Ways to Reduce the Interaction between Glass Melt and Refractory

R. Weigand, H. Hessenkemper, D. Tritschel

Glass as a mass product is indispensable in daily life. The different properties and qualities are defined by the application of the final product. However, at each glass furnace exists degraded material due to the interaction of the refractory and the glass melt. It is necessary to reduce this as a consequence of rising prices for raw materials and energy.

The optimisation of the existing refractory by changing the composition (e.g. the ZrO_2 weight percentage) will be the non-economical way. An alternative solution is the creation of an oxygen depression in the pores of the bricks. Based on this theory the surface tension of the glass melt increases and slows down the process of corrosion. Therefore a decrease of degraded material is possible due to the minimisation of bubbles and stones in the glass melt. Such an oxygen depression can be generated by materials with a high electronegativity.

Crucible tests were done on an industrial corundum brick in contact with sodium silicate glass. Three characterisation methods to specify the corrosion effect were used. Different types of refining methods were used and described. They show that it is possible to decrease the process of corrosion by an economically after-treatment.

1 Introduction

A container glass furnace with a capacity of ca. 100 000 t/a, requires an estimated investment volume of EUR 50 million. Twenty per cent of that is needed for the refractory material. So it is necessary to minimise this costs in order to make the whole process marketable in the future. In the past a market analysis showed that each container glass producer has a lot of costs due to the corrosion of plunger, spout and torque tube. Over the furnace campaign of 12 years the costs added up to EUR 1,2 million. The aim of the project REFRAGLASS is to study a new method to modify those corrodible parts of the glass furnace by generating an oxygen depression due to an infiltration of the bricks with a high electronegative substance. These substances are mostly based on aluminium. The infiltration of the bricks causes an increasing surface tension of the glass melt and therefore a decrease in corrosion. By increasing the service life of the feeder bricks by 5 – 17 %, a cost reduction of about EUR 130 000 can be generated considering a conservative optimisation of 11 % [1].

2 Influence of the atmosphere

At the three-phase interface all three parameters are influencing the interaction between glass melt and refractory which is known as Marangoni effect (Fig. 1) [2, 3]. More resistant bricks will increase the service life. But the costs increase due to their high price and this will not be economically. By changing the redox situation of the glass the surface tension of the melt will be influenced. A reduced melt has a high surface tension. However by changing the redox situation of the glass melt more parameters, e.g. glass transmission and sulphur solubility, will be influenced. So the glass has other properties and is no more sellable.

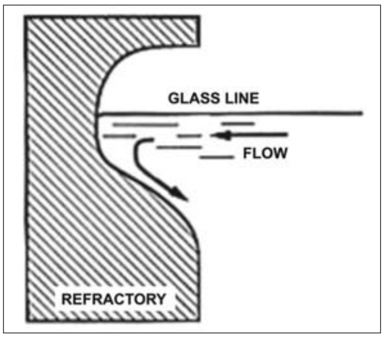

Fig. 1 Three-phase interface in a glass tank

The last parameter which can be influenced is the atmosphere. The atmosphere can be a reducing or an oxidizing one and interacts directly with the melt. By changing the redox situation of the atmosphere the redox situation of the melt is also modified. This change of the atmosphere also affects the surface tension between glass melt and brick.

Rolf Weigand, Heiko Hessenkemper, David Tritschel
Technical University of Mining and Technology Freiberg (TUBAF)
Institute of Ceramic, Glass and Construction Materials (IKGB)
09599 Freiberg
Germany

Corresponding author: *Rolf Weigand*
E-mail: rolf.weigand@ikgb.tu-freiberg.de

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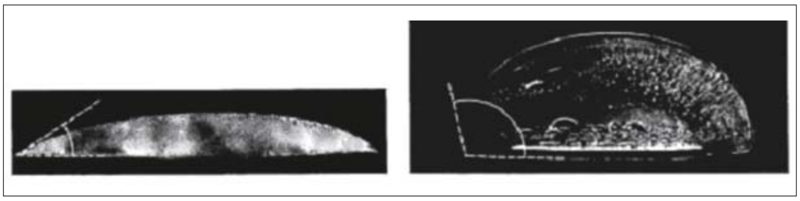

Fig. 2 Same glass drops in oxidising (left) and reducing (right) atmosphere

Jebsen-Marwedel and *Brückner* [4] showed the influence of the atmosphere on the surface tension of the melt (Fig. 2).
Therefore the idea is not to influence the atmosphere of the furnace but rather to affect the three-face interface between refractory, glass melt and pore atmosphere. This can be realised by infiltration of the bricks. The infiltrate creates a so called oxygen depression.

