A View in the Future of the Melting Technology and Refractory Materials for the Glass Industry

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The present article describes a cost-effective alternative to traditional methods for refining refractory bricks in contact with glass melt and two glass melting technologies, which could be applied as future technology in the glass industry. The refractory bricks were treated by integrating aluminium as a reducing agent into the ceramic structure of the bricks. With this technology it is possible to increase the interfacial tension, thus counteracting the infiltration of pores with melt as well as the progress of corrosion. The melting technologies are the submerge combustion melter and the segmented thin film melter. The submerge combustion melter is a technology suitable for melting the batch very fast and has a specific melting rate of about 20 t/(m² · d). The segmented thin film melter has the advantage of lower fining temperature and a similar melting rate like the standard technology.

1 Introduction

For the melting of glass methods have to be developed which allow for producing glass economically. On the one hand, it is necessary to reduce the costs of the refractory materials and to extend the lifetime of the glass furnace. On the other hand, the energy consumption for 1 t of glass has to be reduced. Possible new developments are to be presented by the examples of refining refractory materials and two melting technologies.

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2 Refractory bricks treated with reducing materials

2.1 The aim of the development

The aim of this work was the refining of refractories in contact with the glass melt, linked with an increase in the service life of the refractories. Interactions take place through the contact of the refractory material and the glass melt resulting in corrosion of the refractories. This effect involves undesirable concomitants or production disturbances such as inclusions or streaks. In addition, glass melt infiltrates the pores of the bricks, which results in production disturbances by gas bubbles from the pores [1–2]. Refractories play a decisive role in energy-intensive industries and represent a main part of the investment costs of a plant, therefore the service life of the tank is of high economic relevance. This fact is all the more important in the light of the increasing demand for glass products and rising energy prices. It is necessary for the whole process to increase the corrosion resistance and to decrease the interaction between refractories and glass melt through the design of the tank. To reduce corrosion in the refractory there are two strategic options: to create new material systems or to optimize the processes used in the production and application of existing refractory materials.

A new, cost-effective way is the method described here, which creates an oxygen depression in the pores of the refractory bricks by infiltrating them with reducing materials or solutions. The reducing atmosphere thus generated in the pore space increases the service life of the bricks.

2.2 Pilot tests

The experiments in the past have shown that it is possible to infiltrate refractories with aluminium by wrapping a thin film of aluminium foil around the sample and treating it under forming gas for 3 h at 710 °C and a second series at 910 °C (Fig. 1). Due to the treatment the colour of the bricks changes. For the treatment and the investigation three kinds of bricks were used: fireclay, zirconium-silicate and corundum-zirconium bricks. The first two were selected for their low resistance, and so the success of the treatment became all the more apparent.

Because of the low resistance of fireclay and zirconium silicate, the static finger test was used during the 20-h glass attack at 1360 °C to identify the extent of corrosion in both bricks. The corundum-zirconium bricks were exposed to the dynamic finger test in glass-melt of 1475 °C at 65 rpm for 24 h in reducing atmosphere (N_2). The extent of corrosion was characterised by measuring the corroded area on the fireclay specimens and the maximum corrosion depth of the zirconium-silicate and corundum-zirconium specimens.

The examinations of fireclay, zirconium-silicate and corundum-zirconium bricks have shown that a treatment with aluminium foil increases the corrosion resistance of the bricks significantly (Fig. 2). For the corun-

