ER 2001 SLX – Very Low Exudation AZS Product for Glass Furnace Superstructures

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Fused-cast refractories are widely used in superstructure of soda-lime-silica glass furnaces due to their high resistance to corrosion by the furnace's atmosphere. However, the exudation of the vitreous phase of AZS refractories, at high temperatures, can lead to the formation of defects in the glass, especially during furnace's start-up. The ability of the furnace to digest these inclusions may be not sufficient to avoid production losses for glassmakers. To solve this problem, a new fused cast AZS refractory named ER 2001 SLX has been developed. It offers a zero exudation level under typical glass furnace operating conditions and maintains or enhances all other positive characteristics of fused-cast AZS.

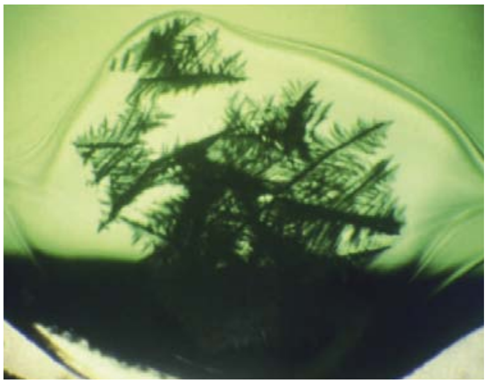

Fig. 1 Glass defect arising from the AZS superstructure

1 Introduction

The most widely used refractories in a glass tank superstructure, except silica, are fused-cast AZS (Alumina Zirconia Silica) materials. They need to provide high resistance to elevated temperature that can vary between 1500 and 1650 °C, and also to chemical attack that comes from batch carry over and from volatile species like alkaline vapours [1, 2]. The glassy phase exudation from fused-cast AZS (expulsion of a part of their vitreous phase at the surface), is a phenomenon which has been widely studied and can be related to a rise in temperature (so generally occurring during furnace heat-up) and also to superstructure attack during the campaign [3–7]. Indeed, the temperature level and/or the aggressive running conditions such as reducing atmosphere, high alkali content and carryover enhance this exudation [8]. This can lead to problems directly affecting the glass quality by generating defects such as vitreous enriched alumina defects with or without secondary zirconia crystals (Fig. 1) [9]. In order to prevent these defects, a new AZS product was developed named ER 2001 SLX with a zero exudation level at high temperature.

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2 Laboratory study of AZS exudation behaviour

To evaluate the exudation of refractory products two main tests were used (Fig. 2). The first one, named "Louisville test", is used as quality control by the company's plants, and consists in measuring the percentage of volume increase of a disc-shape specimen after a test of 16 h at 1500 °C. The second one, named "bar test", consists in measuring the percentage of volume increase on a bar-shaped specimen after two cycles from room temperature to 1500 °C with a 4 h dwelling time. This test enables the assessment of effects, that occur only during transitory temperature operations such as the redox reaction involving impurities (Fe, Ti) and allows identifying clear tendencies on larger size specimens.

3 Chemical and microstructure caracteristics of the new ER 2001 SLX

This new product belongs to the chemical composition area of the AZS (Alumina Zirconia Silica) ternary system (Tab. 1 and Fig. 3).

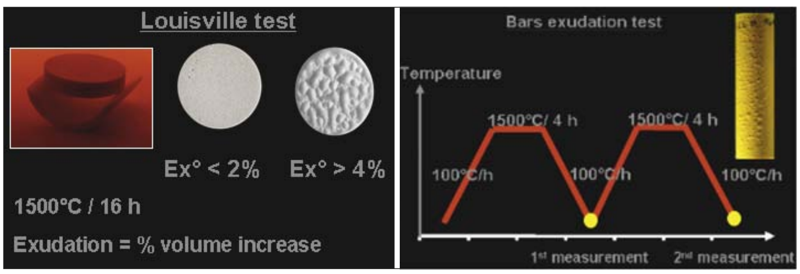

Fig. 2 Exudation tests "Louisville" and "on bars"

Tab. 1 Chemical analysis [mass-%]

