The corrosion resistance of high ZrO_2 fusion-cast Al_2O_3–ZrO_2–SiO_2 glass refractories in soda lime glass

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The corrosion resistance to soda lime glass of fusion-cast high zirconia Al_2O_3–ZrO_2–SiO_2 compositions is evaluated. It is concluded that these materials offer no improvement in corrosion resistance over the typical commercially available 40 wt % zirconia refractory in this glass. Furthermore, it is concluded that an optimum mixture of alumina and zirconia exists which has better corrosion resistance to soda lime glass than either end member. Finally, it is suggested that this trend in corrosion resistance is due to the interdependent solubilities of alumina and zirconia in the glass.

1. Introduction

Zirconia was first added in small amounts to a fused mullite–alumina refractory composition in 1927 to improve manufacturability, i.e. reduce cracking [1]. Later, in 1942, Field [2] demonstrated that zirconia, if partially substituted for silica, improves the corrosion resistance of the refractory. Over the years advancements in composition and processing have been achieved to improve the performance of the fused Al_2O_3–ZrO_2–SiO_2 refractory. The modern product is a void free, oxidized material containing about 25 vol % of a continuous glass phase and between 30 and 42 wt % zirconia.

The most often cited evidence used to explain the corrosion resistance improvement resulting from zirconia additions can be seen in Fig. 1. This figure shows the interface of a typical fused Al_2O_3–ZrO_2–SiO_2 refractory with soda lime glass. The interface consists of a glass matrix and zirconia crystals. The alumina crystals have been dissolved. The conclusion is that zirconia is a more durable phase than alumina and thereby improves the overall corrosion resistance of the body. It follows that compositions with higher levels of zirconia may be even more corrosion resistant than the typical modern product.

High zirconia fusion-cast Al_2O_3–ZrO_2–SiO_2 compositions must be achieved by batching relatively expensive, pure zirconia rather than zirconium silicate. In addition, higher levels of zirconia are known to increase manufacturing difficulties. Nonetheless, high zirconia fusion-cast refractories can be manufactured and are commercially available as evidenced by the patents of Alper and McNally [3, 4] and the publication of Ito *et al.* [5].

The purpose of the study reported here was to evaluate the corrosion resistance of high zirconia fusion-cast Al_2O_3–ZrO_2–SiO_2 refractories in soda lime glass.

2. Experimental procedures

A set of fusion cast compositions was batched as can be seen in Fig. 2. In addition to the alumina, silica and zirconia, sodium oxide was included as a constant 8 wt % of the silica. The sodium oxide has been normalized out of the compositions in Fig. 2. Compositions one to nine in Fig. 2 constitute an experimental design which contains variations in the estimated volume per cent of zirconia and in the molar ratio of alumina to silica. Composition number ten is a composition from US Patent 3632359 [4]. In addition, the composition of a typical commercial alumina–zirconia–silica fusion cast refractory, Unicor I™ is included in Fig. 2. This material was used as a standard in the corrosion tests. The samples were fusion cast from a

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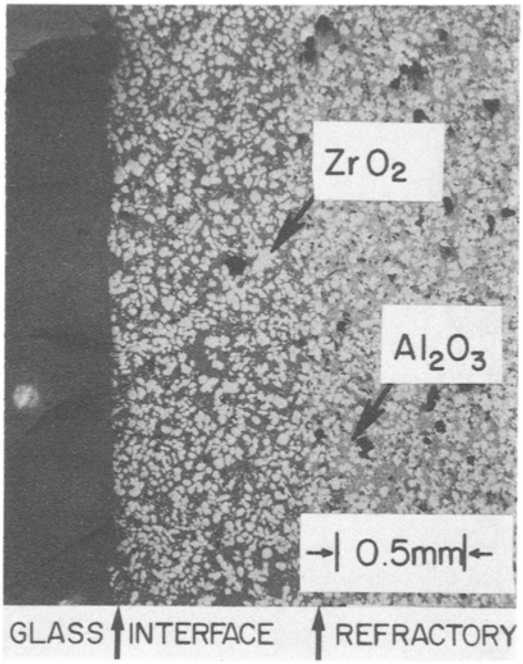

Figure 1 A corrosion interface between soda lime glass and a typcial commercial $Al_2O_3-ZrO_2-SiO_2$ fusion-cast refractory.