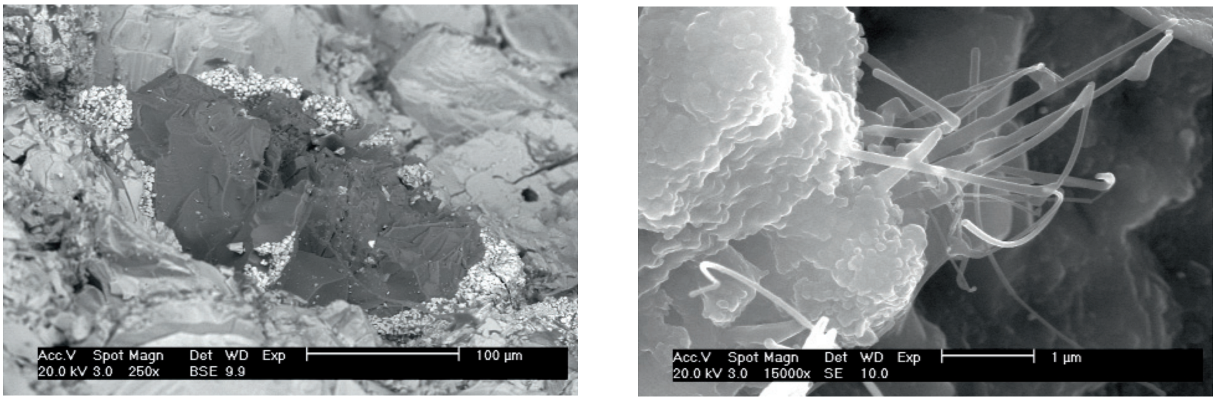

Fig. 1 Integration of aluminium in the microstructure at 710 °C (left) and formation of AlN-whiskers at 910 °C (right)

dum-zirconium bricks, only specimens treated at 910 °C were used for the dynamic finger test because the treatment at 710 °C was less successful due to problems with interface tension. Depending on the glass and refractory systems involved, this increase can vary between 12 and 32 % [4].

2.3 Experimental

After the excellent results of the reducing effect of aluminium in the not optimised pilot tests a lot of experiments with reducing materials on solutions mostly based on aluminium were carried out.

2.3.1 Treatment process

Three kinds of aluminium solutions with different concentrations of aluminium ions and different types of dissolvers were used. The samples were infiltrated at room temperature by hanging the sample for 1 h into the solution. After the infiltration the samples were heated up to maximum 500 °C to vaporise the dissolver. Furthermore, samples were treated with aluminium foil at 710 °C as described in 2.2.

A last series was treated with a phenolic resin. By pressure infiltration up to 5 bar for 45 min the resin fully infiltrates the samples. After hardening the resin at 180 °C and coking the samples up to 700 °C, the surface and surface near graphite were oxidised at 900 °C.

2.3.2 Extent of corrosion

Due to the low resistance of fireclay a static finger test was used during the 20-h glass attack at 1400 °C to identify the extent of corrosion. It was characterised by measuring the maximum corrosion depth of the flux line of the sample.

2.4 Results and discussion

Treating the fireclay achieves a significant increase in the corrosion resistance by testing in clear glass. Fig. 3 shows the normalised corrosion resistance of all samples. All five refining methods or solutions are creating an oxygen depression in the pores of the samples, which increases the interface tension of the glass melt in contact with the brick. Due to this capillary depression in the pores the infiltration of the refractory by glass melt decreases, and as a consequence the service life of the bricks increases.

Through the three aluminium solutions and the treatment with the aluminium foil also another effect takes place. When the aluminium in the pores is oxidised due to the reaction of the oxygen in the glass melt with the atmosphere in the pores, a highly resistant Al_2O_3 phase exists in the pores of the brick and must be corroded by the glass melt before the brick reacts.

The samples treated with aluminium foil show similar results as in the pilot tests (2.2). The increase of around 14 % is not as high as in the past, but the effect is the same. The lower increase can be a result of the higher temperature and the change of the sample dimension.

Due to the treatment with the aluminium solution the increase hovers between 11 and 18 %. The effect depends on the concentration of aluminium ions in the solution and shows the lowest increase at solution II with the lowest concentration. Solution III has also a low concentration of aluminium ions, but contains other ingredients working positive on the service life. Maybe these ingredients react also oxygen depressing in the pores. This has to be investigated in the future to define the effect of the ingredients on the corrosion resistance.

Refining the bricks with a solution at room temperature is a cheep alternative to the other two ways which include a reducing heat treatment above 700 °C.

