Glass melt-refractories interaction

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Introduction

A basic requirement for the production of glass under technical conditions are refractories which guarantee the quality of the glass product and a sufficiently long glass tank campaign. The refractories used in glass melting tanks are subject to permanent corrosive attack. Therefore the most important requirements are a high corrosion resistance of the refractories against glass melts and a low glass defect potential of the used refractory materials in the corresponding glass melts.

An assumption for the selection of the suitable refractory material as well as for their improvement and development of new refractories is the knowledge of the mechanisms of the corrosion and of the formation of glass defects. Therefore the interaction between glass melts and refractory regarding the different influencing factors must be known. These different factors are: diffusion, chemical solution, formation of saturation concentration within the boundary layer refractory/glass melt which leads to a change of the chemical and physical properties, the three types of convection (forced, free density and interfacial i. e. surface tension driven convection), equilibrium processes of polyvalent ions and electrochemical processes.

In this paper the influence of the different factors (with exception of electrochemical processes) and mechanisms regarding the corrosion behaviour and glass defect potential will be discussed to give a survey about the interaction between glass melts and refractories.

Diffusion and chemical solution

The corrosion process of refractory materials by glass melts will be controlled by the transportation kinetics of the solved oxides, away from the reaction point.

Therefore the first step of the interaction between glass melt and refractory is the chemical reaction which is determined by the diffusion of the different ions from the glass melt into the refractory material and vise versa. Furthermore the solubility of different oxides from the refractory material in the glass melt respectively the saturation concentration of the boundary layer refractory / glass melt influences decisively the corrosion behaviour.

A pure diffusion without participation of any kind of convection or chemical reaction is not possible in the system glass melt/refractory [1]. Therefore for this system a moving phase boundary must be considered. For the phase boundary solid / fluid the diffusion movement is proportional to $t^{1/2}$, (t = time) [2].

The diffusion process of the system glass melt/refractory is a multicomponent diffusion problem depending on the inter – or absolute diffusion coefficients of sodium, potassium, alkaline earths, aluminium, silicon, oxygen and so on. Therefore an overall diffusion coefficient was introduced, called the effective diffusion coefficient D_{eff} :

$D_{eff} = f\,(c(Na/Al/Si), D_{Na}, D_{Ca}, D_{Al}, D_{O}, T)$.

These effective diffusion coefficients can be calculated if all the other values of the corrosion equations are determined [3].

By the relationship between the oxides of the refractory materials and of the glass melts the chemical solution of determined oxides of the refractories i. e. Al_2O_3 and Cr_2O_3 influence decisively the formation of boundary layers.

The chemical solution e. g. of „pure" chromic oxide refractories in soda-lime-silica glass melts and in fiber glass melts is so slowly that there is practically no formation of a distinct boundary layer. For the most used refractories in glass melting tanks (glass melt contact material) like fused cast and ceramic bonded AZS, alumina, chromic oxide-alumina and so on it can be assumed that the solution reaction is sufficiently rapid, to reach immediately the saturation concentration of all components within the phase boundary. Thus, the corrosion process will be controlled by the transportation kinetics of solved components, away from the reaction point through which the convection has a decisive influence besides the diffusion.

Corrosion under the influence of various convection flows

A very important assumption for quantitative investigations of corrosion processes at refractories is the knowledge of the influence of convection on corrosion.
There are three kinds of convection in glass melting tanks: forced convection, free laminar density convection, free laminar surface tension driven convection i. e. interfacial convection. These three kinds of convection existing in glass melting tanks have a strong influence on the corrosion rate of the various refractory corrosion tests, too.

Corrosion by the influence of forced convection

In glass melting tanks, the corrosion by influence of forced convection is caused by: bubblers, mechanical stirrers and by the melting rate.The melting rate caused, especially at the throat, a high velocity of flow.

With the exception of the already mentioned causes, that means bubblers, mechanical stirrers and throats, the influence of the forced convection on the corrosion in glass melting tanks has only a subordinated role in comparison with the surface tension convection and density convection. The reason is, that at the forced convection, the flow boundary layers are very large, that means up to a few meters.
However, the investigations of corrosion under the influence of a defined forced convection bring, as corrosion tests, informative directions about the behaviour of refractories in practical use if they take into consideration the particularity of the practice. A very exact method for the determination of the corrosion rate under the influence of forced convection is the rotating cylinder surface method [3-7].

