Industrial Experience with Spinel-bonded Magnesia Checker Bricks in the Regenerator Condensation Zone

R. Bei, B. Schmalenbach, G. Gelbmann, Chr. Majcenovic

This article reviews the literature concerning high spinel bricks and magnesia spinel bricks for application in the glass industry. The characteristics of RUBINAL ESP, a *RHI* developed new spinel-bonded magnesia brick brand, are reported. Based on industrial experience, RUBINAL ESP can be recommended for checkers in the condensation zone of regenerators where high amounts of Na_2SO_4 and SO_3 are expected.

1 Introduction

In the regenerator of glass melting furnaces, the temperature range between 1100 °C and 700 °C is one of the most critical zones for the checker work. Under oxidizing firing conditions, the condensing alkali sulphates as well as the gaseous SO_3 can attack the checker material. Many years ago, chrome-magnesia bricks were widely used because of their high corrosion resistance. However, because of the toxic Cr^{+6} that forms during application of chrome magnesia, the refractory industry has increasingly adopted chrome-free solutions.

In the 1980s, the first magnesia zircon grade RUBINAL EZ was developed [1]. Since this time, step by step magnesia zircon has replaced chrome magnesia as a chrome-free solution. To date, the application of magnesia zircon has been a real success story and more than half the glass-makers producing high grade glass around the world use this type of product. Nowadays, RUBINAL EZ is the benchmark for this kind of application.

Zircon ($ZrSiO_4$) is one of the raw materials in these types of checkers and the coarse magnesia grains (mainly consisting of periclase crystals) are protected by a forsterite ($2MgO{\cdot}SiO_2$) and zirconia (ZrO_2) bonding matrix that forms during the brick firing process. However, as zircon is widely used in different refractory and abrasive resistant products, availability of this raw material cannot be guaranteed in the future. Therefore, it has become important to develop and evaluate the industrial performance of zircon-free magnesia products.

2 Chrome-free and zircon-free magnesia solutions in the literature

There are several refractory solutions that are chrome-free (i.e., environmentally friendly) and zircon-free (i.e., economical) and most of them are based on spinel and magnesia spinel.

High spinel bricks contain more than 90 mass-% magnesium aluminate spinel. The development and application of high spinel bricks for checkers in the regenerator condensation zone (especially when firing with heavy fuel oil) has been reported since the 1980s. In most cases fused spinel was used as a raw material to achieve higher corrosion resistance [2–5], although it was associated with a lower thermal shock resistance [2, 3, 6, 7]. The successful use of sintered spinel as a raw material has also been described [8, 9].

However, spinel is a rather expensive raw material, which makes spinel bricks cost intensive. Consequently, it has been important to look for alternatives, for example magnesia spinel bricks with reduced spinel content and a higher magnesia level.

In the literature there are inconsistent opinions regarding magnesia spinel bricks. For example it was reported that magnesia spinel bricks are less corrosion resistant in comparison to high spinel bricks [8]. In contrast, a much better overall performance was described for magnesia bricks with 25 mass-% spinel compared with the high spinel bricks, especially as a result of their good thermal shock resistance [10]. Spinel-bonded magnesia bricks with 15 mass-% Al_2O_3 have also been reported to demonstrate positive performance [4].

In the refractory industry it is a generally known fact that manufacturing magnesia spinel bricks is difficult. In particular, it is a challenge to achieve good reproducibility and stable magnesia spinel brick quality. Therefore, RHI invested considerable effort to optimize the raw material composition and grain size distribution of this brand. Together with the process parameters specially designed for this material, RHI completed the development in 2006. The result was a new grade of spinel-bonded magnesia brick termed RUBINAL ESP. In this article RUBINAL ESP is compared to the benchmark RUBINAL EZ magnesia zircon brand.

3 Characteristics of RUBINAL ESP

RUBINAL ESP is a magnesia brick with a very strong spinel bonding matrix and this matrix is resistant to sulphate attack. Therefore, RUBINAL ESP can be used in the condensation zone of a regenerator operating under oxidizing conditions. However, the application of RUBINAL ESP in a reducing atmos-

Rongxing Bei, Bernhard Schmalenbach
RHI GLAS GmbH
65203 Wiesbaden
Germany

Gerald Gelbmann, Christian Majcenovic
RHI AG, Technology Center
8700 Leoben
Austria

Corresponding author: *R. Bei*
E-mail: rongxing.bei@rhi-ag.com

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Tab. 1 Chemical composition and physical characteristics of RUBINAL ESP

