State-of-the-Art Refractory Linings for Float Glass Furnaces

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A high quality refractory lining is essential for the production of float glass, especially when the stringent requirements on manufacturers such as product quality, energy consumption and furnace lifetime are taken into consideration. In this article the lining options for float glass furnaces have been described.

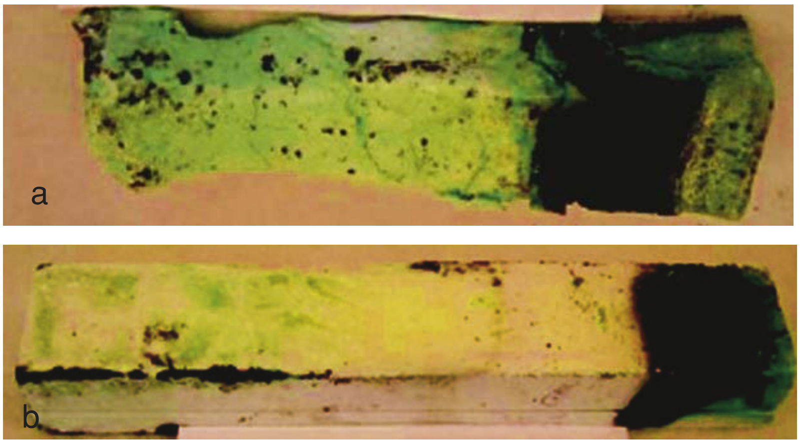

Fig. 1 a) Standard silica grade and b) STELLA GNL after 3 months in an oxy-fuel furnace

1 Introduction

Currently, more than 95 % of the world's flat glass is produced using the float glass process. Since its development in 1959 by Pilkington, the technology has undergone significant improvements. Nearly every year another record regarding the lifetime or capacity of new furnaces is established. Today, float glass facility lifetimes exceeding 15 years are achieved and the largest furnaces have a capacity of 1000 t/d. In addition, float glass quality requirements are continually increasing and even the smallest glass defects that distort product clarity cannot be tolerated. However, achieving these advances is an increasing challenge for float glass manufacturers because of additional demands including more and more stringent environmental requirements (e.g., energy savings and NO_x reduction).

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It is evident that in addition to melting technology and furnace construction improvements, the necessary production developments can only be achieved using high quality refractory products. The following article provides a review of the refractory lining concepts for float glass furnaces to meet the current demands and describes specific grade characteristics.

2 Melter

2.1 Crown

The most important and established refractory for the crown of regeneratively fired float furnace melters is silica. High quality silica materials are characterized, amongst other factors [1], by:

- Low remnant quartz content – typically 0,4 mass-% in STELLA GGS
- Low creep in compression (CIC) value – essential for broadly spanned crowns
- Tight dimensional tolerances to ensure closed joints.

Practical experiences have shown that in highly stressed areas of the crown standard silica materials are at their limits (for example: oxy-fuel fired furnaces). The reason for this is that the wollastonite-bonding phase is easily corroded by alkalis, for example NaOH [2]. As a result of the reaction between wollastonite and NaOH, the formation of glassy phase in the silica brick is initiated, which itself starts to dissolve the coarse silica grains. Rapidly the silica brick becomes enriched with glassy phase and starts to drip. These reactions have been confirmed using thermochemical calculations [3]. Additionally, these investigations demonstrated that high CaO levels in silica grades are detrimental for this application. The only lime-free silica grade available with suitable thermomechanical characteristics is STELLA GNL, comprising 99 mass-% SiO_2. The results of a 3-month test performed in an oxy-fuel furnace to compare a standard silica brick grade and STELLA GNL are illustrated in Fig. 1. Based on the improved purity, additionally STELLA GNL can be used at higher temperatures than standard silica grades which leads to increasing of the production capacity.

2.2 Superstructure

Fused cast Al_2O_3-ZrO_2-SiO_2 (AZS) is routinely used in the superstructure from port 1 to 4, owing to the heavy batch carry-over. All three main types of AZS refractories, differentiated by their ZrO_2 and glassy phase contents, are used for this application. The most important quality characteristic of these grades is the exudation behaviour and the impact of the ZrO_2 content on this phenomenon has previously been described [1]. From port 5, β-alumina grades are most suitable due to the low glass defect potential (e.g., Monofrax H). These grades are described in detail in the following section.