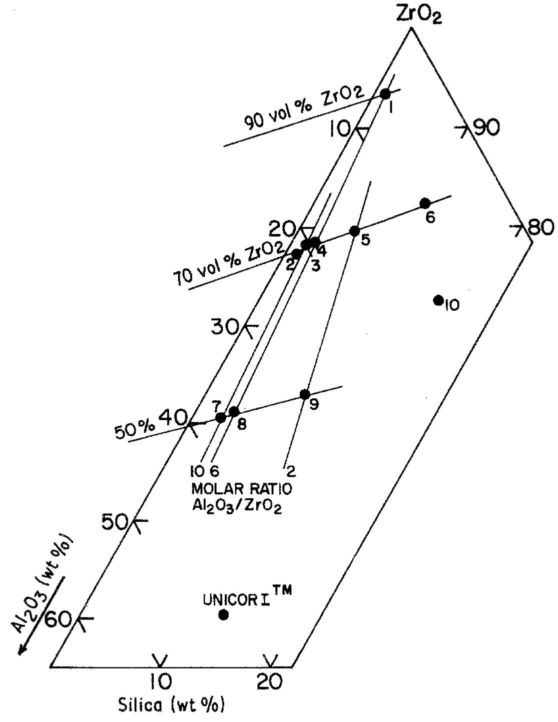

Figure 2 Batched experimental compositions. These compositions also contain Na_2O as a constant 8 wt % of the silica content.

laboratory arc furnace. The melting conditions were adjusted to give dense and oxidized castings. The castings were 7.6 cm x 15.2 cm x 30.5 cm in size and weighed about 13.5 kg.

Samples for corrosion testing, microstructure examination and chemical analysis were removed from identical locations in each block. The chemical analysis was performed by X-ray fluorescence. Two corrosion test samples (1 cm x 1 cm x 3 cm) were taken from each casting. The open porosity of each of these samples was measured by water absorption prior to corrosion testing. The corrosion tests were performed as indicated in ASTM C621-68. The samples were tested in soda lime glass at 1500° C for four days. The composition of the test glass is shown in Table I.

TABLE I Chemical analysis of soda-lime test glass

	wt %
SiO_2	74.4
Al_2O_3	1.7
Na_2O	15.9
MgO	31.
CaO	4.7
K_2O	0.2

3. Results and discussion

Table II lists the analysed compositions of the experimental samples, the average open porosity of the corrosion test samples, and the corrosion test results. Fig. 3 shows the microstructures of four samples that are representative of these compositions. Fig. 3a is the microstructure of a typical commercial fusion cast alumina–zirconia–silica refractory (Unicor I^{TM}). This material contains alumina and zirconia grains embedded in a glass matrix. Fig. 3b is composition No. 2, and it can be seen to contain an increased amount of zirconia over the standard material. It also contains alumina crystals and a small amount of a glass phase. Fig. 3c is composition No. 10. This material can be seen to contain zirconia crystals embedded in a glassy matrix. There are also some mullite needles, but there are no alumina crystals. The alumina in this composition is entirely dissolved in the glass phase. Finally, Fig. 3d is composition No. 1 and it can be seen to consist almost entirely of zirconia. Some alumina crystals are present and also some glass, but these exist as grain boundary phases.