Chemical Composition [mass-%]				
SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3
1,4	23,6	73,6	0,9	0,5
Physical Characteristics				
Bulk density [g/cm³]	Open porosity [vol.-%]	Cold crushing strength [MPa]	Thermal expansion [%]	Refractoriness under load [$T_{0,5}$]
2,95	15,0	60	1,4 (1400 °C)	1590 °C

Tab. 2 Checker refractory concept for the hot chamber of a multiple-pass regenerator

No. Layers	Brand	Brick Type
2	DURITAL K99EXTRA	Sintered high alumina
8	ANKER DG1	Magnesia with MgO-MgO direct bonding
19	RUBINAL ESP	Spinel-bonded magnesia
2	RUBINAL EZ	Magnesia zircon

phere is not recommended. Under reducing conditions, the magnesia brick with MgO-MgO direct bonding – ANKER DG1 – has shown good behaviour in long-term applications. Table 1 details the chemical composition and physical properties of RUBINAL ESP.

4 Field test

Three checker brick grades were tested in the regenerator of a soda-lime container glass furnace. Since the chambers were so-called multiple-pass chambers, the condensation zone was situated between the hot and cold chamber. Therefore, it was possible to test samples without disturbing the checker setting.

The checker brick grades examined were:

- magnesia brick with MgO-MgO direct bonding (ANKER DG1).
- magnesia zircon brick (RUBINAL EZ).
- spinel-bonded magnesia brick (RUBINAL ESP).

The expected SO_3 attack on the magnesia brick (ANKER DG1) started rather quickly, namely after 3 months testing, whilst the RUBINAL ESP and RUBINAL EZ remained in good condition. Microscopic analysis of the checker surface region (Fig. 1) showed that the matrix in the RUBINAL ESP and RUBINAL EZ protected the magnesia.

5 First application in an industrial furnace

At the beginning of 2007, RUBINAL ESP was installed in the regenerator condensation zone of an end-fired soda-lime glass furnace during an intermediate repair. As in the field test, the regenerator was multiple-pass. The checker concept for the hot chamber is detailed in Tab. 2.

After an application period of 3 years, the furnace was cooled down because of a complete rebuild. Macroscopically, the spinel-bonded magnesia brick (RUBINAL ESP)

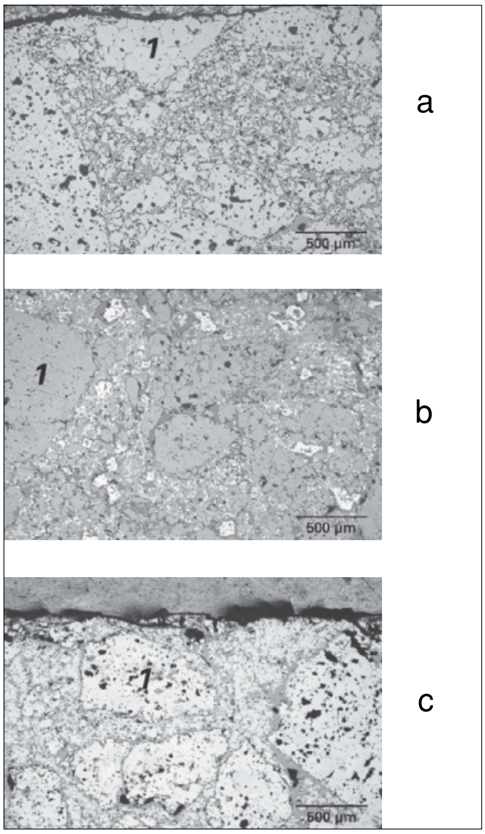

Fig. 1 Microscopic analysis of the checker surface region after 3 months application in the condensation zone:
(a) ANKER DG1 magnesia brick with MgO-MgO direct bonding: matrix corrosion is observed up to a few millimeters from the surface, the pores are filled with Na_2SO_4, and the magnesia (1) has started to corrode; (b) RUBINAL EZ magnesia zircon brick: no attack on the forsterite and ZrO_2 matrix and the magnesia (1) has only minor corrosion;
(c) RUBINAL ESP spinel-bonded magnesia brick: no attack on the spinel matrix is visible and the magnesia (1) has only minor corrosion