Corrosion by the influence of free laminar density convection

In glass melting tanks, the free laminar density convection is caused by temperature gradient in the tank, and by concentration gradients of the dissolved components from the refractory wall. Both can lead to convection flows in the same or opposite direction.
If the reason of the free convection is a density increase of the glass melt saturated with components of the refractories, then the free density convection on the tank bottom is to be neglected in comparison with the convection on the walls.
By reason of the solubility of the refractory material in glass melts, generally there is always a concentration caused density convection.
With concentration-caused free density convection, the space arrangement of wall and sample, respectively, to be investigated is of large importance for the mass transfer. Because in practice, the free convection of vertical walls is of interest for the

determination of corrosion by the free density convection in the lab, the experimental arrangements must be vertically arranged plates [8,9].

Corrosion by the influence of free laminar interfacial conection

The free interfacial convection lead to flux line erosion, bubble drilling and drilling by molten metal droplets. All these kinds of surface tension driven convection cause erosions, which lead to grave losses at the refractories of glass melting tanks. Especially the flux line corrosion and the bubble drilling are always present in glass melting tanks and have the strongest effect in comparison with other convection influences.

Flux line erosion and bubble drilling have the same principle, which means that the convection flow takes place at the two-phasic three-components boundaries: pure glass melt/saturated glass melt with dissolved refractory components/gas atmosphere.
The driving force for the interfacial convection is the difference between the surface tension of the host glass melt and the refractory components-saturated glass melt. Due to the partical or complete miscibility of the components of refractories with the glass melts, there is a continuous supply for the different interface energies.There are interface-energetic balancing processes by the different interface energies on the two-phasic three-components boundary, which lead to a convection flow. This interfacial convection reduce the thickness of the Nernst diffusion layer at a three-components boundary, that means on the fluxline. This leads to an increase of the mass transfer velocity.
As already mentioned by discussing the free density convection, the space arrangement of the wall and sample, respectively, to be investigated is of large importance to the mass transfer. Because in practice the free interfacial convection takes place at vertical walls, the experimental arrangements for the determination of the corrosion by free interfacial convection in the lab must therefore include be vertically arranged plates [3, 7-9].

Influencing factors to the corrosion rate under the action of various convection flows

Table 1 shows the influencing factors and dependence on the corrosion rate under the action of the discussed three kinds of convection.

Table 1: Corrosion rates R as a function f of the influencing factors under the action of various convection flows

Convection flow in general	R	=	f [driving force,	geometry,	kinetics,	solution]
Forced convection	R_{FC}	=	f [$\omega^{1/2}$	-	$D^{2/3}$, $\nu^{-1/6}$	Δc]
Density convection	R_{DC}	=	f [$(g \cdot \Delta\rho/\rho_\infty)^{1/4}$	$y^{-1/4}$	$Deff^{3/4}$, $\nu^{-1/4}$	Δc]
Interfacial convection	R_{IC}	=	f [$(g \cdot \Delta\sigma/\sigma_\infty)^{1/3}$	B	$Deff^{2/3}$, $\nu^{-1/3}$	Δc]

ω = angular velocity of the rotating cylinder; Deff = effective diffusion coefficient; ν = kinematical viscosity; $\Delta c = c_s - c_\infty$, c_s = saturation concentration of the solved component in the phase boundary layer, C_∞ = concentration of this component in the host glass melt; g = gravity acceleration; $\Delta\rho = (\rho_s - \rho_\infty)/\rho_\infty$, ρ_s = density of the saturated glass melt in the phase boundary layer, ρ_∞ = density of the host glass melt; y = current coordinate along the wall; $\Delta\sigma = (\sigma_s - \sigma_\infty)/\sigma_\infty$, σ_s = surface tension of the saturated glass melt in the phase boundary layer, σ_∞ = surface tension of the host glass melt; B = factor dependent on geometrical features of the formed fluxline.
Generally, the corrosion rate in each case depends on the driving force, on the geometry, on the kinetics, and on the difference between the given concentration of the corresponding component in the glass melt c_∞ and the solubility c_s.

The influence of the concentration difference (Δc) enters with the full exponent 1, while the kinetics (D_{eff} and ν), and the driving force (ω, g, $\Delta\rho/\rho_\infty$, $\Delta\sigma/\sigma_\infty$), enter the equations with an exponent lower than 1.

