Lowering of the Refractory Corrosion in High-temperature Processes

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Corrosion of refractories is a problem in any kind of high-temperature process. Since 2008, a new technology for reducing refractory corrosion has been developed at TU Bergakademie Freiberg/DE. With this surface-treatment technology, wear of refractories has been reduced by up to 90 %. In a range of laboratory tests with different kinds of refractory and melt (e.g. finger tests, crucible tests), the effects of the technology were observed. The reason for the reduced interaction between the refractory material and melt was the change in the surface tension and viscosity of the melt in the boundary layer via treatment of the bricks. The different treatments can be used on every kind of porous refractory brick, regardless of manufacturer. After using the surface treatment technology for porous refractories, the bricks show the same corrosion behavior as fused cast bricks. After a range of industrial tests, the results at laboratory scale were confirmed, resulting in considerable savings for operators of high-temperature plants.

1 Introduction

Today, high-temperature processes are becoming ever more complex and require high production standards to ensure successful processing. Temperature ranges of up to 1500 °C, continuous 24-hour melting cycles run over periods of 10 or more years, and corrosive attack by glass melts on refractories are normal in industrial plants. Due to the wetting and infiltration of porous refractories by glass melts, such refractories are exposed to continuous dissolution. The costly results of these effects during production are inclusions, blisters, and cat scratches in the final glass product, as well as costly production downtime during the replacement of the corroded components. For this reason it became necessary to develop technologies to reduce the interaction of porous refractories and glass melts. In the past, many technologies e.g. platinum coating [1–2] were investigated: however, these techniques were not economical enough for industrial-scale glass production, and did not become established. To solve such problems, a surface-treatment technology for increasing the service life of refractories was developed in 2008 at the Institute of Ceramic, Glass and Construction Materials at TU Bergakademie Freiberg. The surface treatment technology lowers the interaction process between glass melt and refractory by up to 90 % [3–5].

2 Surface-treatment technology

The surface-treatment technology refers to a deposition of materials or metal oxides with a high standard electron potential in the pores of the refractory. After the dissolution of the materials and metal oxides in the defined liquids, the refractory samples were impregnated for up to 30 min. After a drying process for 1 h at 100 °C, the samples were heated up to 1000 °C at a rate of 5 K/min and hold a maximum period of 3 h. During this temperature cycle, the deposition was realized in the porous structure of the bricks. The result of the treatment was a so-called oxygen depression in the pores of the brick.

Due to the positive results in creating an oxygen depression in porous refractories, the surface-treatment technologies were optimized step by step over time. Today, over 30 different solutions can be used for the treatment. The aim was the reduction of the interaction of refractory and glass melt by using a technology that could be applied to every refractory material for high-temperature processes. After the first tests on fireclay, where a corrosion reduction of 20 % was detected, the surface-treatment technology was scaled up for industrial bricks from the mass glass industry. A reduction in refractory corrosion of up to 90 % and the amelioration of the crystallization behavior of the glass were observed [5]. Typical refractory bricks were tested, e.g. corundum and zirconium-corundum.

Using the surface-treatment technology for the refractory bricks resulted in strong and wear-resistant refractory components on a par with fused cast products [Fig. 1].

Tests of refractory components in the glass industry at industrial scale confirmed the results in the laboratory. Service life was increased by up to 50 %, and typical problems after the replacement of the components like blistering were reduced by up to 95 %. In addition, the problem of crystallization at the orifice ring (which results in increased production downtimes) was resolved. With the treated orifice ring, crystallization was prevented for over 2 weeks – a

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Fig. 1 Samples after 96-h finger test at 1475 °C: AZS – porous, AZS – fused cast and AZS – porous with surface treatment technology (from left to right)

process which normally takes place after a few hours. Therefore, the surface-treatment technology has been proved in industry.

3 Mechanism of the technology

To understand the effect of the surface treatment technology and its influence on the partial pressure of oxygen in the pores, two identical soda-lime glass samples were melted: one in an oxidizing and one in a reducing atmosphere for 3,5 h at 1400 °C, followed by 30 min at 1450 °C. Afterwards, the samples were cooled down in their respective atmospheres. The temperature of the working point (viscosity of 10^3 Pa·s) was measured on these glass samples using a platinum wire [6]. Upon measurement, the temperature of the working point of the reduced melted sample was found to be 15 K higher than for the sample melted under oxidizing conditions. Using the following equation [6]:

$$\log \eta = A + \frac{B}{T - T_0} \qquad (1)$$

increases in viscosity of about 30 % were calculated at 1400 °C under constant conditions for both glass samples. Due to the oxygen depression in the pores, the viscosity in the boundary layer increased. To quantify the influence of the reducing atmosphere on wetting behavior, the wetting of corundum by clear and amber glass in oxidizing and reducing atmospheres was measured. Under reducing conditions, the surface tension of the melt in the three-phase interface increased by about 10 %. Both effects together – the increasing of the viscosity and of the surface tension of the melt in the boundary layer – resulted in reductions of up to 90 % in the corrosion levels of the refractory material in contact with the glass melt.