The best results shows the series treated with phenolic resin. At high temperatures of

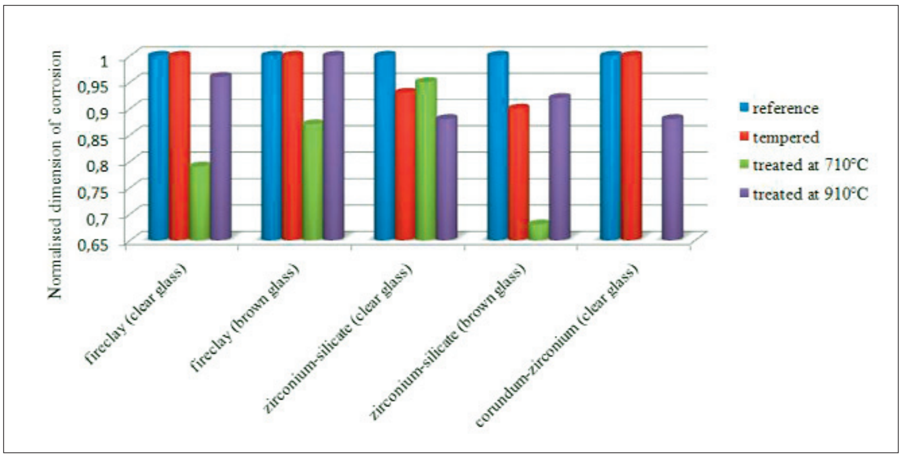

Fig. 2 Corrosion of fireclay, zirconium-silicate and corundum-zirconium in clear and brown glass

1400 °C the graphite in the bricks vaporises to carbon dioxide and under oxygen deficiency to carbon oxide and creates an oxygen depression in the pores. By the time, the gas goes into the glass melt, which has a higher oxygen pressure, and so new gas is build due to the reaction of the graphite with the oxygen. This capillary depression increases the corrosion resistance up to approximately 19 %.
Similar treatments were carried out with brick types typically used for the feeder and also in direct contact with the glass melt. The examination of these bricks shows the same results of increasing the service life due to the refining. These measurements are not completed, so the results will have to be presented in the future.

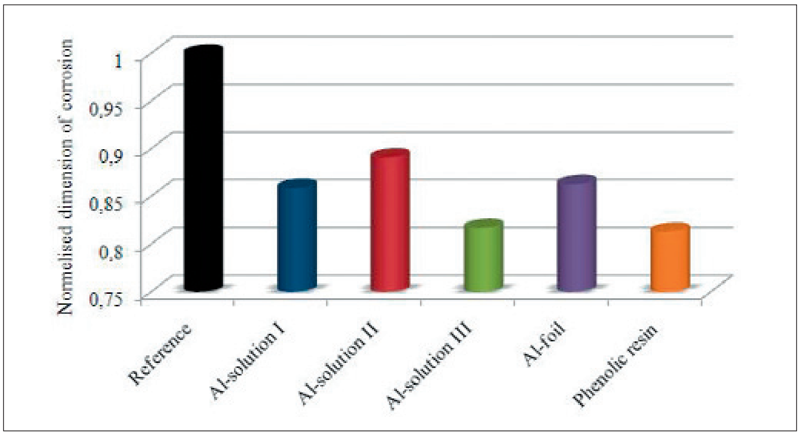

Fig. 3 Corrosion resistance of treated fireclay in clear glass after 20 h at 1400 °C

3 New melting technologies
3.1 Introduction to the melting technologies

New furnace technologies, which have a high specific melting rate or other advantages promised, were not established in the course of the time in the glass industry. Since 1867 the developed furnace technology of *Siemens* with regenerator has been generally used, also nowadays in different variations. Changes of the market in the future could lead to new innovative glass-furnace concepts, which could succeed due to new political environmental guidelines, rising cost for energy, cutthroat competition by new products and therefore rising investment to reach technological improvements.
For the evaluation of new furnace technologies the viewer may not let himself be deceptive of a well sounding specific melting rate and/or apparently low energy consumption.
For example, it would be possible that a furnace technology could have reduced energy consumption, but this only when using a preheated mixture of raw materials. The new furnace seems to be at first sight innovative thereby, however the "old" technology has the same possibilities, if preheated raw materials could be used. Further arguments, e.g. the possible use of fine raw materials with improved specific melting rate in a new furnace technology as argument is attached only, if this new furnace technology offers such possibilities without connected disadvantages.
For comparison of two glass furnaces therefore the following criteria have to be taken into consideration:

- Specific melting rate in dependence on the used raw materials (cullet content, glass composition, raw material granulation etc.)
- Preheating temperature of the batch
- Specific emissions of the furnace per 1 t glass
- Energy consumption per 1 t glass
- Cost of investment
- Operating cost (additional to the energy consumption for melting the glass)
- Economic lifetime
- Glass quality.