The results of the corrosion tests are listed in Table II as average metal line cuts for each com-

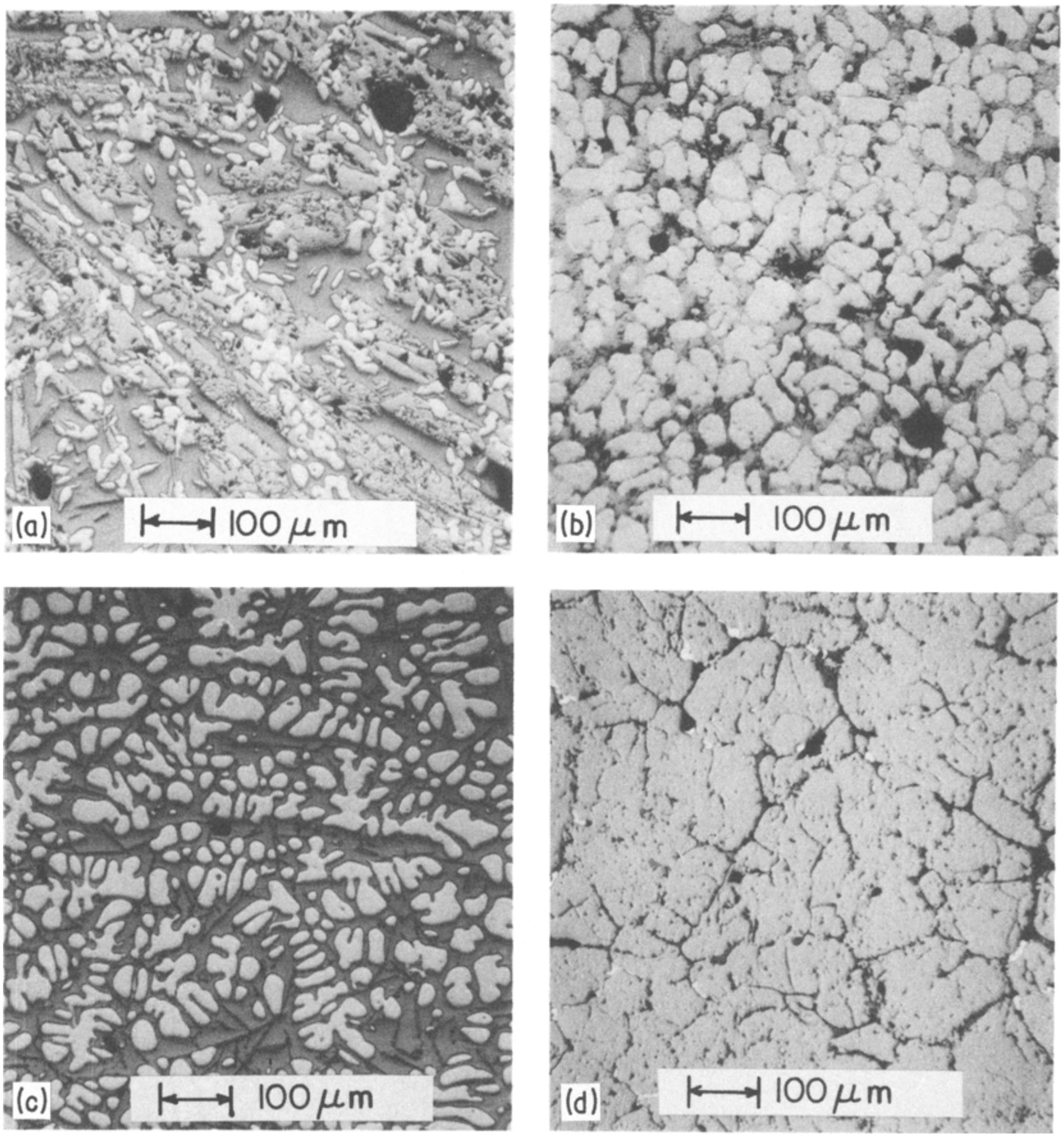

Figure 3 (a) The microstructure of a typical commercial fusion cast Al_2O_3–ZrO_2–SiO_2 refractory (Unicor I^{TM}). (b) The microstructure of composition No. 2. (c) The microstructure of composition No. 10. There are no alumina grains in the structure. (d) The microstructure of composition No. 1.

position. In addition, a corrosion rating has been calculated by dividing the cut on the standard material (Unicor I^{TM}) by the cut on the experimental material and multiplying by 100. A rating greater than 100 indicates corrosion resistance better than the standard and vice versa. Fig. 4 shows the corrosion ratings plotted as a function of composition. Note that the analysed and not the batched compositions have been plotted. As often happens with the fusion casting process, the final cast compositions differ from the batched compositions.