2.3 Glass contact area

In the glass contact area of the melter, fused cast AZS grades are also commonly applied. The most important requirements are a low glass defect potential and high corrosion resistance. REFEL and Monofrax products are proven for this application. The bottom of the melter is usually lined with fused cast pavings (32 mass-% ZrO_2 content). To ensure tight joints the dimensional accuracy of the pavings is extremely important (i.e., 90° angles and tolerances). Underneath the fused cast pavings, a thin mortar settlement layer and a monolithic layer are common. The main role of the monolithic layer is to protect the additional insulation lining below; therefore, it should have a good resistance against glass melt. In addition, it should not shrink during the heat-up process to avoid cracks and gaps forming around the thermocouples and electrode blocks (i.e., enabling melt to infiltrate down to the insulation layer). Depending on the actual bottom construction the following monolithics are suitable for this application:

- RESISTIT ZM260: Ready-to-use ramming mix based on zircon and alumina
- DIDURIT ZM465: Castable based on AZS
- RESISTIT ZS717: Ready-to-use ramming mix based on zircon.

3 Refiner area

Due to lower temperatures in the refiner compared to the melter, the demands on the refractory lining are less severe. However, the requirements for a low glass defect potential are very high and components from the refractory lining should not generate any glass defects. Established grades for this application consist of α/β- and β-alumina. The near absence of a glassy phase in both types of alumina refractories provides certain unique properties and benefits for the end user. Whereas the AZS refractories demonstrate a characteristic glassy phase exudation upon furnace heat up and during the subsequent campaign, both types of alumina refractories are dry upon heat up, which offers a significantly reduced defect potential compared to AZS for superstructure applications. In addition, α/β-alumina provides these advantages in glass contact areas.

High quality fused cast alumina refractories are manufactured by melting high purity raw materials to more than 2000 °C in an electric arc furnace. The molten liquid is cast into graphite moulds. Following a brief period of cooling, whereby a solid skin develops on all surfaces, the refractory block is removed from the graphite mould and annealed in direct contact with an insulating powder for several days.

Fused cast β-alumina is essentially a single-phase refractory, as can be seen from the microstructure in Fig. 2a. Since it is saturated with alkali (i.e., Na_2O), it is chemically very stable in the high alkali and alkaline earth environment found in the superstructure. In service experience has shown that a 1/9,2 ratio of Na_2O/Al_2O_3 in fused cast β-alumina is the most effective composition to ensure the following characteristics:

- High thermal shock resistance
- Chemical stability during exposure to an alkali and alkaline earth oxide-rich environment.

However, since fused cast β-alumina refractory has a relatively high porosity (i.e., ~ 4 vol.-%) and is coarse grained, it does not provide enhanced resistance to corrosion from batch carry-over or glass melt. Therefore, its application is restricted to the downstream superstructure only.

In addition to fused cast β-alumina, silica is a common solution for the refiner superstructure. However, in contrast to the fused cast option the risk of glass defects are higher due to silica melt running down into the glass.

In contrast to fused cast β-alumina, fused cast α/β-alumina consists of two major phases (i.e., α- and β-alumina) with a very small grain boundary phase (Fig. 2b). A phase composition of approximately 40 mass-% α-alumina, 58 mass-% β-alumina, and a 2 mass-% boundary silicate phase shows the best corrosion resistance and is realized in Monofrax M.

Monofrax M is a fine-grained refractory with an open porosity of approximately 2 vol.-%. This is necessary for high corrosion resistance in glass contact applications, for example in the glass contact area of the refiner. However, the temperatures should not exceed 1350 °C. In float furnaces, α/β-alumina refractories are used for the refiner side-