For the acquisition of a glass furnace not all criteria can be evaluated in a sufficient way, but for the glass industry in general the energy consumption per ton of glass and the cost of investment will be the most important criteria.
The energy consumption of the glass is evaluated by measuring the exhaust gas losses, preheating temperatures of the air, the wall losses of the glass furnace plant, which preheating temperatures of the raw materials are considered, and the passage temperatures of the melt.
During this view, however, the most important criterion that has not been considered is the maximum temperature of the melt in the furnace, also common as the fining temperature of the glass.
If the criteria mentioned for the energy consumption of the glass furnace are analyzed critically, then it can be seen that in the unknown wall loss is a part of this energy, which is for the "cooling" of the glass from the maximum temperature to the passage temperature.
The influence on the theoretical energy consumption of the maximum temperature is not to be neglected. Already 3 % of the theoretical energy consumption could be saved reducing the maximum temperature by about 50 K.

3.2 Submerge combustion melter

The submerge combustion melter [5, 6] is a furnace, where a direct combustion in the melt takes place by so-called submerged combustion burners, which are built in the ground or the sidewalls of the melting chamber. The turbulent fluid dynamic in the melt increases the heat and mass transfer between the combustion gases and the glass melt. For the best case, the exhaust gas temperatures have the same temperatures as the glass melt. The high mass transfer is also increasing the corrosion of the refractory material in contact with the melt. Because of this the refractory material is replaced by cooled steel. The glass in contact with the steel formes a cooled glass protective layer, which ensures that the steel wall is not attacked from the glass melt.
Actually, the technology of the submerged combustion melter is not new. In the 30s of the last century the submerged combustion melter was already referred in a patent for a shaft kiln to melt glass [7]. A cooled steel shroud was not installed at that time.
The use of cooled metal alloys as shrouds and "melting glass in glass" is described in a patent [8] of *Glaverbel*. The advantage of the technology is seen in an around one tenth reduced furnace.

Fig. 4 Possible construction of a segmented thin-film melter

A further application, which works with submerged burners, is described by *Pieper* in a patent [9]. The necessary melting area was reduced by 100 m² to 42,56 m² for a pullrate of 270 t/d. The power requirement of the furnace amounted to 2753 MJ/t. A comparable oxy-fuel furnace would need 3020 MJ/t. The exhaust gas temperatures and preheating temperatures of the mixture amounted to 389 °C.

All examples show that the submerged combustion furnace has a lot of advantages. More benefits according to [5] are:

- Energy saving potential of 20 % in comparison with the best commercial furnaces
- Reduction of capital cost of around 80 %
- Reduction of NO_x emission of around 50 %
- Reduction of the refractory material of around 80 %
- Simplified supply possibilities for the batch
- The batch must not have a good homogenisation, because the furnace achieves a good mixing
- Reduction of the melting chamber dimensions of around 85 %.

Five submerge combustion melters with a melting rate of 75 t/d in each case are operated in Ukraine. The furnaces show very good results in NO_x formation (100 ppm) connected with small CO values.

3.3 Segmented thin film melter

The segmented thin film melter is a melting technology, which is discussed at the *Professorship of Glass and Enamel Technology* of the *Technical University of Mining and Technology Freiberg* [10].

The segmented thin film melter is divided into three zones, whereby in the connection as in all other glass furnaces still the working end follows. These zones are, as shown in Fig. 4, the melting zone (ASZ), the rest quartz dissolution zone (RQLZ) and the fining zone (LZ).

3.3.1 Melting zone

In the melting zone the batch is heated with burners from the superstructure. A thin layer of melt will be created at the surface of the batch, which flows into the rest quartz dissolution zone due to the force of gravity. Hence the colder batch will come in contact with the radiation of the superstructure and the heat transfer will be increased. A high melting rate could be achieved for this zone. For example, a further solution for the melting zone is given by the "rust melting furnace" of *Schelinski* [11].

