Bubbles as Criteria for Refractory Corrosion by Glass

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Measurements of blistering in contact of glass melt and refractory were done. Two different methods were used to detect blistering. To prevent blistering the used porous brick was treated with a substance which creates an oxygen depression in the pores of them. Due to this the surface tension of the glass rises which is shown as extremely lowered blistering up to 50 %. The surface tension of the glass increases in such a level, that the refined bricks show the same low blistering like fused cast bricks. Savings up to EUR 16 000 per year for a rolled glass producer are possible.

1 Introduction

While the quality requirement of the consumers raises the bubble content in glass products decreases in the last few years. After changing refractory components like plunger, torque and spout during the production of container glass, bubbles were generated after the infiltration of the pores by glass melt of the new component. The costs for changing (material + production losses) sum up to 100 000 EUR/a [1]. The same problem takes place at a rolled glass plant after changing the porous lip stone. So it was necessary to find a way to reduce the interaction of glass melt and porous refractory. In the past different expensive methods e.g. platinum coating [2–3] were investigated but these technologies are not economic for the mass glass industry and were not implemented. An alternative to traditional methods is the creation of an oxygen depression in the pores of the bricks by an economical refinement. So this technology can be used for every combination of glass melt and refractory world-wide.

2 Blistering

Glass melt and refractory mainly based on the same oxides. In consequence of this the melt wets the refractory and infiltrates it. Following *Wasburn*, the effect and infiltration depth h is a function of the surface tension of the melt σ, the wetting angle θ, the viscosity of the melt η, the radius of the pores r and the time t [4]:

$$h = \sqrt{\frac{\sigma \cdot \cos\theta \cdot r \cdot t}{2\eta}} \qquad (1)$$

The gas from the pores forming bubbles in the melt which rising up. The rate of ascent v_B is a function of the bubble size r_B, the viscosity of the melt η, the gravity acceleration g and the difference of the density of melt and gas ρ_{GB} which were described by the *Stokes*-equation [5]:

$$v_B = \frac{2 \cdot g \cdot r_B^2 \cdot \Delta\rho_{GB}}{9\eta} \qquad (2)$$

The research work of *Berg* [6] shows that the conditions in a glass melt are more complex as the approach of Stokes. The bubbles interact during the blistering which results in different shaping of the bubbles. So the bubble rising cannot be explain exactly with the Stokes-equation. This interaction and the resulting influence of the bubble rising is not part of this paper. In this article the blistering as number of bubbles in a defined area was detected and analyzed.

3 Refining technology

Due to positive results of creating an oxygen depression in porous refractory the technology was optimized step by step in the past. The aim was lowering the interaction of glass melt and refractory by using a technology which can be applied on every combination of glass melt and refractory. After tests on fireclay [7] the refinement technology was scaled up to industrial bricks which are in glass melt contact. A minimization of the refractory corrosion up to 80 % and an extremely prevention of the crystallization behavior of the glass were measured [8].

The refinement technology based on the deposition of metals with a high standard electron potential which work as oxygen depression in the pores of the brick. The tests in the past mainly based on solutions containing aluminum. To correlate the results from the past with the new test methods the refinement RW II was used for the blistering tests. The method is similar to the RW I method shown in the past [8] but after the infiltration of the bricks they were heat treated by a defined flame. Due to the color change of the samples after the temperature process the treatment success of them can be visually detected.

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Fig. 1 **Test setup static blistering test before and after the test**

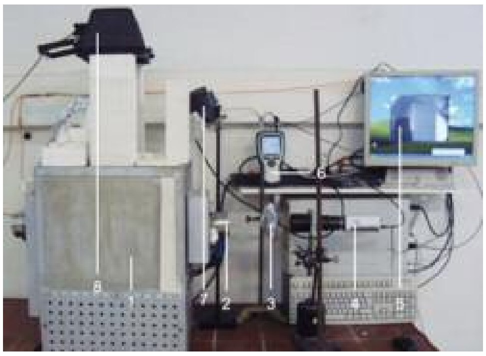

Fig. 3 **Test setup dynamic blistering test: SiC tube furnace; water cooled tube; black glass; CCD camera; user interface; ALMEMO-instrument; air cooler; lightining**

4 influencing the surface tension

The surface tension of the glass melt plays an essential role and influences the interaction between refractory and glass melt. Following the *Young* equation [9]:

$$\cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma} \tag{3}$$

The surface tension of the melt σ, the surface energy of the refractory σ_{sv} and the surface energy between refractory and glass melt σ_{sl} defines the wetting angle θ. By refining the samples and creating an oxygen depression the surface tension of the melt is changed.