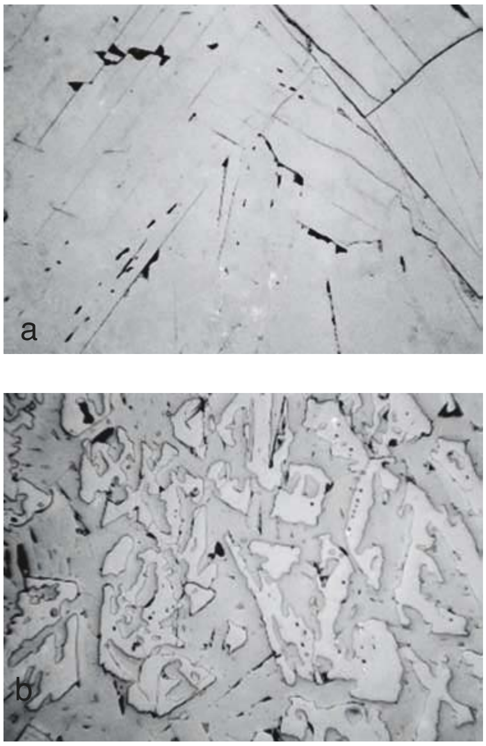

Fig. 2 **a) Monofrax H fused cast β-alumina refractory ($\beta \sim Na_2O \cdot 9{,}2\ Al_2O_3$) and**
b) Monofrax M fused cast α/β -alumina refractory (α = Al2O3 and $\beta \sim Na_2O \cdot 8{,}2\ Al_2O_3$)

walls, pavers, canals, and lipstone. In these applications, Monofrax M is preferable to AZS due to its lower defect potential. The absence of zirconia and a viscous glassy phase in Monofrax M results in a lower stoning and viscous knot potential. Furthermore, α/β-alumina refractories produce considerably less seeds and blisters in glass than AZS.

A critical component in the float process is the lipstone. For several years, RHI Monofrax has offered a complete lip spout assembly encased in steel for convenient installation in a float furnace (Fig. 3).

4 Regenerator

4.1 Regenerator checker work

In modern float furnaces the regenerators are solely equipped with thin-walled checkers, namely ceramically bonded chimney blocks or fused cast checkers. These types of checkers are characterized by a high thermal efficiency. In addition to this fundamental requirement, the corrosion resistance of grades used for the demanding conditions is important. The conditions in the regenerator vary from the charging end to the refining

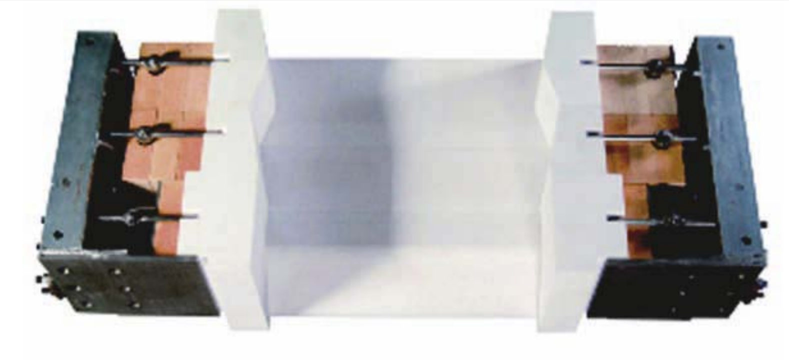

Fig. 3 **Monofrax M lipstone in a spout lip assembly**

area and this must also be considered for appropriate refractory selection.

The first two ports are characterized by a high loading with batch dust. This mainly influences the grade selection for the regenerator crown and the upper courses of the checker work since it is necessary to install materials with a high resistance against the SiO_2-containing batch carry-over. For oil-fired furnaces, vanadium oxide attack must also be taken into account.

Magnesia-zircon material (i.e., RUBINAL VZ) has proved to be effective in the upper checker courses when aggressive SiO_2 attack occurs. In these grades periclase is protected by a fringe of forsterite and zirconia; thereby, forsterite bursting is minimized. In addition, products based on 99 mass-% fused alumina grains (i.e., DURITAL K99EXTRA) possess a high resistance to the corrosive agents present in the top courses.

Less critical is the grade selection for the area below the top courses down to temperatures of 1100 °C, especially when the furnace is heated with natural gas. In such cases the use of Ca_2SiO_4-bonded MgO (i.e., ANKER DG1) is recommended. In cases where the furnace is fired with heavy oil the use of checkers with a low CaO content and strong forsterite bonding, for example a magnesia-zircon grade (i.e., RUBINAL VZ) is common, because it exhibits a high resistance against V_2O_5.