The geometry does not enter the forced convection flow, but only for the special case of the rotating cylinder end face. However, in other cases the geometry plays an important role, for example: B for the fluxline corrosion and $y^{-1/4}$ for the case of density convection flow.

With the knowledge of these influence parameters it is possible to derive suggestions for the reduction of the corrosion rate and suggestions for the improvement of the corrosion resistance of refractories [10].

To demonstrate the strong influence of the physical properties of the saturated boundary layer the example of the viscosity will be briefly discussed. Figure 1 shows the viscosity (log η) of a container glass melt and that of the saturated boundary layer fused cast AZS 41/ container glass melt corresponding to the chemical composition of table 2 as a function of temperature. The viscosity of the saturated melt is much higher (at 1.400 °C log η_s = 4,15 respectively η_s = 14.223 dPas) than that one of the pure container glass melt (at 1.400 °C log η_∞ = 2,21 respectively η_∞ = 161 dPas) due to its higher alumina and lower silica concentration [3]. This high viscosity of the saturated glass melt effects as a diffusion barrier against aggressive ions from the glass melt like sodium. Furthermore the high concentration of 27 % Al_2O_3 reduces the solubility of zirconia in this boundary layer to $\leq$ 2 % [12 and 13].
The other physical properties (surface tension and density) show similare behaviour and influence strongly the corrosion behaviour corresponding to the factors in table 1.
All these parameters are responsible for the relative high corrosion resistance of fused cast AZS 41 materials (i.e. Monofrax CS5) against alkali oxide – alkaline earth oxide – silica glass melts.

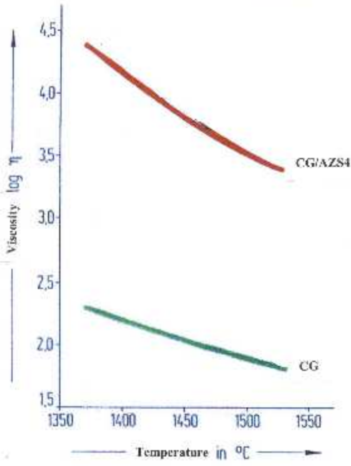

Figure 1: Viscosity (log η) of a container glass melt
and that of the saturation boundary layer of
container glass melt /fused cast
of temperature

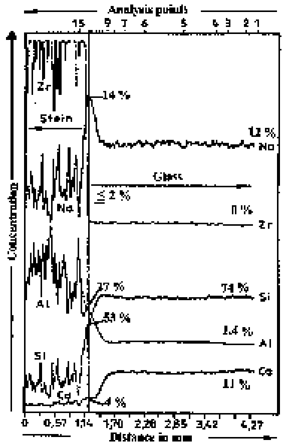

Figure 2: Concentration profil of a soda
lime silica glass melt/fused cast the
combination AZS 41 boundary layer after
AZS 41 as a function 192 hours at 1.400 °C.

Formation and behaviour of boundary layers

The formation and behaviour of the boundary layers of various refractory / glass melt types are partly complete different. On the one side there are refractory / glass melt combinations which form a relativ thick reaction layer, on the other side there are refractory / glass melt combinations with very thin boundary layers (no visuell reaction layer).

In the following part of this paper one example of each will be discussed: fused cast AZS / soda-lime-silica glass melt in the first case (thick reaction layer) and chromic oxide / soda-lime-silica glass melt in the second case (no visuell reaction layer).

Boundary layer of fused cast AZS / Soda-lime-silica glass melt

For the production of alkali oxide- alkaline earth oxide-silica glasses fused cast AZS materials are the mostly used refractories in the glass contact area. In case of the combination fused cast AZS /Soda-lime-silica glass melt the velocity of the chemical solution is much faster than the convective-diffusive transportation. This is the reason for the formation of saturation concentration in the fused cast AZS /Soda-lime-silica glass melt boundary layer [11].

Figure 2 shows a typical concentration profile of different ions within the reaction zone of a fused cast AZS 41 / container glass melt after 192 hours reaction time at 1.400 °C. The saturation concentration of silica, alumina, zirconia and calcium oxide appears as a shoulder, the saturation concentration of the sodium oxide is given by the maximum of the concentration profile.