Not one of the high zirconia compositions displayed corrosion resistance to soda lime glass better than the standard 40 wt% zirconia refractory. In fact, at very high zirconia levels and at low molar ratios of alumina to silica, the corrosion resistance appears to be lower than the standard material. Both test samples of composition No. 6 were cut off in the corrosion test. As can be seen in Table II, the open porosity of the samples does not appear to have any affect on the corrosion results since the porosity is uniformly low for all of the samples.

TABLE II Chemical analysis and corrosion test results

Composition number	ZrO_2* (wt %)	Al_2O_3* (wt %)	SiO_2* (wt %)	Na_2O* (wt %)	Per cent open porosity	Average metal line cut (mm)	Corrosion resistance rating
1	95.1	4.6	0.5	0.04	0.52	1.47	86
2	81.6	16.7	0.5	trace	0.75	1.33	95
3	79.1	21.1	0.1	trace	0.76	1.36	93
4	84.6	15.3	0.4	0.03	3.0	1.43	89
5	82.7	15.9	2.6	0.2	‡	1.33	95
6	85.8	7.9	5.1	0.4	0.70	cut off	0
7	61.5	38.0	0.6	0.05	‡	1.30	98
8	61.6	34.1	4.4	0.4	0.93	1.31	97
9	62.8	31.9	5.4	0.4	1.58	1.43	89
10†	71.5	11.5	15.0	2.0	‡	2.44	52

*Actual X-ray fluorescence results – not normalized.
†Typical analysis.
‡No measurement.

The boules of glass that remained after the corrosion tests were analysed quantitatively by X-ray fluorescence. Table III indicates the amounts of alumina and zirconia dissolved in the glass expressed as moles of refractory cation per 100 g glass. The alumina content of the virgin glass has been subtracted so that the values in Table III represent only those ions dissolved from the refractory. As might be expected, the amounts of the individual ions that are dissolved in the glass from a particular refractory composition is directly proportional to the amounts of those ions in the refractory. On the other hand, the total number of refractory cations (Zr^{4+} + Al^{3+}) dissolved in the glass per unit volume is relatively constant, i.e. independent of the composition of the refractory sample. The total moles of refractory cation per 100 grams of glass is plotted as a function of analysed refractory composition in Fig. 5.

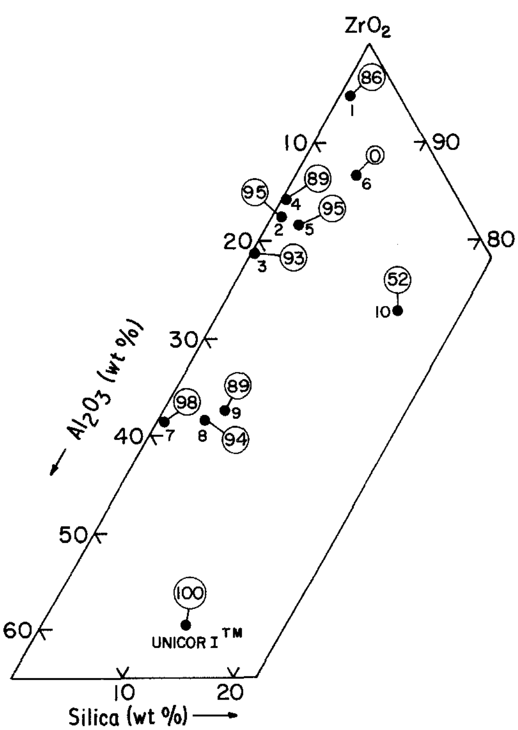

Figure 4 Corrosion ratings as a function of analysed composition. Unicor I^{TM} = 100.

