Microstructural Analysis of Magnesia Bricks Operating under Altered Conditions in the Regenerator Condensation Zone of Glass Melting Furnaces

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Refractory producers need to offer lining solutions tailored to the different operating conditions occurring in glass melting furnaces [1]. For example, in the regenerator condensation zone (700–1100 °C) it is necessary to adapt the lining concept to the specific atmosphere resulting from the waste gas composition. For oxidizing conditions, forsteritic-bonded magnesia-zircon checker bricks are a well-proven lining concept providing satisfactory lining performance, while in a reducing atmosphere pure, low-iron magnesia bricks offer the best performance in this temperature range. However, the requirement to fulfil environmental regulations by implementing for example NO_x reduction measures in addition to severe operating problems can significantly change the typical regenerator atmosphere. In such cases, the corrosive load on the lining from waste gases is highly intensified. In this paper an insight into the microstructural changes occurring in brick linings located in the condensation zone when the atmosphere is drastically changed are discussed with examples from post mortem investigations and a laboratory trial.

Fig. 1 Glass tank regenerator: the condensation zone has a temperature range of approximately 700–1100 °C (source: RHI AG)

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1 Introduction

Flue gases in oil or gas fired soda-lime glass melting-furnaces consist mainly of fossil fuel combustion products such as SO_x (in the case of oil firing), CO, CO_2, HCl, NO_x, O_2, and N_2. Additional components in the flue gas can be SO_2, stemming from the refining agent, and NaOH, mainly originating from the glass melt [1]. Under oxidizing operating conditions, volatiles like sodium and SO_3 condense in the so-called condensation zone of the glass melting tank regenerator, resulting in the final formation of Na_2SO_4. This condensation zone occurs in the temperature range of approximately 700–1100 °C (Fig. 1). In the case of oxidizing operating conditions and excess SO_3, aggressive free sulphate is formed besides sodium sulphate. This resulted in the development of forsteritic-bonded magnesia-zircon bricks [2], which provide the highest corrosion resistance against sulphate attack. Since the glass industry is a major combustion source, in recent years it has had to solve several problems to reach government environmental regulations, for example NO_x emission targets. This can be achieved by using oxy-fuel combustion as well as by operating the furnace under reducing conditions [3], defined as a CO content >1000 ppm (vol) [1]. Reducing conditions can be reached for instance by decreasing the combustion air flow to under stoichiometric conditions or by introducing natural gas into the waste gas stream (i.e., *Pilkington* 3R process) [4] before it enters the regenerator. Another possibility is to inject ammonia into the exhaust gas stream in the regenerator zone where the temperature lies within the effective NO_x reduction range of between 870–1090 °C [5].

The effect of reducing conditions on the waste gas in the condensation zone is that SO_3 is not stable and as a result sodium sulphate cannot form in the condensation zone. As a consequence, aggressive sodium remains in the flue gas [1]. Since sodium has a high reaction potential with SiO_2-rich brick materials, pure, low-iron magnesia bricks are an appropriate lining recommendation for the regenerator condensation zone operating under reducing conditions. In sodium silicate glass melting tanks, particularly in the case of gas firing where there is a very high load from NaOH in the flue gas, pure magnesia bricks show the best performance.

In summary, depending on the furnace atmosphere, suitable and well-proven refractory lining recommendations can be made. However, in cases where during operation the atmosphere within the regenerator heating phase changes drastically from the usual oxidizing to reducing conditions and vice versa, serious chemothermal attack on the previously well-performing refractory lining can arise. In extreme cases, the regenerator lining lifetime can decrease drastically.

The following examples provide a comprehensive view of the microstructural changes that occurred when bricks were subjected to a drastically changed atmosphere in the regenerator. The samples were investigated microscopically and compared to unused material.

2 Investigation procedure

To generate results with the highest possible quality and accuracy levels, sample investigations were carried out according to international standard procedures. For example calibration was performed using internationally certified standards. Na was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 26845), which covers the range from parts per billion to high mass-% sulphur determination (DIN 51085) using *LECO* CS 200 covered a range of 0–30 mass-% sulphur in a refractory sample with an accuracy of ±0,1 mass-%. The microscopic investigations were carried out on polished sections by optical light microscopy and using a *JEOL* 6400 scanning electron microscope equipped with an energy dispersive spectrometry (EDS) analysis system to provide chemical microanalyses.