To understand the influence of the reducing atmosphere realized with the oxygen depression the glass were heated up under air and forming gas. The wetting angle at 1000 °C were measured which increase from 76,5 °C in air to 102,5 °C under forming gas. By using the results and calculations

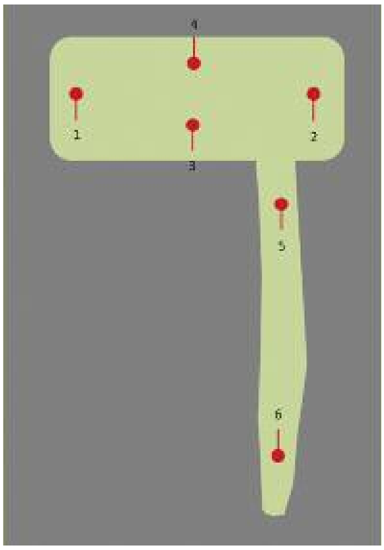

Fig. 2 **Measuring points static blistering test**

of *Gauckler* [10] and *Kucuk* [11] whose worked on the field of surface tension and surface energy of the glass melt, an increasing of the surface tension of the glass melt up to 8 % under reducing atmosphere were calculated. This correlates with the results between corrosion and crystallization behavior in the past [8].

5 Detecting blisters

The blistering tests were done on porous lip stone (Arkal 60PR), which was treated with the RW II method and fused cast material (Jargal M) in contact with flat glass. Two different methods were used to detect the bubbles in the melt. The used temperature of 1050 °C is the same temperature like in the industry when the glass flows over the lip stone.

5.1 Static blistering tests

The flat glass panes (20 mm × 50 mm × 2 mm) were fixed at the top of the refractory samples (100 mm × 65 mm × 5 mm). To realize the angle of the industrial lip stone of around 30° [12] both were localized on a prepared brick (Fig. 1). The test setup was realized in dependence on the ASTM-method [13].

After 1, 42 and 84 h heating of the refractory the glass plates were put on it for one hour and then cooled down. The bubbles were detected along a defined cross at six points (Fig. 2) by using a camera controlled microscope and the software Image Focus.

5.2 Dynamic blistering tests

For this test cylinders of refractory (∅ 32 mm, h = 10 mm) and glass (∅ 32 mm, h = 28 mm) were heated up in a silica glass cup in a camera controlled tube furnace like *Dunkl* [14] shows. The blistering was analyzed after 6, 12, and 24 h using the software Image J. Fig. 3 shows the used test setup. To minimize blisters from the basic glass cullets were melted at 1450 °C for 4 h before casting the glass cylinders.

6 Results

The results of the static blistering test show Fig. 4. The bubble content of the porous Arkal 60PR (reference) of 17 bubbles in an area of 0,3 mm² was normalized to 1, which increases over 42 h around 90 % and 125 % after 84 h. This is a result of the changing of the pore structure, the oxygen situation and the glass phase which influences the gas solubility in the glass melt. Also the infiltration depth and so infiltrated vapour volume defines the blistering level. The fused cast brick (Jargal M) generates a constant blistering over the test time. Due to the interaction with the glass melt an increasing of the aluminum content in the melt is possible as a result of diffusion process [15]. This influences the gas solubility in the glass melt which will be lowered by increasing the aluminum content due to a closer glass network and forming bubbles. By treating the porous brick with RW II method an oxygen depression in the pores is formed. This increases the surface tension of the melt which slows down the infiltration of the brick. So a decreased blistering up to 50 % was detected. Also the lower interaction with the glass melt slows down the blistering as a result of changed gas solubility. The results correlate with measurements about infiltration and corrosion in the past [16].

The dynamic blistering test shows the same results like the static test (Fig. 5). The glass infiltrates the porous Arkal 60PR (reference) and generates bubbles. The bubble content of 220 of the reference after 6 h was normalized to 1 again. Over the time the blistering slows down about 13 % over the 24 h due to a decreasing of the infiltration depth. A reason can be a change of the capillarity over the time. The fused cast brick (Jargal M) shows a lower blistering as the porous one. Here the blistering is defined by the change of the gas solubility of the glass by modify the aluminum content during the refractory corrosion. Also the blistering slows down over the 24 h about 15 %. By treating the porous brick with the RW II method the refractory infiltration and corrosion slows down, which was already shown in the past [16]. This lowers the blistering about 25 % in comparison to the porous Arkal 60PR which is under the level of the fused cast brick.

Fig. 6 shows the blistering of the three series after 12 h. The porous brick generates a heavy blistering which is extremely lowered by treating it with the RW II method. The fused cast brick (Jargal M) is nearly in the same level of the RW II treated brick.

