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The influence of zircon in a model aluminosilicate glass tank forehearth refractory

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Abstract

Standard aluminosilicate forehearth refractories are normally fabricated with a small proportion of zircon to improve their performance. To identify possible bases for the action of the zircon, fine-grain aluminosilicate materials of similar compositions were prepared and tested, to model the behaviour of the finer grain bond phase in the standard refractory. The reference materials contained a range of proportions of zircon, and further sets of materials were prepared in which the zircon was replaced by varying amounts of very fine alumina, silica or zirconia powders. The alumina and zirconia powders increased the strength at room temperature of the base aluminosilicate, with zirconia having the largest effect; silica had only a slight effect. It appears that the zircon increases strength through three mechanisms: the reduction in porosity brought about by improved efficiency of the particle packing, a faster rate of sintering of the fine grained bond phase, and a transformation toughening of the bond phase, caused by tetragonal zirconia formed in situ by high temperature dissociation of the zircon.

Keywords: Al_2O_3; Porosity; Refractories; SiO_2; Strength; ZrO_2; $ZrSiO_4$

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1. Introduction

Glass tank and associated liquid glass processing systems commonly use aluminosilicate based refractories in which zircon is incorporated to improve corrosion resistance.[1–4] Coarse alumina and mullite powders and grits are used in the construction of these materials, and during powder processing and sintering very little, if any, overall shrinkage occurs. Therefore in order to achieve maximum fired density, and in consequence mechanical strength and resistance to corrosion by molten glass, very efficient particle packing is required in the green state. The starting materials are prepared by blending carefully controlled proportions of components having particle sizes covering the range of multi-millimetre to sub-micrometre. Accessible porosity in the sintered product is normally in the region of 15–20%. The refractory can therefore be considered to be a very coarse grained material, bonded by an interspersed aluminosilicate phase consisting of much finer grain size material and a small quantity of glass. Strength is considered to be developed by the bonding of the finer fractions of particles to each other, and to the surfaces of the large grains. Because the overall strength of the refractory is likely to be largely determined by that of the finer grain bond phase, studies of the influence of additive oxides on strength can conveniently be carried out using materials consisting of the bond phase components alone, with omission of the coarser grain materials.

In the context of a detailed study of a zircon-containing refractory used in a glass tanks forehearth, we have examined the consequences of substituting other oxides for the zircon. In the standard forehearth refractory the zircon in is incorporated as a fine powder, in amounts of ~17% by weight. Materials prepared with omission of the zircon have lower resistance to corrosion, and decreased

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mechanical strength. The present study has concentrated specifically on determining the consequences for strength of the partial, or complete, removal of the zircon, and its replacement by other oxides, specifically alumina, silica and zirconia. It has therefore been concerned with the clarification of the function of the zircon component in the standard refractory.

The particle sizes used for the construction of test materials were restricted to <1 mm. These materials were therefore representative of the bond phase of the normal refractory, and the finer scale of the microstructure also allowed strength measurements to be made on samples of small dimension. The materials examined were essentially aluminosilicates, prepared from a blend of moderately fine alumina and mullite powders, with proportions representative of the finer components used in the forehearth refractory. Test materials were first prepared containing a range of amounts of zircon. Further materials were prepared using a base composition from which zircon had been omitted, and incorporating small amounts of much finer alumina, silica, or zirconia, powders. Measurements of porosity, and mechanical strength at room temperature, formed the bases for comparisons between materials.

2. Experimental

The starting powder blend used, based on the composition of a standard commercial material, is shown in Table 1. This composition formed the basis for all materials prepared. The very fine (submicron) oxide powders incorporated are listed in Table 2. These powders were added in amounts of 9, 17, and 26% by weight of the total mixture, which gave proportions corresponding approximately to 0.5, 1.0, and 1.5 times the weight of zircon present in the normal refractory. Powder mixtures were blended dry with alumina media over 2 h, using 2 wt.% of polyvinyl alcohol (PVA) added as an isopropanol solution to provide adequate green strength for subsequent handling. Silica was added as appropriate volumes of a solution of tetraethylorthosilicate (BDH, Poole, UK) in isopropanol, which was hydrolysed after blending by the addition of dilute (10%) aqueous ammonium hydroxide. Powder mixtures were dried at 110 °C, and passed through a coarse sieve to break up large agglomerates. Powders were then compacted into 25 mm diameter discs by uniaxially pressing at 60 MPa. The quantity of powder used in the die was chosen to give a constant disc thickness of ~4.5 mm. Discs were sintered in air at temperatures between 1500 and 1600 °C with hold times of up to 5 h. These temperatures are slightly higher than those used in present commercial practice, but allowed measurable strengths to be developed in shorter times. Heating and cooling rates were 600 °C h^{-1}. Most samples for strength measurement were prepared at 1600 °C with a hold time of 4 h.

