</td>
<td>4.7</td>
</tr>
<tr>
<td>float glass</td>
<td>7.2</td>
</tr>
<tr>
<td>tableware</td>
<td>8.0</td>
</tr>
<tr>
<td>E-Glass fibers</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Reference: Beerkens, 2006
Complexity of melt and refractory

Factors:

- Furnace: temperature/time/atmosphere
- Glass melt: composition/viscosity/surface tension
- Refractory: composition/grain distribution/capillarity/porosity/pore atmosphere
- Surface-volume-ratio: glass melt-refractory

References:
- HVG, 1996
- RHI, 2014
- Mertens, 2014
**2 Technology**

**Principle - ancorro**

*beading effect in nature*

*beading effect in the laboratory*

- **Strong infiltration/attack without ancorro-technology**
- **Infiltration/attack reduced significantly with ancorro-technology**

*Patented process*
Principle - ancorro

- surface-treatment-technology of ancorro creates reducing atmosphere in the pores
  → reducing atmosphere increases in the boundary layer:

  surface tension of the glass

Reference: Jebsen-Marwedel & Brückner, 2011
2 Technology

Principle - ancorro

- surface-treatment-technology of ancorro creates reducing atmosphere in the pores

→ reducing atmosphere increases in the boundary layer:

\[ \frac{dm}{dt} = D \cdot F \cdot \frac{c_S - c_{G,\infty}}{\delta_N} \]

\[ \Delta \eta \approx 30\% \]
Principle - ancorro

- surface-treatment-technology of ancorro creates reducing atmosphere in the pores
  → reducing atmosphere decreases:

\[ h = \sqrt{\frac{\sigma \cdot \cos \theta \cdot r \cdot t}{2\eta}} \]

Reference: Gerthsen Physik, 2006
Since 2008 ancorro investigate materials to improve porous refractory.

measurement and analysis:

• static finger test (corrosion measurement)
• dynamic finger test (corrosion measurement with flow simulation)
• evaluation and measurement (using a 3D-scanner)
• crucible test (measurement infiltration depth)
• blistering studies (measurement blistering formation)
• crystallization measurement (determine crystallization temperature)
• glass analysis (detailed analysis of glasses)
3 Research and results

Results corrosion minimization

• 90% lower corrosion after 21 hour static finger test on zirconium-corundum brick at 1450 °C in green glass

samples after the finger test

Reference
ancorro

normalized flux line depth
Implementation of the ancorro-technology on different refractories and melts.

**Refractories of the type:**
- fireclay
- bricks containing chrome
- bricks containing zircon

**Melts of the type:**
- soda lime glass
- lead glass

**Effect of the ancorro technology on different refractories, reference (left) and ancorro treated (right):**

- Zirconium-corundum
- Sillimanite
- Mullite
- AZS-joint compound
Examples

**AZS - soda-lime glass**

**sillimanite - enamel**
Crystallization

• homogeneous nucleation:  
  – temperature gradient
  – no interface present

≠ industrial glass production

• heterogeneous nucleation:  
  – temperature and/or saturation gradient
  – interface present

  → wetting

= comparable with industrial glass production

homogeneous and heterogeneous nucleation

Reference: Leibniz Institut Dresden, 2012
3 Research and results

Crystallization

- nucleation in the glass melt:
  → homogeneous nucleation
  \[ \Delta G_{\text{max}} = \frac{16\pi \cdot \sigma^3}{3 (\Delta g_V)^2} \]

- heterogeneous nucleation
  \[ \Delta G^*_{\text{max}} = \Delta G_{\text{max}} \cdot [ (1 - \cos \varphi)^2 \cdot \frac{(2 + \cos \varphi)}{4} ] \]

Reference: Jebsen-Marwedel & Brückner, 2011; Varshneya, 2006
3 Research and results

Crystallization

- influence of the refractory corrosion to the liquidus / crystallization temperature of the glass:

![Graph showing the relationship between content of refractory oxides and liquidus temperature. The x-axis represents the content of refractory oxides in the glass (%), and the y-axis represents the liquidus temperature (°C). The graph shows a significant increase in liquidus temperature with increasing content of refractory oxides.]
3 Research and results

