
Technical Report

Influence of glass composition on high zirconia fused cast refractory corrosion

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Chemical composition and microstructure of individual phases of corroded high zirconia fused cast (HZFC) refractory have been examined in various places and distances from the interface with molten glass of different compositions. An unused HZFC block (ER 1195 RT) as well as blocks corroded by lead glass for lighting purpose, container white glass and Simax glass, respectively, have been investigated. Static crucible corrosion tests have been carried out at 1450 °C for 100 h. Samples of refractories were studied by means of scanning electron microscopy with energy dispersive X-ray spectroscopy and X-ray diffraction. The greatest changes were observed only in the glassy phase composition of individual corroded samples.

1. Introduction

Fused cast refractories containing various amounts of ZrO_2 are used extensively in glass tank construction because of its considerable resistance to corrosion by molten glass and to the glass melting environment. For this reason alumina-zirconia-silica (AZS) refractories are widely used in glass melting furnaces [1]. However, it is known that glass defects such as viscous knots, stones and bubbles of refractory origin will typically come from fused cast AZS refractory due to variable dissolution rates of alumina and zirconia phases [2]. Thus the search for refractories for use in contact with glass with a lower potential for causing defects began. Whereas the corrosion of fused AZS refractory by glass is characterized by the formation of a two-phase interface, high zirconia fused cast (HZFC) refractory corrosion by glass is characterized by the phenomenon of frontal dissolution of zirconia in the glass [3]. Dissolution of zirconia takes place in the absence of biphasic interface between the glass and refractory, thus eliminating the source for some glass defects. Corrosion of HZFC refractory by lead crystal glass and, in part, colour TV panel glass was studied previously [4 and 5]. The main interest was the origin of defects in glass. The main purpose of this work was to study the chemical composition and microstructure of individual phases of corroded HZFC refractory in various places and

distances from the interface with molten glass of different compositions.

2. Experimental

The samples of unused HZFC refractory (ER 1195 RT, SEPR, Le Pontet (France)) contained (in wt%): 94.2ZrO₂, 1.2Al₂O₃, 4.0SiO₂, 0.3Na₂O and < 0.3TiO₂ + Fe₂O₃. The mineralogical composition of this material is 94 wt% of monoclinic zirconia (baddeleyite) and 6 wt% of the glassy phase. From these compositions we calculated the chemical composition of glassy phase (in mol%): 0.56ZrO₂, 13.66Al₂O₃, 77.26SiO₂, 5.62Na₂O and about 2.90TiO₂ + Fe₂O₃.

The average chemical compositions of the glasses used for static isothermal corrosion tests are given in table 1.

Samples (5 × 5 × 4) cm³ for the present investigation were obtained from commercial fused cast ER 1195 RT blocks. The crucible test was carried out by placing glass cullet into holes with diameter 2.6 cm and depth 3 cm in the samples. The test samples thus obtained were placed on a platinum foil and heated in air at 1450 °C for 100 h. A heating rate of 10 K min⁻¹ and spontaneous cooling were used. The corroded crucible was sectioned to obtain samples for microstructural and compositional examinations (figure 1). Samples were ground and polished using standard ceramographic techniques. The surface of the samples was cleaned

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Table 1. Chemical composition of glasses used in this work in mol%

	Simax glass	lead glass	container white glass
SiO ₂	83.20	76.83	72.66
Al ₂ O ₃	1.71	0.92	1.14
Na ₂ O	3.56	9.17	11.52
K ₂ O	0.47	5.74	0.89
CaO	0.22	0.28	10.74
MgO	0.15	=	3.03
B ₂ O ₃	10.64	-	-
PbO	-	6.95	=
Sb ₂ O ₃	-	0.08	-
Fe ₂ O ₃	0.03	0.03	0.02