In the regenerator, the temperature zone between 1100 and 800 °C is the most critical region for the checker work. Condensing alkali sulphates as well as gaseous SO_3 corrode the checker material. Since more than 20 years RUBINAL EZ magnesia zircon blocks have been installed in this area giving excellent results over long campaigns. In these checkers zircon ($ZrSiO_4$) is one of the raw materials. The coarse magnesia crystals are protected by a bonding matrix of forsterite and zirconia that are formed during the firing process of the bricks.

Since zircon is widely used in different refractory products, the availability of this raw material cannot be guaranteed. Therefore, zircon-free magnesia products have become important. RUBINAL ESP was developed for this purpose. RUBINAL ESP is a magnesia brick with a very strong spinel bonding matrix whereby a part of the spinel is formed in situ, namely during the firing process. The spinel bonding matrix is resistant to sulphate attack and protects the periclase. Therefore RUBINAL ESP chimney blocks can be used in the condensation zone of the regenerator under oxidizing conditions.

Since the beginning of 2007, RUBINAL ESP has been installed in the condensation zone of regenerators of glass furnaces. To date the performance has been satisfactory and will be monitored further.

In the last two ports the conditions alter considerably because the influence of batch carry-over and exhaust gases is reduced. Therefore, the use of a forsterite-bonded magnesia grade (i.e., ANKER DG 3) in the condensation zone is appropriate.

4.2 Regenerator casing

Due to the large dimensions of float furnace regenerators, the casing has a significant impact on the investment costs. Many different refractory lining solutions are common for this application. Nearly every float glass manufacturer has its own philosophy and has a positive experience with a specific lining strategy that is optimized to the specific operating conditions. Predominantly, four types of lining concepts for the upper part of the regenerator casing exist:

- Silica (crown) + mullite (walls)
- Silica (crown) + magnesia (walls)
- Magnesia (crown and walls)
- Silica (crown and walls).

High quality silica in the crown is a cost-efficient solution with excellent thermomechanical characteristics, especially high creep resistance. Whilst a high degree of additional insulation is necessary, silica has a high corrosion resistance against SiO_2 attack. However, a critical aspect is liquid slag formation due to alkali attack, which can lead to a premature wear. In addition, the current tendency towards lower temperatures and a reducing atmosphere in the regenerators is detrimental for standard silica. For this situation *RHI* offers the improved silica grade STELLA GNL. Due to the absence of lime bonding this grade has a higher corrosion resistance against alkalis compared to that of standard silica.

A more effective solution compared to silica for regenerator wall applications is mullite. Pure mullite grades (e.g., DURITAL E75EXTRA) exhibit excellent characteristics, for example high creep resistance and high resistance against SiO_2 and V_2O_5 attack. However, pure mullite refractories are expensive because they are based on synthetic raw materials and require high firing temperatures. Therefore, grades based on andalusite with corundum addition have been developed (e.g., DURITAL S70), which form mullite during the firing process.

However, a disadvantage of mullite is that with decreasing sand carry-over the risk of alkali corrosion, especially nepheline formation, increases.

In service experiences have shown that a refractory lining combination of silica in the crown and MgO walls should be avoided since silica melt from the crown runs down over the walls and corrodes the MgO. This results in softening of the MgO and forsterite spalling.

A MgO concept is a cost-efficient option for the casing. ANKER DG10 is an appropriate grade for the crown and upper regions because of its excellent creep behaviour up to 1600 °C that enables effective insulation. The main reason for the excellent creep resistance is the use of large crystal sinter in this grade. However, in certain cases a particular detrimental phenomenon has been observed with magnesia in the first month of operation. If fine cullet is used during the start-up this component reaches the regenerator and can result in forsterite spalling. This phenomenon concerns only the furnace start-up period and causes no general problems for further furnace operations. To avoid this issue, extremely fine cullet should be not used to fill the furnace during start-up.

5 Tin bath

5.1 Tin bath bottom blocks

The tin bath is the core of every float bath facility and refractory selection for this unit has an enormous influence on the glass quality over the lining lifetime. The history and development of tin bath bricks has been reviewed in detail [5]. Common fire clay tin bath bottom blocks exhibit the following characteristics:

- Alumina content of approximately 38 mass-%
- Glassy phase content of approximately 30 mass-%
- Cold crushing strength of approximately 50 N/mm^2 to ensure a good surface appearance with a low risk of transport and installation damage
- Hydrogen diffusivity in the range of 50 mm WG.