The foregoing results suggest that the glass can accomodate just so many aluminium plus zirconium ions per unit volume, i.e. that the two ions assume similar structural roles in the liquid. This further suggests an explanation for the trends in corrosion resistance in the alumina–zirconia–silica system. The hypothesis is that the solubility limits of alumina and zirconia in soda lime glass are not very different; however, the rate of

TABLE III Analysis of corrosion test glass

Composition number	Moles of refractory ion dissolved per 100 grams of soda lime glass		Total (Zr^{4+} + Al^{3+})
	Zr^{4+}	Al^{3+}	
1	0.27	0.05	0.32
2	0.15	0.20	0.35
3	0.16	0.24	0.40
4	0.14	0.23	0.37
5	0.15	0.19	0.34
8	0.07	0.32	0.39
Unicor I^{TM}	0.06	0.31	0.37

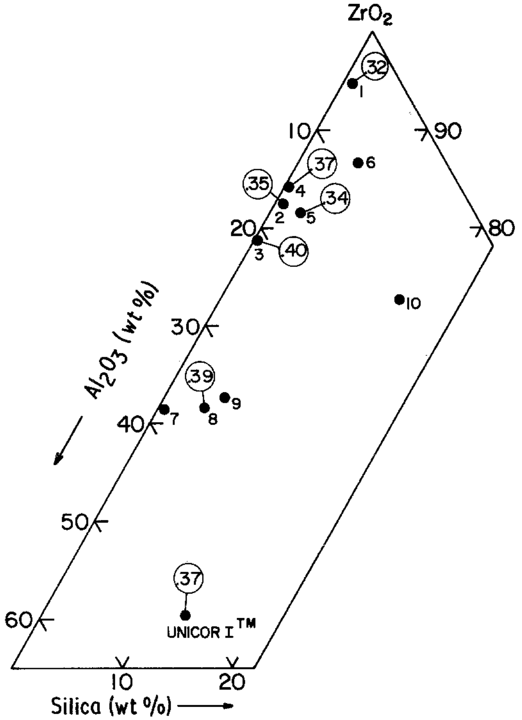

Figure 5 Moles of dissolved Zr^{4+} and Al^{3+} cations per 100 grams of glass plotted as a function of the analysed refractory composition.

dissolution of alumina in soda lime glass is greater than the rate for zirconia. As alumina dissolves in the glass, it creates an alumina-saturated glass interface next to the refractory. Table IV shows a microprobe analysis of the glass at an interface which confirms that its composition is rich in alumina. As the interface in Fig. 1 shows, zirconia has a low solubility and, therefore, a low rate of dissolution in the alumina-saturated interface glass. Therefore, as zirconia is added to an alumina refractory composition, it serves to create a more stable and durable interface, and it raises the corrosion resistance of the refractory.

As more and more zirconia or silica is added to the alumina refractory composition, a point is reached where the alumina is sufficiently diluted so that the refractory can no longer saturate the glass at the interface with aluminium ions. The

TABLE IV Microprobe analysis of interface glass between AZS refractory and soda lime glass

	Soda lime glass	Interface glass
SiO_2	72.9	50.4
Al_2O_3	1.7	33.5
Na_2O	16.8	8.5
CaO	5.2	3.1
MgO	3.4	1.0
ZrO_2	0	3.6

results in Table III and Fig. 5 suggest that the solubility of zirconia in this unsaturated glass is increased and, therefore, so is the rate of zirconia dissolution. This increase in the dissolution rate apparently occurs to the point that at high zirconia contents, the corrosion resistance of the refractory in soda lime glass is less than that of some optimum mixture of alumina and zirconia.

4. Conclusions

1. Fused alumina–zirconia–silica refractories with high zirconia contents (> 50 wt %) do not offer improved corrosion resistance to soda lime glass. There is an optimum mixture of alumina and zirconia that has corrosion resistance superior to either alumina or zirconia in soda lime glass.

2. The reason for this trend in corrosion resistance appears to be the interdependent solubilities of alumina and zirconia in soda lime glass.

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