3 Mechanism of the oxygen depression

The pores of the bricks were infiltrated by substances with a high electronegativity. Those substances have a heavy oxygen affinity. Fig. 3 shows the effect of the oxygen depression schematically. The untreated bricks (Fig. 3a) were infiltrated with melt and generate bubbles which results in a rising of degraded material. This effect did not appear at treated refractory material (Fig. 3b). The infiltrate consumes the oxygen in the pores and at the surface of the melt which is in direct contact to the brick. So a reducing atmosphere is generated which increases the surface tension of the melt. The assumption is that the silica from the melt is reduced by aluminium in the pores. A barrier of silicon and on the opposite a barrier of alumina is formed. This silicon barrier can only be destroyed by an oxidation process. The so-called cascade effect increases the service life of the bricks. Due to the non-infiltration of the refined bricks the bubble content in the melt and therefore the amount of degraded material decreases dramatically.

4 Refining of refractory

Seven different refinements were designed in order to create an oxygen depression in the pores. Most of them based on aluminium, which is a low melting metal with a high electronegativity. Based on earlier studies, where a significant decrease of the corrosion attack at feeder bricks by 5 to 17 % could be found [1], refinements with an aluminium foil (AlF) and an aluminium solution (AC) were tested again. For treating the bricks with AlF they were wrapped in one layer aluminium foil and treated above 700 °C for 150 min in forming gas. The treatment with AC as a refinement solution was performed by using two concentrations (AC_1 and AC_2 with $C_2 > C_1$). The samples were dipped for 60 min into the solution and then dried and heated up to 300 °C for 1 h. Also two other treatments based on aluminium were part of the investigation. The first method was a solution (AlH) which was applied similar to the AC while the second is based on a pressure filtration of pure aluminium melt (AlS) below 900 °C under oxygen-free atmosphere. Additionally two more solutions without aluminium were tested. These were on the one hand a solution for a low temperature treatment (LTS) which was applied similar to the AC and on the other hand a solution for a high temperature treatment (HTS) which was headed up after dipping like the series with AlF.

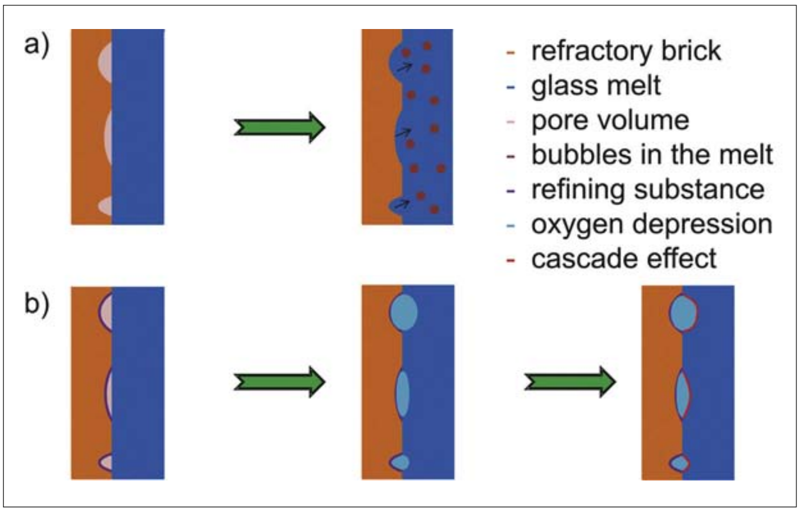

Fig. 3 Untreated brick (a) and treated brick (b) with increasing glass surface tension (middle) and cascade effect (right)

5 Test parameters

An industrial corundum brick was tested with a sodium silicate glass. After a 24-h crucible test at 1550 °C the samples were cooled down and axial sawed. For the crucible test samples of 18 g sodium silicate glass were used, which were coloured with cobalt for a better illustration of the reaction zone. At some bricks the content of aluminium in the glass was measured to characterise the corrosion effect as a function of the glass compositions after the attack.

6 Results

The analysis of the corrosion tests was done optically. After cutting the samples the flux line depth (FL) and the thickness of the reaction zone (RZ) were measured on both halves (Fig. 4). So on every half two values of the flux line and three values of the reaction were determined. The results of the reference were normalised to one and the other series were plotted in the percental difference to the reference.
The effect of the oxygen depression can be characterised by measuring the flux line depth (Fig. 5). With all refinements a decrease of it can be detected. The substances in the pores increase the surface tension of the melt and according to the theory of the cascade effect a barrier is formed which protects the bricks from corrosion. By treating the bricks with aluminium based solutions at low temperatures (AC1, AC2, AlH) an increase of 5 up to 16 % was measured. This is in the same range as the increase which was found at feeder bricks in former studies [1]. The refining solution with the lowest aluminium content (AC1) shows the best results of the three aluminium-based solutions. Due to the lower concentration of aluminium in

the solution a formation of fine accumulations with a high specific surface area took place in the pores of the brick. Those can create a higher oxidisation of the melt as well as a higher oxygen depression.