7 Savings

Based on data from an own market analysis the blistering time after changing the lip stone at a rolled glass furnace with a capacity of 250 t/d is around 4 h. Including the working time for this, losses of ca. EUR 20 000 per change are created. With one change after 6 months losses of EUR 40 000 per year were generated. Based on the results with a lowering of 25 % blistering and also increasing the life time of about 25 %, which was shown in the past [8, 16], costs of around EUR 10 000 per year can be saved.

Not included are the costs for the lip stone which rise the saving up to around EUR 16 000 per year. So the refinement technology enables around 40 % savings for the part lip stone. In the calculation the winnings of higher quality and lower energy loses due to possible replacement of fused cast brick by refined porous brick are not containing and increasing the savings over the shown value.

8 Summary

Blistering is still a problem after changing porous refractory in glass melt contact. The refinement technology of ancorro can lower this effect up to 50 %. This based on the effect of the created oxygen depression due to the refinement, which increases the surface tension of the glass melt. An oxygen depression can be realized by infiltration of the pores with metal based substances. For a rolled glass producer savings of EUR 16 000 per year are possible.

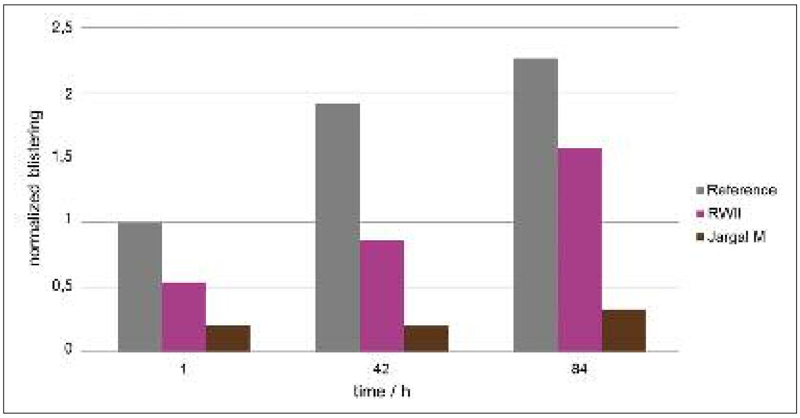

Fig. 4 Normalized blistering of the static blistering test at 1050 °C

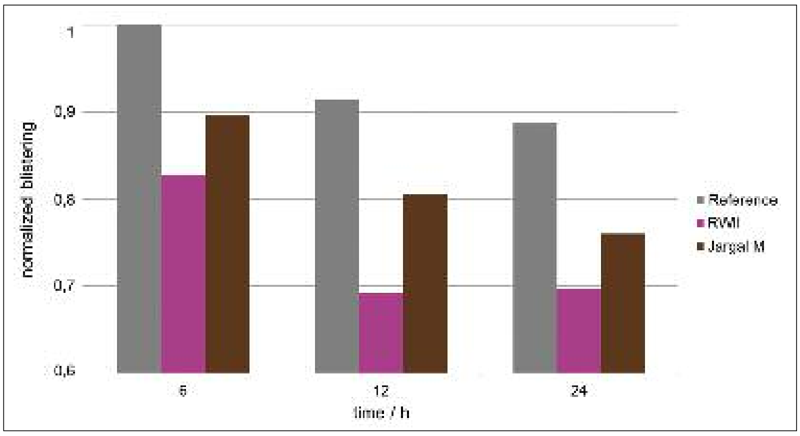

Fig. 5 Normalized blistering of the dynamic blistering test at 1050 °C

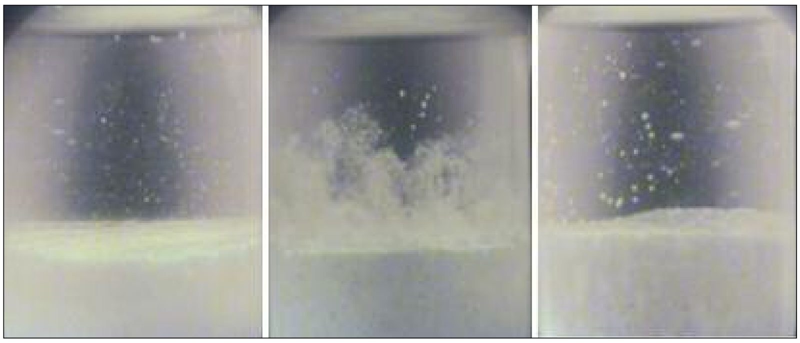

Fig. 6 Blistering of Jargal M (l.), reference Arkal 60PR (middle) and RW II (r.) after 12 h at 1050 °C

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