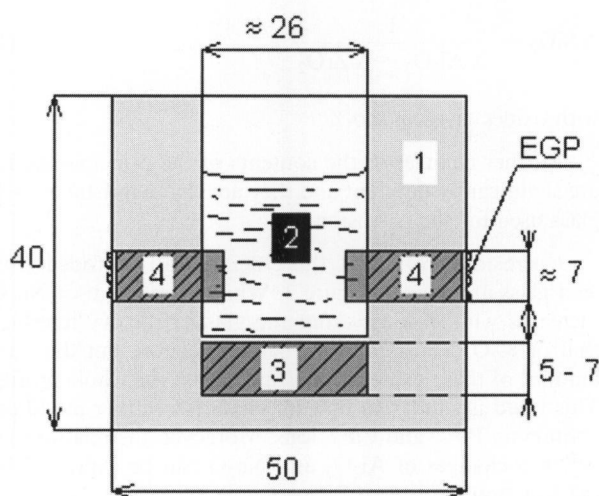


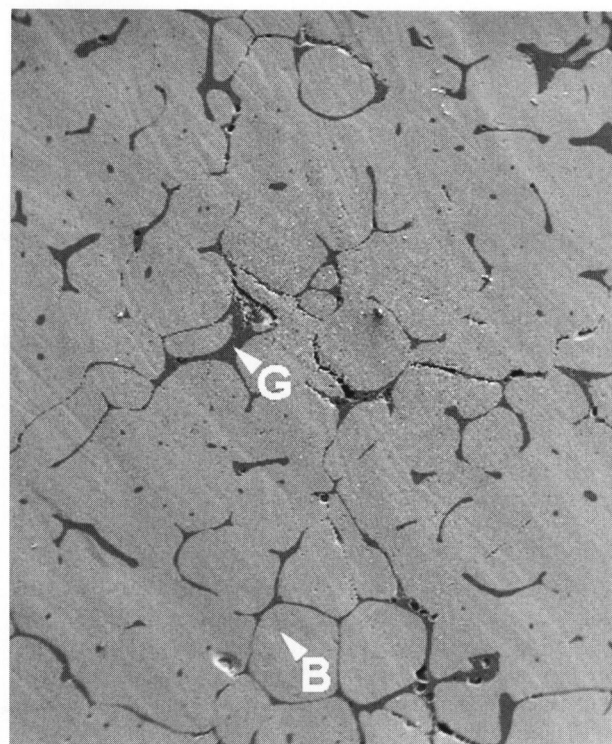
Figure 1. Crucible for static corrosion test and places from which samples were taken (dimensions in mm); 1: refractory material ER 1195 RT, 2: glass used for corrosion test, 3 and 4: samples sawn from bottom and sides, respectively, EGP: exuded glassy phase.

thoroughly in deionized water for about 30 min using an ultrasonic stirrer.

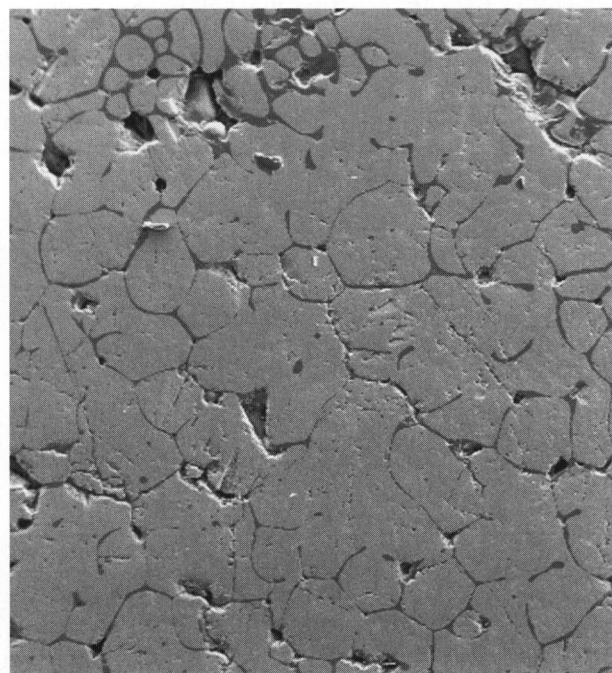
The microstructures of the samples were investigated by scanning electron microscopy (SEM). The phase analysis of the crystalline components was carried out on polished samples by X-ray diffraction (XRD) (CuK α radiation). The chemical composition of the crystals as well as that of the glassy phases in all samples were determined by energy dispersive X-ray spectroscopy.