	ZrO_2	Al_2O_3	SiO_2	Na_2O	Zirconia	Corundum	Vitreous phase
ER 1681	32,5	51,2	15,0	1,3	32	47	21
ER 1851	36,0	53,1	10,0	0,9	35	51	14
ER 2001 SLX	17,0	68,3	13,0	1,7	16	63	21

Tab. 2 Exudation level of ER 2001 SLX compared to classical AZS material

Exudation [%]	Louisville test	Bar test (1st cycle)	Bar test (2nd cycle, cumulated)
ER 1681	1,5	2,7	5,4
ER 1851	0,7	2,6	3,4
ER 2001 SLX	0	0	0

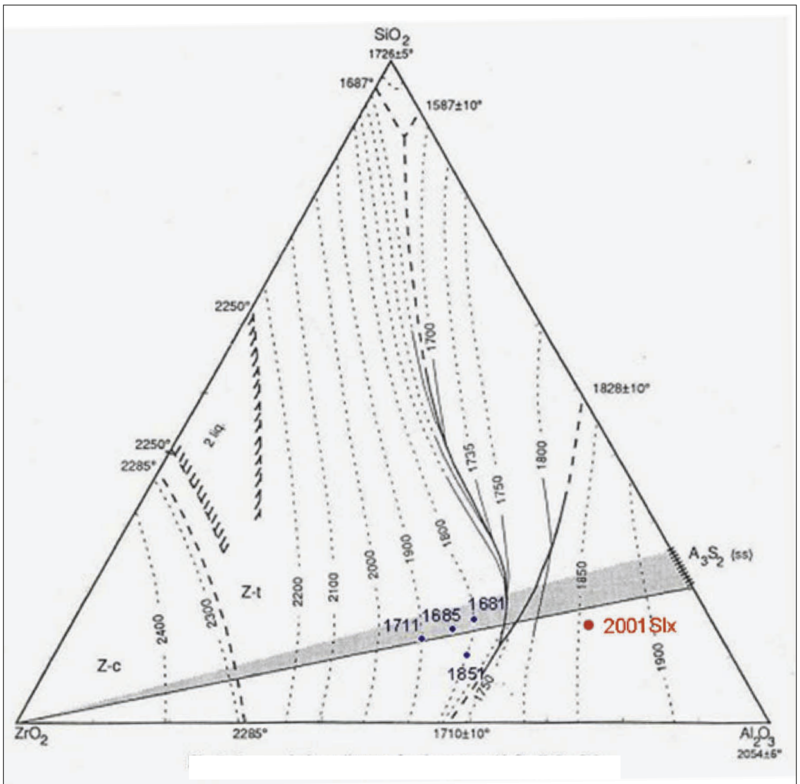

Fig. 3 Situation in the AZS ternary system

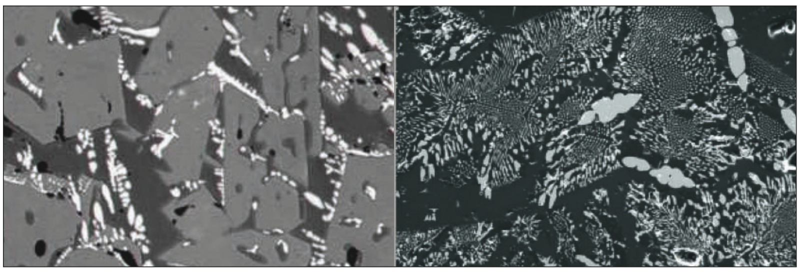

Fig. 4 Microstructure of ER 2001 SLX (left) and ER 1681 (right) (2D section)

This composition leads to a microstructure made of separated corundum and zirconia crystals (without eutectic arrangement), with an alumino-silicate glassy phase (Fig. 4).

4 Exudation test results

The exudation measured with the two different tests on the new product ER 2001 SLX are compared to typical values of ER 1681 and ER 1851 in Tab. 2. These tests have been repeated several times to obtain reliable values. These results clearly indicate that the exudation level of the new AZS material ER 2001 SLX is zero (see Fig. 5).