3.3.2 Rest quartz dissolution zone

Inside the rest quartz dissolution zone the rest quartz will be solved in the primary melt. Further this zone is to serve as a glass reservoir, in order to be able to adjust fluctuations in the melting rate of the melting zone. The use of bubbling, electric heating boosting, fine raw materials and other methods like the oxy-hydrogen-bubbling [12] is applied with the objective to accelerate the rest quartz dissolution. The glass melt level in the rest quartz dissolution zone can be adapted depending upon conditions and will be probably between 0,6 – 1 m.

3.3.3 Fining zone

In the fining zone the melt will be cleaned of blisters and solved gas in the melt should be set free. The principle of the fining zone is that the glass melt level is lowered in such a way that degassing will be increased due to the homogeneous temperature distribution in the fining zone. This zone could be constructed in form of a fining shelf. In patents [13, 14, 15] the use of a fining shelf can be found, whereby in particular the patent [15] for high-melting glasses shows constructional conditions similar to the fining zone in a segmented thin film melter. *Nebel* reports [16] about the construction and usage of a fining shelf and shows that the corrosion of the refractories for the fining shelf is not increased due the lower glass level.

The physical process of the bubble rise in the fining zone / fining shelf can be described by equation (1), when no thermal convection will occur:

$$\dot{m} = \frac{2}{9} \cdot g \cdot \rho_l^2 \cdot \frac{R_{C+P}^2 \cdot \cos(\alpha)}{\eta_l} \cdot b \cdot L \qquad (1)$$

$\dot{m}$ – maximally possible mass flow in the fining zone, where no glass quality problems arise
g – gravity acceleration
ρ_l – density of the melt
R_{C+P} – the smallest bubble radius, which should have to be removed inside the fining zone
b – width of the fining zone
L – length of the fining zone
cos (α) – angle between the melting bath surface and the horizontal, the value can be set as 1
η_l – viscosity of the melt.

Equation (1) shows that there are constructional possibilities given in the fining zone to degrade the viscosity of the melt for the same mass stream. *K.A. Pchelyakov* et al. report [17] that when using a thin film fining zone with a daily output by 100 t/d of dark green glass with a 6 m width fining shelf the length of the fining zone could be reduced from 5,5 m to 2,3 m. If the length of the fining zone will be unmodified and it is assumed that the blister quality remained the same, the viscosity of the glass melt could be increased by the factor 2,3. For a standard container glass a decrease of the fining temperature from e.g. 1480 °C (7,8 Pa · s) to 1370 °C (17,9 Pa · s) would be theoretically conceivable. Practically 1350 – 1400 °C is needed for the rest quartz dissolution and also the influence of fining agents should be taken into account.

However, it becomes evident that the fining shelf offers advantages, which could make it possible to reduce the maximum temperature in the glass furnace.

Further research of the fining zone has to be accomplished by the *Technical University of Mining and Technology Freiberg*, with the help of the fining shelf and changed bound-

ary conditions inside the fining zone. The aim is to decrease the minimum bubble radius and the maximum temperature inside the glass furnace in connection to the melting zone and rest quartz dissolution zone.
The advantages of the segmented thin film melter are:

- The maximum temperature inside the segmented thin film melter can be decreased with the help of the fining zone (perhaps up to 1400 °C).
- The temperatures at the top of the furnace inside the melting zone will be comparable to the temperatures in standard glass furnaces. In the other zones the top furnace temperatures could be decreased in order to warm up and to hold the glass on maximum temperature.
- The use of sodium sulfate could be reduced.
- The burner technology (e.g. Flox combustion burner) can be adapted to each zone. The combustion burners should provide an optimized heat transfer and a small concentration of emissions (NO_x and CO).
- Energy saving potential is given by the reduced maximum glass melt temperature.
- The emissions of the glass melt will be smaller due to the decreased maximal temperatures; gas/oil-heated glass furnaces could become attractive for special applications with high emissions of the melt.
- Corrosion of the fining shelf should not become larger in the case of a suitable construction [16].
- The reduction of refractory materials in contact with the melt is possible. The order of magnitude of saving refractories for the melting chamber could be between 10 – 20 %. For the superstructure is no reduction of the refractory demand expected.