Table 2: Chemical composition of fused cast AZS 41, AZS 32 and its glassyphase, container glass, and its saturation layer

% by weight	fused cast AZS 41	fused cast AZS 32	Glassy phase of AZS 32 at 1550 °C	Container glass	Saturation boundary layer
SiO_2	**12**	**15**	**66**	**74**	**53**
Al_2O_3	**46**	**49**	**23**	**1,4**	**27**
ZrO_2	**41**	**33**	**4**	**-**	**≤ 2**
Na_2O (+K_2O)	**≤ 1**	**≤ 2**	**6**	**12**	**14**
CaO	**-**	**-**	**-**	**11**	**4**
Others	**0,2**	**1**	**1**	**2**	**-**

Table 2 shows the chemical composition of a fused cast AZS 41, of a fused cast AZS 32 and its glassy phase, of a container glass and of the saturation concentration of the boundary layer fused cast AZS 41 / container glass.

By the relationship between the oxides of the refractory material and of the glass melt the diffusion of the different species in both opposite directions leads to the presented chemical composition of the saturation concentrations of table 2. The large difference between the chemical composition of the pure container glass melt and the saturation concentration of the fluid boundary layer leads to different physical properties of each one i. e. the saturation concentration of the boundary layer has a very important role regarding the corrosion and glass defect potential.

Figure 3: Typical microstructure of a fused cast AZS 41 material- Monofrax CS 5

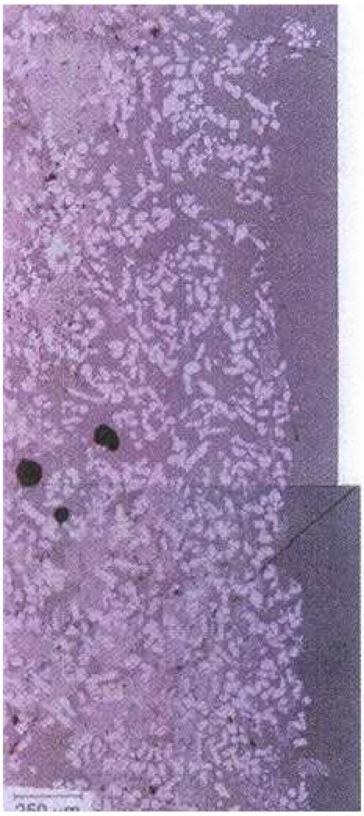

Figure 4: Boundary layer area of a fused cast AZS 41 block- Monofrax CS 5 (left) with a soda-lime silica glass (right) after a reaction time of 120 hours at 1500 °C.

Figure 3 shows the typical microstructure of a fused cast AZS 41 material (41 % ZrO_2, 46 % Al_2O_3, 12 % SiO_2) i. e. grey alumina crystal with embedded white baddeleyite, the coarse white „free“ baddeleyite and the darker grey glassy phase.

Figure 4 shows the boundary layer area of a fused cast AZS 41 block (left) with a soda-lime- silica glass (right) after a reaction time of 120 hours at 1.500 °C. Within a distance of about 500 µm in the boundary layer area of the fused cast AZS 41 material the alumina crystals are solved in the glass melt in which the baddeleyite seam (white) is embedded. On the top of the picture a part of the knot glass with baddeleyite is moving to the host glass melt. Possibly, bubbles were the reason for pushing out these particles of the boundary layer to form glass defects.

Mechanism of knot formation in the reaction zone fused cast AZS / Soda-lime-silica glass melt

Figure 5 shows the schematical representation of the reaction zone between a high alkali oxide-alkaline earth oxide-silica glass melt and a fused cast AZS block. The corundum is dissolved by diffusion processes, especially of alkali ions from the glass melt into the liquid glassy phase of the AZS block and by their subsequent reactions. Because of these processes, a baddeleyite seam – embedded in a high viscous glassy reaction layer – is formed on the block side of the phase boundary. The chemical composition of this glassy reaction layer corresponds to that of the glass knots. At an increase of temperature, there is the formation of oxygen bubbles, caused by redox equilibrium processes of polyvalent ions, such as iron oxide in the glassy phase of the AZS material. The gases set free in the glassy phase of the AZS block can only exit through the reaction zone. The bubbles push out portions of the glassy reaction layer and carry along ZrO_2-crystals of the baddeleyite seam. Because the surface tension of the glassy reaction layer is larger than that of the host glass melt, the former contracts into „spheres“ and leads, therefore, to knot formation.