In order to obtain this new AZS that exhibits zero exudation, there were combined:

- the same controlled amount of glassy phase, with quite identical chemistry, low level of impurities and oxidation level, as in conventional AZS materials such as ER 1681 and ER 1851
- and a highly imbricated microstructure associated to the particular chemical composition and solidification path. Indeed, the percolation of the glassy phase is much higher in ER 1681 / ER 1851 than in ER 2001 SLX (see the products on Fig. 6 cleaned out of their vitreous phase after a treatment in HF solution), which explains why it is harder for the glassy phase to be exuded from ER 2001 SLX. Moreover this phase is less compressed by the zirconia transformation during heating up (inducing shrinkage) as the zirconia content is lower in the product.

5 Dynamic exudation tests

Some exudation tests under stronger conditions were also performed (at temperature up to 1675 °C), under video observation (Fig. 7). In such tests, the exudation of ER 2001 SLX remains very low.

At very high temperature, the very low exudation of ER 2001 SLX induces the preservation of its original microstructure and internal crystalline cohesion without creating porosity as in other AZS refractories (Fig. 8). This will make it very resistant to corrosion by carry over and alkaline vapours in operating conditions.

6 Vapour phase corrosion resistance

The ER 2001 SLX product has also a good behaviour in vapour phase corrosion tests. Penetration of soda seems especially limited

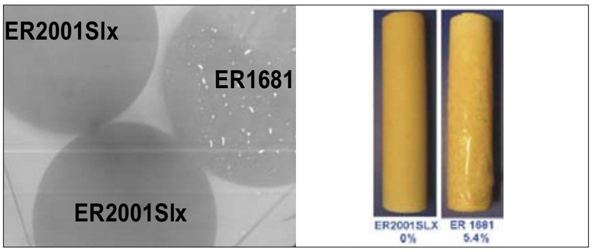

Fig. 5 Louisville test (at 1500 °C) and bar test specimens after testing on ER 2001 SLX and ER 1681