3. Results and discussion

The characteristic microstructure of ER 1195 RT refractory (figures 2a and b) consists of grains of baddeleyite separated from each other with a thin glass layer. A comparison of the SEM micrograph of the corroded refractory with that of the unused refractory showed that the microstructure was not affected significantly. The major differences can be observed in the form and size of originally larger crystals of



a) | 100 μm



b) | 100 μm

Figures 2a and b. Typical scanning electron micrograph of a) unused ER 1195 RT refractory and b) the same refractory after corrosion test with Simax glass; B: baddeleyite, and G: glassy phase.

ZrO₂, some of which disintegrate into smaller crystals or particles, probably due to the phase transformation of ZrO₂ at about 1100 °C. It seems, however, that during the corrosion test the ZrO₂ crystals were also partially dissolved.

Table 2. Average chemical composition of glassy phase in mol% of unused refractory material ER 1195 RT and that of samples from the bottom of the crucibles after corrosion testing with various glasses

	unused refractory	lead glass	container white glass	Simax glass ^{*)}
SiO ₂	78.57±0.48	60.87±4.94	72.69±0.78	63.42±5.09
Al ₂ O ₃	12.61±0.28	7.27±1.37	12.47±0.11	12.67±1.52
ZrO ₂	1.74±0.49	13.59±2.52	4.43±0.86	12.58±7.51
Na ₂ O	5.47±1.10	9.71±3.38	7.01±0.42	8.73±1.79
K ₂ O	-	2.31±0.51	0.90±0.05	1.04±0.12
CaO	0.92±0.11	2.28±0.40	2.50±0.07	1.56±0.17
PbO	-	3.97±0.30	-	-
TiO ₂	0.68±0.05	-	-	-

^{*)} The B₂O₃ content was not determined.

In all samples (unused and corroded refractories) only monoclinic ZrO₂ (baddeleyite) was confirmed in the X-ray diffraction patterns. However, the relative intensities of individual peaks were often different, which can be explained in terms of various orientations of ZrO₂ crystals in compact polished samples.

The chemical composition of individual phases was determined by EDS microanalysis on the surfaces of both unused and corroded samples. In all samples the quantitative analysis of crystalline phases confirmed that their composition was consistent with ZrO₂. Substantial changes were observed only in the glassy phase composition of individual samples. The average compositions of glassy phase of samples removed from the bottom of the crucibles are given in table 2. Analyses from at least five places on the surface of each of the samples were recorded. The chemical composition of glassy phase of unused material compared with that calculated (theoretical) from the average chemical and mineralogical composition shows very little deviation in content of all oxides present, except the content of ZrO₂. This is probably due to higher dissolution of ZrO₂ grains into the glassy phase during the refractory material production. Because of this difference, comparison of measured data only of both unused and corroded material is used in this work.

The glassy phases in the corroded refractories are always richer in ZrO₂, Na₂O, K₂O and CaO. On the other hand, the SiO₂ content decreases, while the Al₂O₃ content remains unchanged except for the corrosion by the lead glass. Moreover, it was found that the total amount of SiO₂, Al₂O₃ and ZrO₂ was approximately constant in every analysed region of the glassy phase in the same sample. This suggests that all of these oxides act as glass-forming oxides and the others are modifiers (except TiO₂). While the total amount of glass-forming oxides decreases in the glassy phase of corroded refractories that of typical modifiers (Na₂O, K₂O and CaO) increases. However, the ZrO₂ content always increases. From the results obtained we conclude that both the high temperature and the penetration of Na⁺, K⁺, Ca²⁺ and Pb²⁺ ions from the molten glasses into the refractory cause dissolution of the baddeleyite grains. However, the resulting compositions of the glassy phases do not unambiguously correlate with the modifier contents of the glasses (see table 1).

As well as the corrosion of the bottom of the crucible, the influence of the molten glasses on the glassy phase compositional changes of samples sawn from sidewalls of the test crucibles has been examined. Concentration profiles of the principal oxides in the glassy phases of corroded samples are shown in figures 3 to 5. The composition of the glassy phase was measured at the same distance at least three times (maximum deviation was about 0.1 mm).

The greatest changes in oxide contents of all the corroded samples were observed up to a distance of about 1 mm from the molten glass/refractory interface. Some of the overall changes are common for all of the corroded samples. The total amount of the glass-forming oxides, SiO₂, Al₂O₃ and ZrO₂, is nearly constant. If significant changes in these oxides were observed, the relationship between them may be expressed as:

$$\Delta \text{SiO}_2 \approx \frac{1}{\Delta \text{Al}_2\text{O}_3 + \Delta \text{ZrO}_2} \quad (1)$$

with oxides given in mol%.