3 Results and discussion

3.1 Magnesia-zircon bricks – oxidizing atmosphere and high sulphate load

Forsteritic-bonded magnesia zircon brick brands like RUBINAL EZ and RUBINAL VZ are a suitable lining material for regenerators operating with an oxidizing atmosphere where there is an excess of sulphate in the flue gas. One important microscopic feature of this brick type is that initial magnesia and zircon brick components completely react during the firing process to form magnesia, forsterite, and zirconia. Well-selected raw materials that form a dense microstructure with homogeneously distributed components, a strong forsteritic bonding structure in the brick, and the development of a forsterit-

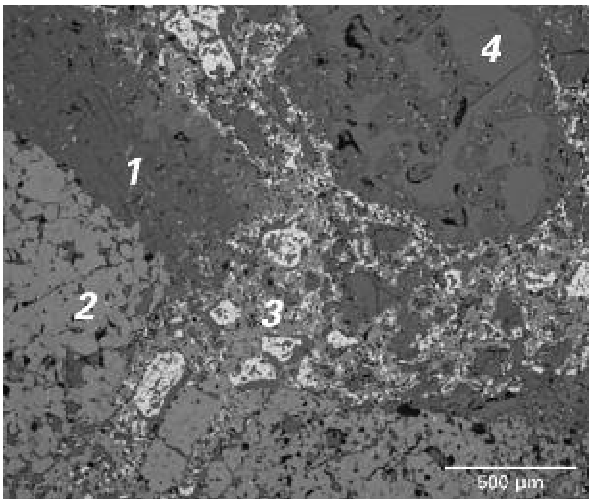

Fig. 2 Magnesia-zircon checker brick after 17 years in service. At the near surface, up to a maximum of 5 mm from the hot face, corrosion of magnesia (2) due to the formation of a sulphate phase (1) is visible. The forsteritic matrix shows very high resistance against sulphate attack (3) and pores (4) are indicated (source: RHI AG)

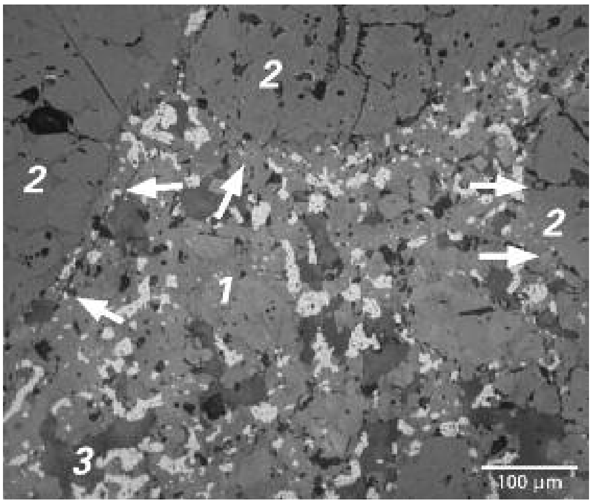

Fig. 3 Microstructural detail 7 mm from the surface of a magnesia-zircon checker brick after 17 years in service: no corrosion of the forsteritic bonding matrix (1). The forsteritic belt (arrows) protecting the magnesia grains (2) and Na-Mg-sulphate in the pores (3) are indicated (source: RHI AG)

ic belt protecting the magnesia provide the microstructural basis for a satisfactory lining life. Due to its acidic character, forsterite does not react with sulphate. This has been confirmed in several postmortem studies of samples, not only from the glass industry, where magnesia with Ca_2SiO_4 in the interstitial phase is corroded by sulphate to form merwinite, monticellite, and finally the stable