The results of the metallic aluminium (AlF and AlS) are in the range of 9 to 13 %. Due to the small diameter the realisation of the contact between foil and internal side of the crucible during the treatment with AlF was very complex. Therefore the lower content of metallic aluminium results in a less oxygen depression. For treating the samples with AlS the crucibles were filled with aluminium grains. These results in a defined amount of melt which was pressure-infiltrated. During the treatment the level of the glass melt was slightly higher than the aluminium melt. As a consequence, only diffused aluminium could work as an oxygen depression in the flux line area during the corrosion.

Treating the samples with a low (LTS) and high (HTS) temperature solution decreases the flux line depth between 2 to 46 %. Samples treated with LTS show the poorest results due to the low electronegativity of the used substance in this solution. Series HTS has shown the best result because of a high and dispersed metal content with a high standard electron potential which formed the biggest barrier and increases the surface tension of the melt up to the highest level. Furthermore, the result of this series is well reproducible due to the low standard deviation.

The results of the reaction zone show the same effects (Fig. 6). By creating an oxygen depression in the pores the surface tension of the melt rises which can be detected by a lower infiltration. However there are two other effects which influence the infiltration (eq. 1) [5]:

$$h = \frac{2 \cdot \gamma_{lv} \cdot \cos\theta}{r \cdot \rho_G} \qquad (1)$$

H = depth of the infiltration
γ_{lv} = surface tension of the melt
θ = wetting angle
r = average radius of the pores
ρ_G = density of the glass melt

At the flux line the erosion parameter of the interfacial convection defines the process of corrosion and can be influenced by the surface tension of the melt. Below the surface of the glass melt only the effects of diffusion and density convection exist. The average radius of the pores is changing by the infiltration which influences the infiltration depth. The infiltrate is in the pores but also in the ceramic matrix and diffuses into the melt as a function of time and concentration difference. So the density of the melt changes in the reaction layer and influences the infiltration depth. This has the strongest effect at the bottom of the glass tank because there is no or only a very low convection.

The solutions based on aluminium decreased the reaction zone up to 20 %. Also here AC2 shows the best result of these solutions due to the low concentration which results in fine accumulations with a high specific surface. By treating the samples with metallic aluminium the infiltration depth rises between 11 and 40 %. AlS shows the better results of the metallic aluminium treatment due to the higher content of aluminium which creates a higher surface tension and barrier in accordance with the theory of the cascade effect. The low and high temperature solutions slow down the process of infiltration up to 53 to 43 %. Here the low temperature solution offers the best

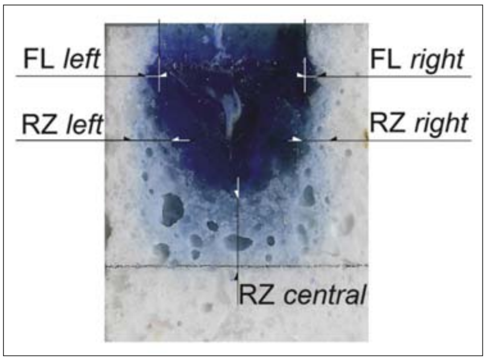

Fig. 4 **Measuring of the flux line (FL) and reaction zone (RZ) at the crucibles**

result. The solution has the lowest reducing effect but changes the density of the reaction zone so extremely that the infiltration slows down in the same way as treating the brick with the high temperature solution.

To detect the lower interaction between glass melt and brick without measuring the flux line and reaction zone three glass samples (Reference, AC1 and HTS) were analysed to determine their Al_2O_3 content since there is no alumina in the sodium silicate glass. Fig. 7 demonstrates that there is