3.4 Further questions about the two glass furnace concepts

For the segmented thin film melter it cannot be stated to the present moment whether an increase of the specific melting rate is possible. Theoretical computations for the melting zone could show up to now that about 5,5 – 8 t/m² · d is conceivable for this zone [18]. For the whole furnace the specific melting rate is insufficient according to a smaller value and will be probably in the order of 3,5 t/(m² · d). Further research on the possible melting rate and the usage of the melting zone should be carried out in the future. A problem of the segmented thin film melter might be the intersection between the melting zone and the rest quartz dissolution zone. The flowing down of the primary melt with unresolved rest quartz could increase the corrosion in this region. Furthermore, new concepts of the batch supply for the melting zone and new refractory materials should be investigated.
The submerged combustion melter has a high specific melting rate. However, this is valid only for a melting chamber without fining. A fining zone inside the submerge combustion melter must be constructed additionally, if the glass should have no blisters. This fining zone cannot have a cooled steel shroud and refractory materials should be used. Due to high temperature gradients between the steel shroud and the refractory the intersection between the melting chamber and the fining zone should be taken into account. Corrosion of the refractory material and high thermal tensions inside it might be seen critical.
The usage of the submerged combustion melter for the production of container glass with the necessary higher fining temperature might not achieve lower energy consumption. On the one hand, the melt in the melting chamber must be warmed up to fining temperature and thereby, on the other hand, the associated wall losses will become larger.
If there is no demand for a fining zone, just like for glass wool, the submerged combustion melter could be the best choice. The low investment cost and the low energy consumption for the submerged combustion melter in such a case are profitable.

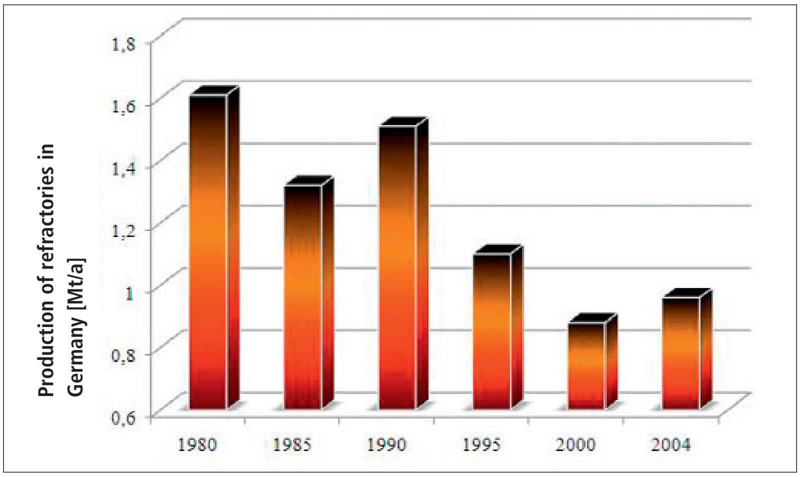

Fig. 5 Production of the German refractory industry

4 Summary and outlook

It was shown that the infiltration of refractories with metallic aluminium, aluminium-based solutions and a phenolic resin is possible. A temperature annealing of the samples is necessary to vaporise the dissolver or to overcome the surface tension in case of the aluminium foil. The atmosphere and temperature are depending on the refining method. By refining the bricks with the substances an oxygen depression is formed in the pores of the bricks and increases the surface tension of the glass melt. So the infiltration of the porous refractory with glass melt is decreased. Depending on the refining method of the refractory system the increase of the corrosion resistance can vary between 11 and 19 %.
Furthermore, the service life of new refractory bricks, e.g. for the feeder, was measured. These measurements have shown the same tendency of increasing the service life due to the refining. Therefore, it is necessary to optimise the treatment and examination parameters shown in this work and to measure a lot of brick types to show the applicability of this method. Furthermore, other important brick properties, e.g. wetting angle, thermoshock resistance etc., have to be measured.
The results shown here are based on unoptimised test conditions. It is therefore necessary to optimise the treatment and examination parameters shown in this work. The principle of increasing the service life by a new treatment of refractories as presented

here should be implemented in energy-efficient technological applications.

Taking into account that the production of the German refractories industry (Fig. 5) [19] amounts to 0,9 Mt/a, then there is a chance to save money with the new refining technology of refractories.

It was also shown that new melting technologies will be developed for the future. As long as there is no benefit for the glass industry the new melting technologies will not be used. The question for the future of new melting technologies will be if they can solve the requirements of the glass industry for low investment cost and/or low specific energy consumption to melt the glass.

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