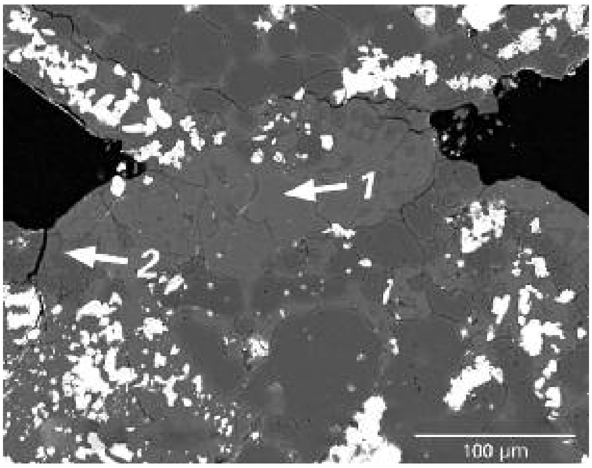

Fig. 4 **Magnesia-zircon brick sample that had undergone a laboratory corrosion test where the heating and cooling phases were under alternating reducing and oxidizing conditions, respectively. 96 cycles were performed between 800 °C and 1100 °C. Mainly sodium attack occurred. Newly formed Na-Mg-silicate (1), minimal Na-sulphur phases (2), corroded forsteritic matrix (3) with ZrO_2 (white), MgO (4), and pores (black) are indicated (source: RHI AG)**

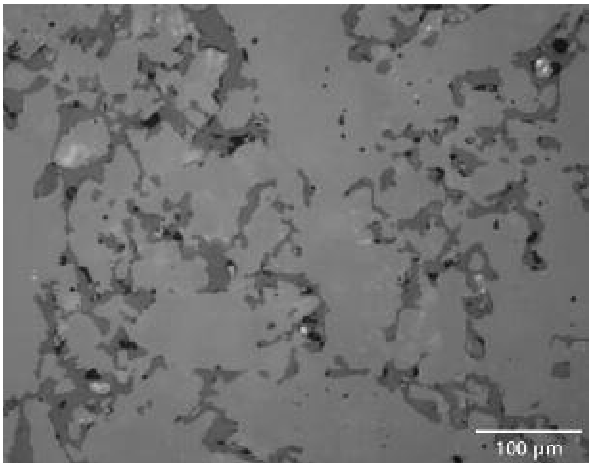

Fig. 5 **High fired pure magnesia brick.: the fines develop a strong bonding matrix (source: RHI AG)**

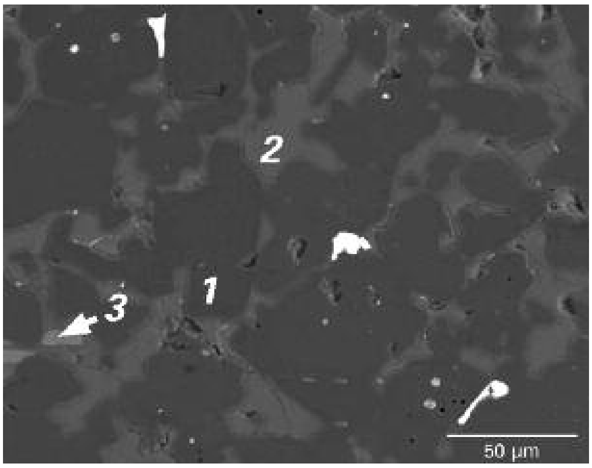

Fig. 6 **Pure magnesia brick, approximately 1,5 mm from the hot face brick, after sulphate attack caused by an oxidizing atmosphere: some residual MgO bonding bridges remain. MgO (1), Na-Mg-(K)-Ca-sulphate (2), and Ca-sulphate (3) are indicated. SEM-EDX analysis of point 2 detected 11,6 mass-% Na_2O, 18,7 mass-%, MgO, 66,0 mass-% SO_3, 1,2 mass-% K_2O, and 2,5 mass-% CaO (source: RHI AG)**

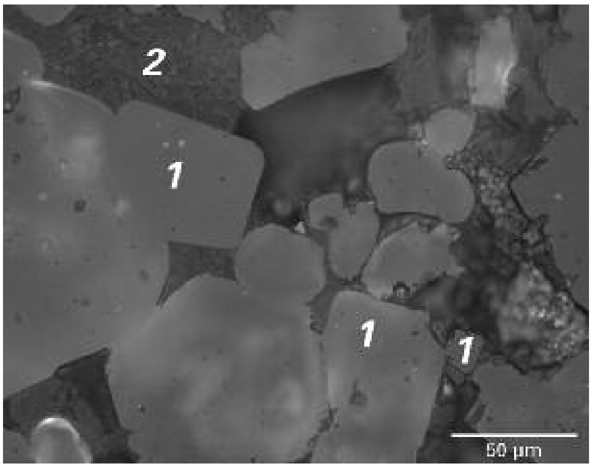

Fig. 7 **Pure magnesia brick after sulphate attack caused by an oxidizing atmosphere: precipitation of idiomorphic, cubic shaped MgO (1) from the sulphate melt (2) is visible (source: RHI AG)**