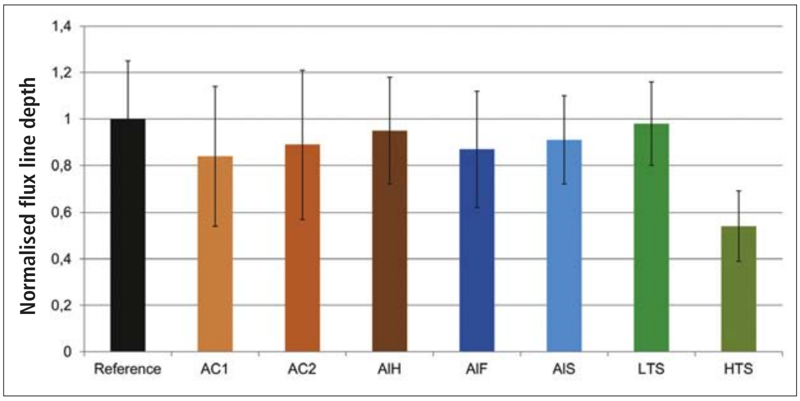

Fig. 5 **Normalised flux line depth of the bricks after glass corrosion at 1550 °C after 24 h**

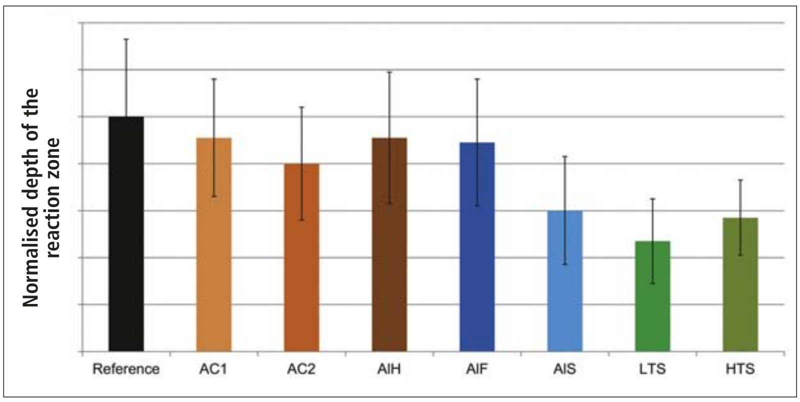

Fig. 6 **Normalised thickness of the brick reaction zone after glass corrosion at 1550 °C / 24 h**

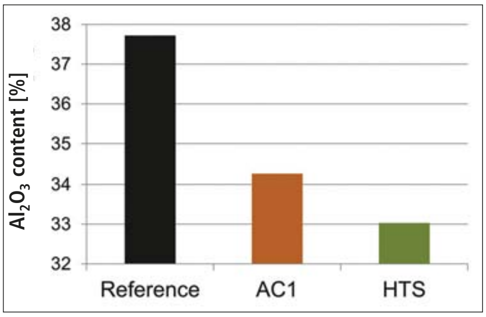

Fig. 7 **Alumina content in the glass after corrosion of the refractory brick**

a high content of alumina in the glass after the crucible test. In industrial applications there will not be such a high rise of the alumina content. Meanwhile a smaller glass volume is in a longer-lasting contact with a high volume of refractory during the laboratory test. Nevertheless it can be shown indirectly that through the refinement the corrosion slows down as a result of lower alumina content. The higher oxygen depression of HTS results in a lower content of Al_2O_3 in comparison to AC1. However both refinements reproduce the effect which was detected by measuring the flux line and reaction zone.

7 Summary

It is possible to infiltrate refractory bricks with solutions and metals which cause an oxygen depression. These substances are mostly based on aluminium. After a 24-h crucible test with sodium silicate glass at 1550 °C the interaction between corundum brick and glass melt can be minimised. Due to the refinement a decreasing of the flux line depth up to 46 % and of the reaction zone up to 53 % were found. The infiltrate increases the surface tension of the melt which slows down the corrosion. Furthermore a barrier is formed due to the reduction of the glass melt surface in contact with the pores which decreases the infiltration as well as the corrosion process. The effect can also be shown by measuring the alumina content in the glass melt after the interaction with the brick.

8 Outlook

By increasing the service life of a glass furnace a significant reduction of costs is possible. The surface tension of the melt decreases due to the oxygen depression. This results also in a minimisation of the crystallisation based on a lower contact area between refractory and glass melt. Crystallisation takes mainly place at the orifice ring of a container glass furnace. Due to the possible decrease of the interaction between melt and orifice ring based on the refining, the batch can be changed. By increasing the content of calcium oxide in the batch from e.g. 10 to 12 %, a decrease of the fining temperature of 30 K can be realised but on the other side the liquidus temperature increases in the range of 30 K. By treating the orifice ring the problem of crystallisation can be controlled. The batch change increases the service life of about 15 %. This means a rising of the furnace campaign from 12 to 14 years. Thereby the physical amortisation decreases up to EUR 600 000 per year. Furthermore there is the possibility of energy saving in a range of EUR 700 000 annually. The return of investment for the refinement is around 4 month. To quantify this investigation industrial tests will be done in the future.

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