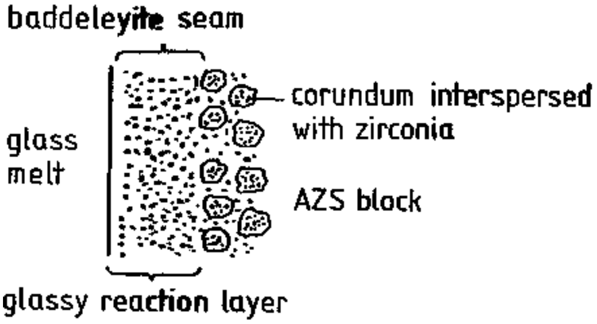

Figure 5: Schematical representation of the reaction zone between the highly alkali oxide-alkaline earth oxide-silicate glass melt and the fused cast AZS-block.

Figure 6: Polished section of boundary layer region between an AZS block (left) and a glass melt (right), with bubbles and knot glass rising from art the part of the ZrO_2 seam.

Figure 6 presents the boundary layer region between an AZS block (left hand side) and the glass melt (right hand side) with bubbles and glass knots rising from the part of the ZrO_2 seam that has been pushed outwards. The gas content of the most bubbles consists primarily of oxygen [14].

A conclusion of this behaviour should be to avoid many and strong temperature increases during operation of glass melting tank to reduce such glass defects i. e. blisters, stones, knots and cords.

Boundary layer of isostatic pressed chromic oxide CR95WA / Soda-lime-silica glass melt

Figure 7 shows an isostatic pressed CR95WA (96 % Cr_2O_3, 4 % TiO_2) on the left hand side with the dense microstructure. After a reaction time with the soda-lime-silica glass melt (right hand side) of 120 hours at 1.450 °C there is no visible reaction zone. The reason for this behaviour is that there is nearly no solubility of chromic oxide in such a glass melt. Therefore the velocity of the chemical solution of the isostatic pressed „pure" chromic oxide in a soda-lime-silicate glass melt is much lower as the convective transport processes i. e. there is no possibility for the formation of a saturation concentration in the boundary layer area. Therefore has such an isostatic pressed chromic oxide material a very good corrosion resistance and no glass defect potential.

Figure 7: Boundary layer area of an isostatic pressed CR95WA block (left-96 % Cr_2O_3, 4 % TiO_2) with a soda-lime silicate glass (right) after a reaction time of 120 hours at 1.450 °C.

Figure 8: Boundary layer of an isostatic pressed CR95WB block (left – 96 % Cr_2O_3, 4 % TiO_2) with a soda-lime silicate glass (right) after a reaction time of 120 hours at 1.450 °C.

Boundary layer of isostatic pressed porous chromic oxide CR95WB / Soda-lime-silica glass melt

Figure 8 shows the microstructure of an isostatic pressed CR95WB (96 % Cr_2O_3, 4 % TiO_2) which has a lower bulk density and a higher porosity but an improved thermal shock resistance in comparison to the above discussed CR95WA. The CR95WB (left) shows a coarse dense Cr_2O_3-grain within a fine sized Cr_2O_3-matrix which has a higher porosity. After a reaction time of 120 hours at 1.450 °C there is a little larger corrosion in the matrix area recognizable but no reaction zone is visible analogous to the CR95WA. This is the reason why the CR95WB has a very good corrosion resistance against soda-lime-silica glass melts and no glass defect potential. This fact is confirmed by the application of the CR95WB material in more than 50 glass melting tanks in which this chromic oxide material is installed in throats, weir walls, as dog house corner blocks, bubbler blocks and as overcoating tiles.

Here are only two different examples shown from a lot of possible combinations refractory material/ glass melt, but it presents how important it is to consider the formation and behaviour of boundary layers for the selection of refractory materials.

Further examples of different combinations refractory / glass melt regarding formation and behaviour of boundary layers are described in [15].

Conclusions

All discussed parameters which occure at the interaction between glass melt and refractories influence strongly the corrosion resistance, the formation of boundary layers and therefore the glass defect potential. The knowledge about the different influencing factors to the glass melt – refractories interaction is very important: For the selection of the suitable refractories which effect the productivity of glass melt tanks, for the improvement and development of refractories, as well as to optimize the operation conditions of glass melting tanks.

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