reaction product forsterite [1, 6, 7]. Fig. 2–3 provide impressive microstructural examples of a forsteritic-bonded magnesia-zircon checker brick that achieved a lining lifetime of 17 years in the condensation zone despite very high sulphate load. Even in the centre, the SO_3 load was 6,77 mass-% with a molar alkali/SO_3 ratio of 0,32. At the immediate surface there was magnesia corrosion due to sulphate attack (Fig. 2) involving the formation of Na-Mg-sulphate. However, the forsteritic bonding matrix was stable and almost unaffected. At a depth of 7 mm there was Na-Mg-sulphate infiltration and densification of the open pores but no bonding structure corrosion and only very minor corrosion of the forsterite protected magnesia grains (Fig. 3).

3.2 Magnesia-zircon bricks – reducing conditions and sodium attack

The following example is a magnesia-zircon brick sample that was exposed during a laboratory trial to a reducing atmosphere containing an excess of sodium compared to sulphur. The temperature was cycled from 800 to 1100 °C and back to 800 °C. Firing during the 30 min heating phase was under reducing conditions (3–5 % CO) whilst the 30 min cooling period was under oxidizing conditions.

A total of 96 cycles was performed. The forsterite reacted with the supplied sodium to form Na-Mg-silicate (Fig. 4). This resulted in a corroded, softened bonding structure, especially near the surface. Under strongly reducing conditions the forsteritic bonding structure in magnesia-zircon bricks is corroded by sodium attack, which increases with the exposure time and begins at the brick surface. In extreme cases even ZrO_2 can be corroded to form Na-zirconate or Na-Zr-silicate.

3.3 Pure magnesia bricks – reducing conditions and sodium attack

The usual lining recommendation for the condensation zone in the case of reducing conditions and the resulting sodium attack is a pure, low-iron magnesia brick such as ANKER DG1 or RUBINAL VS [1]. As a basic oxide, MgO has the highest resistance against basic sodium attack. The typical microscopic feature of this brick type is a very strong bonding structure between the magnesia grains (Fig. 5). In addition, the magnesia raw material purity, which should generally have a low Fe-oxide content, is highly important. The higher the sodium load, the purer the raw material should be as well as the higher the brick firing temperature.

3.4 Pure magnesia bricks – oxidizing conditions and sulphur attack

Under oxidizing conditions and a resulting molar alkali/sulphate ratio <1, corrosion of the pure magnesia brick bonding structure can occur. At a lower alkali/sulphate ratio the corrosion becomes more severe. The effect can be demonstrated with a post-mortem sample that had become affected when the atmosphere was severely changed by the operating conditions. In this extreme example a 6,8 mass-% SO_3 content with a molar Na_2O/SO_3 ratio of 0,31 was found even in the centre of some bricks. Generally, preferential corrosion of the Ca_2SiO_4 interstitial phase as well as MgO can occur. Sulphate attack in combination with a certain amount of sodium and MgO results in the formation of Ca-sulphate, Ca-Na-sulphate, Ca-Na-Mg-sulphate, and forsterite (Fig. 6). Consequently, there is also corrosion of the MgO bonding structure. As a result of MgO participating in the sulphate attack, the formation of idiomorphic, cubic shaped MgO – periclase – can also occur (Fig. 7). This can be explained by the slight thermal changes and related MgO saturation limit changes in the salt melt. Higher thermal load results in an increased ability for MgO to dissolve in the melt. When this MgO saturated sulphate melt cools, MgO precipitates, forming idiomorphic, cubic crystals within the sulphate.

4 Conclusion

There are well-proven solutions to line the regenerator condensation zone in glass melting furnaces that are selected according to the operating conditions such as the fuel type and whether the waste gas atmosphere is oxidizing or reducing. The microstructure of the various refractories is optimized for the special operational requirements in this critical lining zone.

However, when during the heating phase the usual atmosphere in the regenerator is drastically changed, the flue gas also significantly changes its corrosive potential. Atmosphere changes can occur for instance in the case of operating problems or due to NO_x reduction measures taken during the life cycle of an existing regenerator lining. Therefore, a possible impact on the existing glass tank regenerator lining and its performance must be considered. In extreme cases drastically lowered lining performance can occur.

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