Fig. 2 The spinel-bonded magnesia brick (RUBINAL ESP) after 3 years application

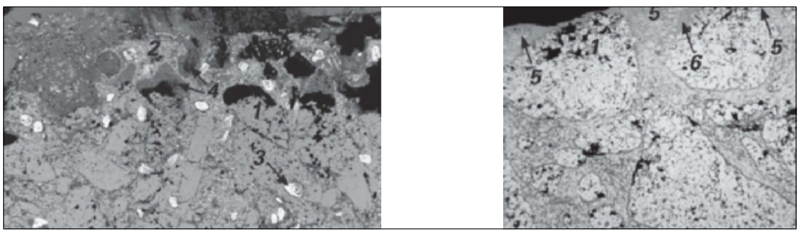

Fig. 3 Microscopic analysis of the checker brick surface region after a 3 year campaign in the condensation zone: (a) RUBINAL EZ magnesia zircon brick: premature wear of magnesia (1) is evident up to a depth of 1 mm from the surface and the forsterite-zirconia matrix (2), ZrO_2 (3), pores (4) filled with reaction product are indicated;
(b) RUBINAL ESP spinel-bonded magnesia brick: slight corrosion of the magnesia (1) and the spinel matrix (5) was only corroded up to 0,5 mm from the surface. The resin (6) for sample preparation is indicated

showed good performance after 3 years application in the condensation zone (Fig. 2).

The magnesia zircon brick (RUBINAL EZ) from the second layer and the spinel-bonded magnesia brick (RUBINAL ESP) directly above this RUBINAL EZ layer were analysed in detail to provide a direct comparison between the two grades (Fig. 3).

Microscopic examination of the magnesia zircon brick (RUBINAL EZ) showed no visible attack on the matrix comprising forsterite and ZrO_2 (Fig. 3a). Whilst the periclase crystal on the hot face had minor corrosion, directly under the surface the original brick structure was unaffected.

The spinel-bonded magnesia brick (RUBINAL ESP) microstructure showed only slight visible attack on the spinel matrix (Fig. 3b). Similar to the magnesia zircon sample, the periclase crystal on the hot face demonstrated only minor corrosion and directly under the surface the brick bonding structure was unaffected.

6 Conclusion

For soda-lime glass production under oxidizing conditions, the main attack in the regenerator condensation zone is caused by Na_2SO_4 and SO_3. In this atmosphere the spinel-bonded RUBINAL ESP checker brick showed good performance. Following a field test lasting 3 months and industrial application for 3 years, macroscopically and microscopically the bricks showed high resistance against Na_2SO_4 and SO_3. RUBINAL ESP can be recommended for the regenerator condensation zone of end-fired furnaces and for the first few chambers of cross-fired furnaces, because in these chambers high amounts of Na_2SO_4 and SO_3 are expected.

References

[1] Schmalenbach, B.; Weichert, T.: Soda lime glass tanks checker material for regenerative chambers wear mechanism and lining recommendations. World Glass 2 (1987) 2–4

[2] Schmalenbach, B.; Weichert, T.: Weiterentwicklung chromfreier Steine für die mittleren Lagen von Regenerativkammern. Didier Technical Information, Wiesbaden 1984

[3] Schmalenbach, B.; Weichert, T.: Further development of chrome-free bricks for the middle layers of checkerwork. Didier Technical Information, Wiesbaden 1989

[4] Kettner, P.; Christof, G.: MA-spinel brick in glass furnace regenerators. Radex-Rundschau (1986) [1] 3–11

[5] Olbrich, M.; Rostami, F.: Sodium sulphate attack on magnesia aluminate spinel bricks. Glastechn. Ber. 63 (1990) 204–209

[6] Künstner, D.: Verhalten feuerfester Steine in den mittleren Lagen von Regenerativkammern. Presented at Fachausschuss II der Deutsche Glastechnische Gesellschaft, Karlsruhe, Germany, 22 March 1983

[7] Dhupia, G.; Krönert, W.; Goerenz, E.: Untersuchungen an Gittersteinen für die mittleren Lagen von Regenerativkammern. Presented at XXVIIIth Int. Coll. on Refractories, Aachen, Germany, 10–11 Oct. 1985, 149–181

[8] Ichikawa, K.; et al.: Application of spinel checker brick for glass furnace regenerators. Taikabutsu Overseas 15 (1995) [3] 30–35

[9] Kurashina, Y.; et al.: Chrome-free lining for glass furnace regenerators. Shinagawa Technical Report 45 (2002) 61–68

[10] Bartha, P.: Entwicklungstendenzen bei spinellhaltigen feuerfesten Steinen für die mittleren Lagen von Kammergitterungen ölbeheizter Glasschmelzöfen. Glastechn. Ber. 58 (1985) 288–294