This type of material, with an alumina content of 38 – 40 mass-%, has been in service since the beginning of the 1980s. However, whilst in certain instances campaigns of 12 years or more have been reached without problems, in most cases nepheline peeling has occurred.

Nepheline is a reaction product of Al_2O_3, SiO_2, and Na_2O and results from Na_2O diffusing from the glass, through the tin bath, to the bottom block. However, the time period between installation and first peeling varies between 5 and 10 years, depending on the alumina and the glassy phase contents of the refractory. To circumvent these problems *RHI* developed a grade mainly consisting of calcium aluminate, termed SUPRAL CA. The characteristics and advantages of this grade have previously been described in detail [6] and include:

- No chemical reaction with tin
- No reaction with alkalis dissolved in the tin bath
- No influence of the reducing atmosphere present in the tin bath
- Good mechanical strength to enable perfect grinding and drilling as well as to eliminate handling damages
- A smooth surface and sharp edges are obtained after grinding and drilling
- Thermal expansion comparable to fire clay blocks: The design of the expansion joints does not have to be modified when replacing the fire clay with SUPRAL CA
- Thermal conductivity is lower compared to fire clay material
- Thermal resistance is higher in comparison to fire clay blocks: SUPRAL CA can work at a maximum temperature of 1200 °C, whereas fire clay starts to creep at 1100 °C
- Hydrogen diffusivity is at a very low level of approximately 10 mm WG: The formation of bubbles under the glass ribbon caused by thermal transpiration during the campaign can be excluded completely.

There were thermodynamic calculations showing a possibility of formation of calcium sulphite (CaS). This phenomenon was not observed in the practice, also no sulphate has been found in the used tin bath blocks. Currently, there are more than 20 float baths in operation with SUPRAL CA bottom blocks by several leading float glassmakers around the world. The first campaign started in 2004, and to date no problems have been observed.

5.2 Mixes for tin bath stud holes

In addition to the blocks, the selection of unshaped refractory products to close the stud holes in tin bath bottom blocks is important. The ramming mix based on zircon mullite is most common for this purpose. This practice has following disadvantages:

- A longer installation time.
- The mix is not dense enough and cracks can be formed after heating up (Fig. 4a).

RHI has developed a self-flowing castable based on calcium aluminate (DIDOFLO D345) [6], which can be poured easily into the holes and is self-levelling. It simplifies the installation process and saves time. The homogeneous structure ensures a high quality filling. DIDOFLO D345 is not only suitable for SUPRAL CA blocks, but also for SUPRAL 40FG (fireclay) tin bath bottom blocks.

DIDOFLO D345 has the following advantages:

- Self-flowing and therefore easily to install.

Volume stability: no open joints and no crack formation (Fig. 4b)

- High resistance against tin infiltration
- High resistance against alkali attack.

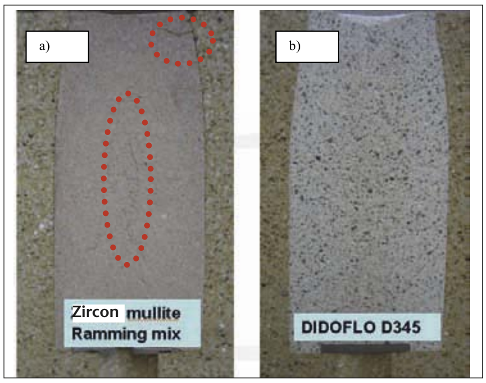

Fig. 4 a) The stud hole filled with ramming mix based on zircon mullite, after firing at 1100 °C: cracks formed b) The stud holes filled with DIDOFLO D345, after firing at 1100 °C: no cracks or open joints

6 Conclusions

A high quality refractory lining is essential for the production of float glass, especially when the stringent requirements on manufacturers such as product quality, energy consumption and furnace lifetime are taken into consideration. In this article the lining options for float glass furnaces have been described.At *RHI* the prerequisite chemical and physical material properties, in addition to the required brick specifications are achieved through tight manufacturing tolerances and functional quality monitoring.

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