Crystallization

- detecting crystallization via gradient furnace
- refinement of the refractory samples to minimize crystallization
- reduction of the crystallization temperature about 140K - inhibition of the heterogeneous nucleation

![Crystal formation in the contact zone glass melt - refractory](image.png)
4 Application and implementation of the technology

Industry

Since 2010 tests have been carried out continuously in collaboration with industrial partners.

results:

• fireclay pots - life extension by 50%
• plungers - reduction of blistering after change up to 95%
• orifice rings - reduction of crystal formation in the glass by factor 6
• orifice rings - life extension from 3 to 5 weeks

Further tests are conducted with the following components:

tank block, stirrer, lip stone, superstructure of the feeder,
regenerator bricks, plunger, torque, fireclay pots
5 Value and potential

Value for industry

- porous bricks show the same properties as expensive, fused cast refractory
- increasing service life and reduction of production downtimes
- reduction of rejects
- energy savings through lower heat losses / minimized CO₂ emissions
- flexibility - applicable to all refractories
- enormous savings through batch conversion (container glass)
• crystallization at the orifice ring
  → gob temperature ca. 1150°C
• increasing the lime content
• elimination of the crystallization due to ancorro-technology

<table>
<thead>
<tr>
<th>composition [in wt. %]</th>
<th>Glass I</th>
<th>Glass II</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>72.6</td>
<td>71.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>12.5</td>
<td>11.9</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>CaO</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>fining temperature [°C]</td>
<td>1465</td>
<td>1445</td>
</tr>
<tr>
<td>liquidus temperature [°C]</td>
<td>1038</td>
<td>1093</td>
</tr>
</tbody>
</table>

Glass I: untreated orifice ring

Glass II: orifice ring treated by ancorro
5 Value and potential

Potential batch conversion

- Lowering the batch free time about 33% by increasing of CaO-content
- Minimization of the residue quartz dissolution
- Same thermal stress of the furnace
  - = increasing of the tonnage
  - → rise of capacity
  - → depending on forming machines
  - → realizable often only for new construction
- Increase of turnover about 5.5 million EUR/a possible

Glass I untreated orifice ring

Glass II orifice ring treated by ancorro

Reference: TNO; 1997
Non-glass contact refractory materials:

Silica crown material: Two aspects

a.) Improvement of the heat transfer by radiation

b.) Corrosion improvement especially against NaOH attack

Higher crown temperature below 1700 °C could be an answer to a.)

Limited due to corrosion problems

Coatings could be a possible answer

New cheap and effective coatings for the problems of a.) and b.)
5 Value and potential

Radiation Black Body / Emissivity Silica (Bauer, W. / TUBAF)

\[ T = 1773,15\, K \]
5 Value and potential

![Radiation Transmitted by the Atmosphere Diagram]
5 Value and potential

Examples

silika brick– NaOH-atmosphere
(1500°C – 3 hours)

ancorro after the treatment
ancorro after the test
Reference after the test
5 Value and potential

Potential batch adjustment

- container glass furnace with a tonnage of 250 t/d and campaign of 10 years
- refinement of the orifice ring to prevent crystallization
  → increasing of CaO-content possible
- lowering of the fining temperature by ≈20K
  → > 3 % energy savings/ minimization of CO₂-Emission
  → reduction of the thermal stress of the furnace
    = decreasing of cat scratches
    = ≈10% service life increasement
- reduction of costs by soda ash
- total savings > 500,000 EUR/year and glass furnace possible
- payback time < 3 months

Reference: Martinek, Zwiesel 2007
Conclusion

• reduction of the refractory corrosion // blistering // crystallization of the glass
  → porous refractories show properties of fused cast refractories

• scale-up of the ancorro-technology from laboratory into industry realized
  → 50% increasing service life fireclay pots
  → 95% lower blistering after plunger change
  → prevent of crystallization at orifice ring by factor 6
  → >65% increasing service life orifice ring

• saving potential container glass > 500,000 EUR/ year and furnace
Outlook

Further fields of application

metallurgy, cement industry, special glasses, waste incineration, dust and condensation zones in high temperature processes

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We are looking for further industrial partners to implement and improve our process.

Reference: Schweizer Fleisch, online 2011
Reference: http://www.cfoworld.de, online 2013