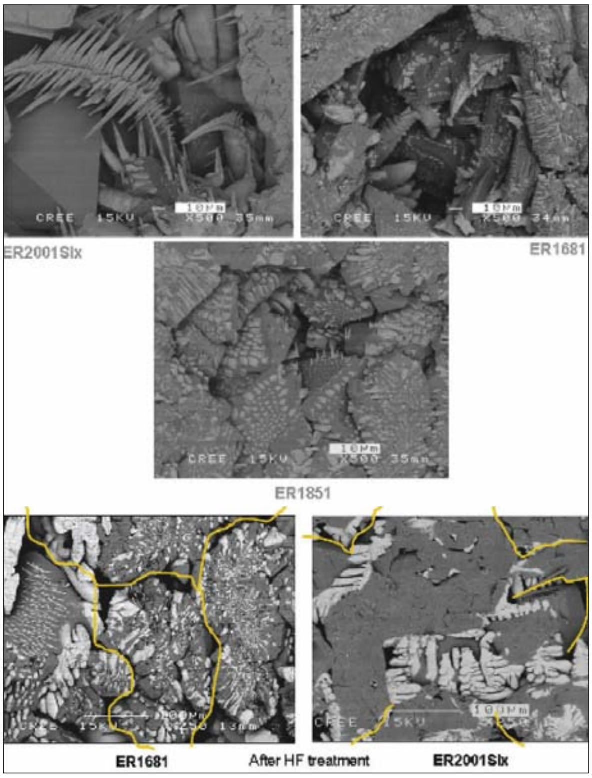

Fig. 6 SEM on AZS after HF treatment in ER 1681 vs ER 2001 SLX

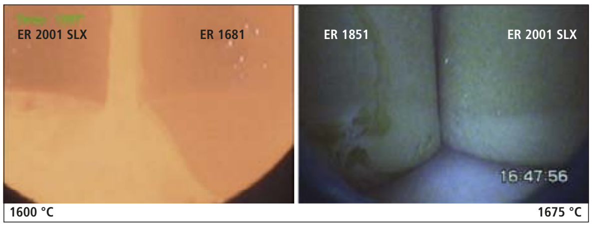

Fig. 7 Pictures taken during high temperature bar test

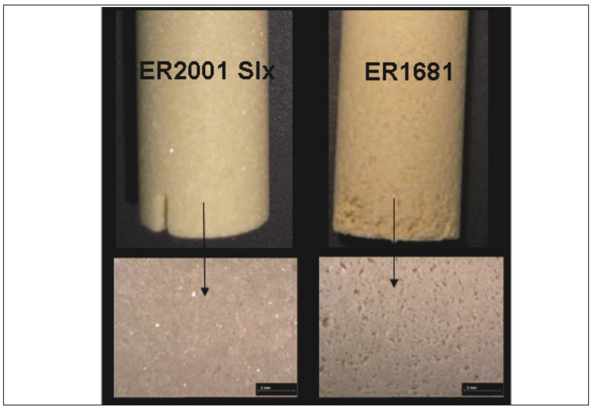

Fig. 8 Bars after exudation test at 1650 °C

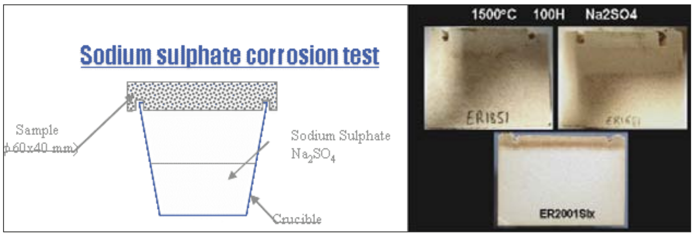

Fig. 9 Alkaline vapour phase corrosion test; specimens' attack faces after test

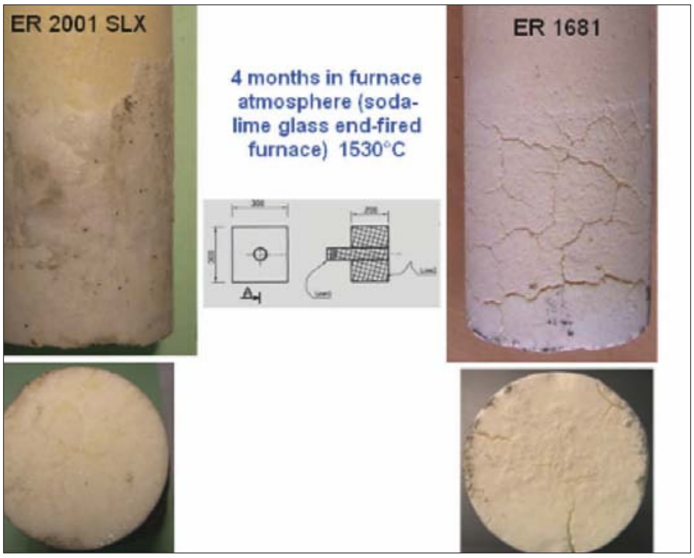

Fig. 10 ER 2001 SLX vs ER 1681 after 4 months in an end-fired glass furnace

by the low percolation of vitreous phase (Fig. 9).

7 Industrial experiences

Some samples were tested in industrial furnaces melting soda-lime-silica glass. These confirm that ER 2001 SLX exhibits excellent performance, in vapour phase and carryover corrosion. After few months in real conditions, one can easily differentiate the behaviour of the ER 2001 SLX compared to regular 32 % AZS material: porosity and enrichment in alkaline species in ER 2001 SLX is lower (Fig. 10 and Tab. 3).

Moreover, since 2005, many furnace superstructures have been built with ER 2001 SLX. There was the opportunity to perform some endoscopic observations in some furnaces to verify and illustrate the good behaviour of the product in operating conditions, as expected (Figs. 11, 12).