4 Calculation of the corrosion

During contact between a glass melt and a refractory material, convection takes place at a three-phase interface. This typically results in flux-line erosion. Due to the fact that the oxides of the glass melt and refractory material are the same, wetting takes place at the high temperatures found in the glass tank. During dissolution and diffusion in the boundary layer, a secondary melt is created [7–8]. For a typical soda-lime glass for example, the secondary melt has a higher surface tension than the basic glass melt, as it has a higher alumina content due to corrosion of the refractory. The convection at the three-phase interface, which can be described as an alkali pump [8], constantly transports new glass melt material to the interface.

The corrosion at the flux line is called the *Marangoni* (Ma) effect, which can be described by the following equation [9]:

$$Ma = \frac{\Delta\sigma \cdot l_P}{\eta \cdot D} \qquad (2)$$

Equation (2) was used to understand the effect of the surface-treatment technology on the refractory corrosion. After a typical finger test, the basic glass and the secondary glass in the boundary layer were analyzed chemically. Afterwards, the surface tension σ was calculated using the database of *Kucuk* [10]. The data for the diffusion coefficients were taken from *Guloyan* [11]. Furthermore, the influence of the surface-treatment technology on the surface tension and viscosity of the melt were included in the calculation. Due to the surface treatment of the samples, the calculated surface tension difference $\Delta\sigma$ across the interface boundary increases. Therefore, the *Marangoni* convection decreases, which resulted in 75 % lower corrosion of the refractory by the glass melt. The calculated values correlate with the measured effects of the finger tests carried out previously [5]. The higher the oxygen depression generated in the pores, the higher was the increase in the service life of the bricks [Fig. 2].

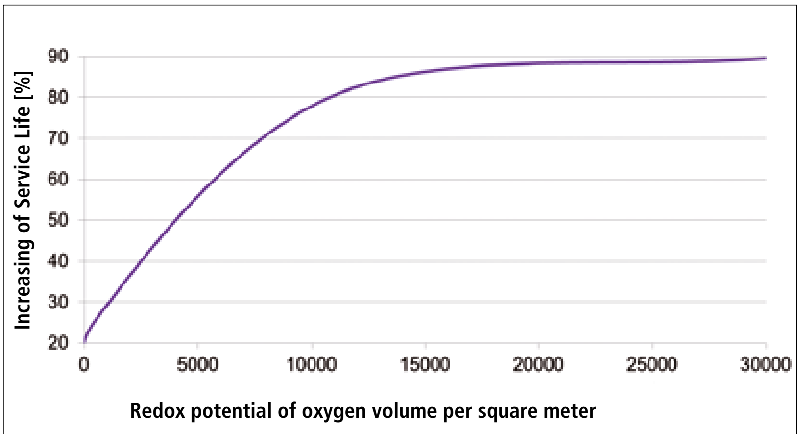

Fig. 2 Influence of the oxygen depression on the service life of the refractory material

5 Economic potential

In addition to the increase in service life, the inhibition of crystallization or heterogeneous nucleation between the refractory material and the glass melt were detected. This is because of the "protection layer" of high viscosity and surface tension in the boundary layer. Therefore, an increase in the CaO content of the glass batch is now possible, as the crystallization issues caused by increasing CaO content can be solved with the refractory surface-treatment technology described. The economic potential of this batch change is significant. An increase in CaO content with a concurrent decrease in crystallization behavior at the orifice ring results in a reduction of the fining temperature in the glass furnace of about 20 K. For an average container glass tank with a tonnage of 250 t/d, energy savings of up to three per cent and a reduction in CO_2 emissions of up to 165 t per furnace and year can be achieved. With the increase in the CaO content, a reduction of the Na_2O content in the batch can be realized. Over 80 % of the costs for the batch are defined by the costs for soda ash as a raw material for Na_2O. Reducing soda ash costs leads to considerable reductions in raw-material costs. In addition, the thermal stress the thermal stress on the furnace is lowered. A reduction of the temperature by about 100 K lowers the corrosion rate by about 50 % [9]. Due to the fact that the service life of the refractory material defines the furnace campaign, a decrease in the fining temperature of about 20 K should increase the service life of the glass tank by up to 10 %. Combining all the savings, up to 500 000 EUR in costs per year and furnace can be eliminated. Approximately 1500 container glass tanks are in operation worldwide, so the potential savings for this industry are huge.

6 Outlook

Further applications, e.g. the surface treatment of refractories for use in the ferrous metal, nonferrous metal, and cement industries are now the focus of further research. An initial test of refractory material for the production of aluminum lowers the infiltration of the bricks by up to 30 % using the surface-treatment technology. To bring this technology to the market, the foundation of an independent company is planned for autumn 2014.

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