Further changes in the contents of the principal oxides are significantly different and they are characteristic of each glass used for the corrosion test.

Corrosion profiles of the crucible wall corroded with lead glass are given in figure 3. While the content of Na₂O increases with distance from the glass/refractory interface that of K₂O decreases in the same direction, but the total amount of these oxides is constant across the whole profile. This trend is similar to that for changes of other modifiers containing Pb²⁺ and Ca²⁺ ions. Moreover, the relationship between changes of Al₂O₃ and Na₂O can be expressed by the equation:

$$\Delta \text{Al}_2\text{O}_3 \approx \Delta \text{Na}_2\text{O} \quad (2)$$

with oxides given in mol%.

A comparison of the above results with those obtained from the bottom samples or from the unused material shows

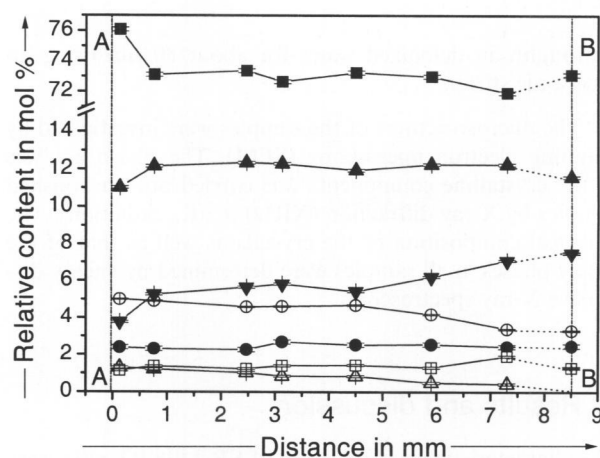


Figure 3. Concentration profiles of the principal constituents of the glassy phase in samples from sidewall corroded by lead glass; ■: SiO₂, ▲: Al₂O₃, ▼: Na₂O, ○: K₂O, ●: ZrO₂, □: CaO, △: PbO; section A-A represents lead glass / ER 1195 RT refractory interface, and B-B represents refractory material / furnace environment interface.

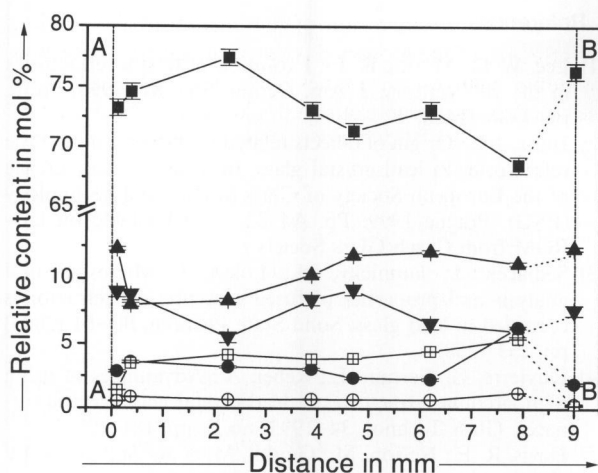


Figure 4. Concentration profiles of the principal constituents of the glassy phase in samples from sidewall corroded by container white glass; ■: SiO₂, ▲: Al₂O₃, ▼: Na₂O, □: CaO, ●: ZrO₂, ○: K₂O; section A-A represents container white glass / ER 1195 RT refractory interface, and B-B represents refractory material / furnace environment interface.