8 Conclusion

During recent years, glass furnace performances have been driven by the requirement for an ever increasing improvement in glass quality. One source of glass defect comes

Tab. 3 ER 2001 SLX vs ER 1681 after 4 months in an end-fired glass furnace, chemical analysis (Enrichment in Na_2O [mass-%])

Distance from high temp. surface / Products	0 cm	2 cm	5 cm
ER 2001 SLX	2,65 (+ 56 %)	2,40 (+ 41 %)	1,84 (+ 8 %)
ER 1681	2,94 (+ 126 %)	2,74 (+ 111%)	2,47 (+ 90 %)

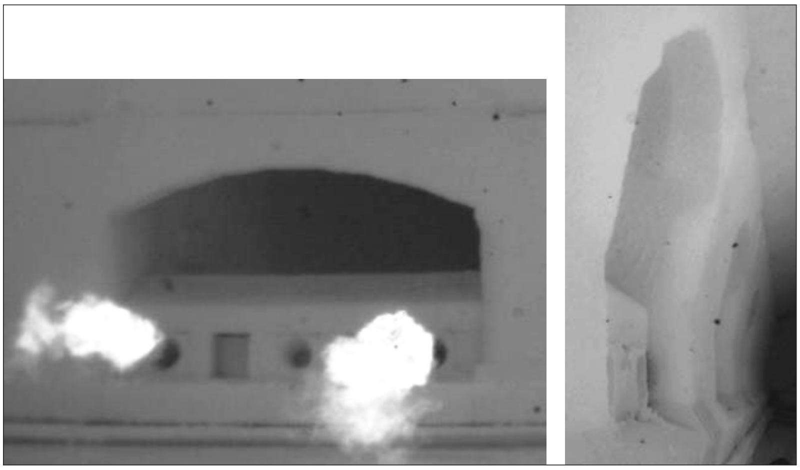

Fig. 11 Endoscopic observation in a float furnace after 2 ½ years of ER 2001 SLX use (T ~ 1585 °C)

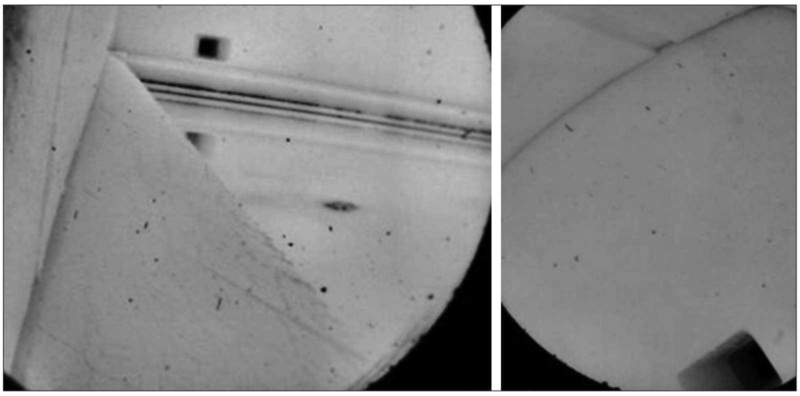

Fig. 12 ER 2001 SLX tuckstones and frontwall in a pattern glass furnace after 2 years of use (T ~ 1530 – 1580 °C)

from thermal and chemical interactions of the furnace atmosphere with the refractories. In soda-lime-silica glass furnace superstructures, AZS fused-cast refractories are widely used as they provide high resistance to high temperature. In order to help glassmakers regarding glass quality issue, there was developed the new AZS fused-cast product ER 2001 SLX that exhibits a zero exudation at high temperature. This behaviour also induces a lower reactivity with the furnace atmosphere, compared to a current fused-cast AZS product, which can become more porous during furnace operation, due to the glassy phase exudation, thus being more sensitive to vapour attack. This new material is made of separated corundum and zirconia crystals, and is characterized by a very low level of glassy phase percolation. This microstructure confers also to the product a good resistance regarding alkali vapour attack, as it results in lower diffusion of alkaline species into the refractory. This has been confirmed by the analysis of specimens picked up in industrial glass furnaces. Furthermore, a low thermal expansion coefficient, reflecting the lower zirconia shrinkage, will help to close the joints between the blocks with this product.

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