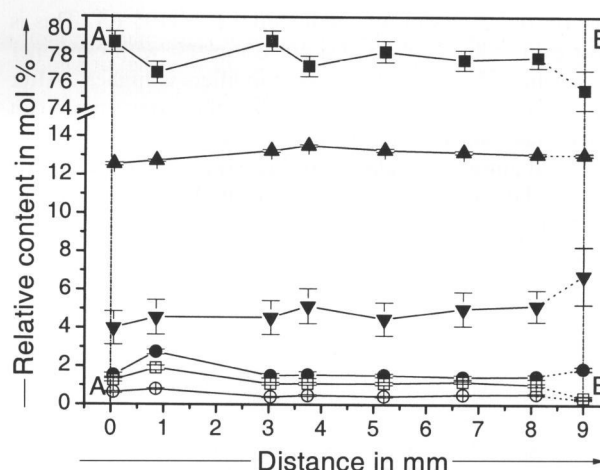


Figure 5. Concentration profiles of the principal constituents of the glassy phase in samples from sidewall corroded by Simax glass; ■: SiO₂, ▲: Al₂O₃, ▼: Na₂O, ●: ZrO₂, □: CaO, ○: K₂O; section A-A represents Simax glass / ER 1195 RT refractory interface, and B-B represents refractory material / furnace environment interface.

that: a) the average amounts of SiO₂, Al₂O₃, ZrO₂ and Na₂O are close to the contents of these oxides in the glassy phase of unused material, b) the content of PbO decreases with distance from the interface with glass and it is always lower than that observed in the sample from the bottom, c) the content of K₂O is much greater than that at the bottom.

These statements result from the significant changes in K₂O and PbO contents at the sidewalls resulting from corrosion by the lead glass compared with the composition of the glassy phase of unused refractory. The diffusion of K⁺ and Pb²⁺ ions from the glass melt into the refractory ER 1195 RT occurs during corrosion by lead glass and their contents decrease with increasing distance from the refractory/glass interface. Differences between the composition of glassy phase of the samples from bottom and sidewall can be explained in terms of various diffusion rates at both interfaces with lead glass. From technological practice and from our previous study [3] it is known that in glass tanks the content of PbO increases toward the bottom due to gravity. It may be stated that with the static corrosion test, even though it was isothermal, a similar phenomenon occurs. The Pb²⁺ richer glass then acts as diffusion barrier for the K⁺ ions at the bottom. On the other hand, since this barrier does not occur at the sidewalls so much, the K⁺ ions can penetrate into the glassy phase of refractory to a higher degree.

The results obtained from the crucible wall corroded with container glass are given in figure 4. In this case both the most significant and the most irregular changes were observed in the corrosion profiles of the principal oxides. The contents of modifiers K₂O and CaO gradually increase with the distance from the molten glass/refractory interface, whereas the content of Na₂O changes irregularly. Moreover, the changes of Na₂O content are usually directly proportional to those of Al₂O₃.

The average contents of the principal oxides in the glassy phase of the sidewall samples are nearly the same as those

obtained from the bottom samples. Only the CaO content significantly increases owing to the greater diffusion of Ca²⁺ ions from the molten glass into the refractory wall.

Corrosion profiles of the crucible wall corroded with Simax glass are given in figure 5. The contents of K₂O and CaO are almost constant, whereas the content of Na₂O increases with the distance from the refractory/glass interface. The relationship of the content changes among Na₂O, Al₂O₃ and SiO₂ may be expressed as:

$$\Delta \text{Na}_2\text{O} \approx \frac{\Delta \text{Al}_2\text{O}_3}{\Delta \text{SiO}_2} \quad (3)$$

with oxides given in mol%.

The composition of the glassy phase of the wall samples is nearly identical to that in unused material but there are some differences in SiO₂, Al₂O₃, Na₂O and K₂O contents when compared to those of the bottom samples.

4. Conclusions

In summary, it may be stated that the microstructure of the corroded samples of high zirconia fused cast refractory (ER 1195 RT) was not affected significantly. It seems, however, that during the corrosion test the ZrO₂ crystals were partially dissolved. The greatest changes were observed only in the glassy phase composition of individual corroded samples. The most compositional changes of the glassy phase in samples were observed by the corrosion in the lead glass and, especially, in the samples from the bottom of the test crucibles. On the other hand, the composition of glassy phase of the crucible wall corroded with Simax glass is nearly identical to that in unused material. We may conclude from the above results that the relative contents of individual modifiers in molten glass have significant influ-

ence on the corrosion of the material ER 1195 RT. This is most evident in the case of a corrosion test with container glass, where the content of glass modifiers is highest. After their diffusion into the refractory the other constituents can easily penetrate too due to glassy phase structure release. The total amounts of glass-forming oxides and modifiers as well as their relative proportions in molten glasses are of importance too, as they have different influence on glass structure.

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