Table 1
Base composition

Powder	Type	Nominal particle size	Amount (wt.%)
Alumina	Alcan RMA 325	15 μm	71.4
Mullite	“Fused”	0.5–1 mm	12.5
	“Sintered 35#”	325 μm	12.0
Clay	ball	~1 μm	2.1
	china	~1 μm	2.0
Total			100.0

Powder suppliers: alumina: Alcan, Burntisland, Fife, UK; mullite: Washington Mills, Trafford Park, Manchester, UK; clays: English China Clay, St. Austell, Cornwall, UK.

Table 2
Added oxides

Raw materials	Measured (d_{50}/μm)
Zircon (zircozon Z)	0.7±0.1
Alumina AKP 50	0.4±0.1
Zirconia (monoclinic) (Tosoh)	0.5±0.1
Zirconia (tetragonal 3 mol% yttria stabilised, Tosoh)	0.5±0.1

Accessible porosity was measured directly using penetration by boiling water, according to a standard method (BS7134). Each reported value is the mean of four determinations. Although the accessible porosity levels were generally quite high (~30%), weighing the water-saturated samples in air in practice presented no difficulties, probably because the small pore entrance diameters in these fine grain materials prevented loss of internal water after removal of the samples from the water. Values of repeated measurements reproduced satisfactorily, giving density values with a mean standard deviation of ~1%. Bulk density (ρ_b) was measured for all materials by a standard water immersion method from which:

$$\rho_b = \{w_1/(w_2\text{-}w_3)\}\rho_w \quad (1)$$

where w_1 is the dry weight of the sample, and w_2 and w_3 are its weights saturated with water (by impregnation under vacuum) in air, and pre-saturated with water and suspended in water respectively. ρ_w is the density of water at the test temperature. With selected materials bulk density was also measured by the standard mercury immersion method: values obtained by mercury immersion agreed to within ±0.5% of those obtained using water, justifying the use of the more convenient water immersion method. Total porosity was estimated by comparisons of the measured bulk density values, and values for theoretical solid density estimated using the simple rule of mixtures. Pore size distributions were measured in representative materials by a standard mercury intrusion porosimetry method.

Strengths of discs were measured in the as-sintered state, using diametral compression[5] in a tensile testing machine (Instron Model 1185) and a loading rate of 1 mm min^{-1}. At least four (normally six) measurements were made on each material, and the results averaged. In this mode the strength (S) is given by:

$$S = 2P/(\pi.d.t) \qquad (2)$$

where P is the load, d the disc diameter and t the disc thickness. Disc thickness was maintained approximately constant at 4.5±0.1 mm because in practice values of S vary with sample thickness to an extent not exactly expressed by the simple reciprocal relationship implied by Eq. (2). Thicker discs could not be used because of the requirement for t to be significantly less than d. This restriction, coupled with the difficulty of producing larger diameter discs of uniform density, created the potential problem that because the disc thickness was only a factor of 4–5 larger than the largest grain size populations of the material forming the disc, considerable scatter in strength data would be obtained. In fact the spread of strength values for each material was not abnormal, and at about ±15% of the mean. Because the intention was to compare and rank the strengths of very similar materials (differing primarily only in the nature of the finest particle size component), it was considered that would be satisfactory to have strength values which were consistent, rather than very precise.

X-ray diffraction (XRD) analyses using copper K_α radiation (154.05 pm) with a Philips APD 1700 system diffractometer (45 kV, 35 mA and 9 mm oscillation amplitude) were made on finely crushed samples.

3. Results and discussion

The base composition attained reasonable strength after 30 min sintering at temperatures of 1500 °C and above, as shown in Fig. 1. Total porosity was in the range 25–35%. These porosity values were considerably higher than those typically measured for the forehearth refractory (~20%), but not unexpected in view of the omission of the coarsest powder fractions from these model compositions. Increasing the hold time to 5 h gave only small further increases in strength and had no effect on porosity. The influence of alumina, zircon, and zirconia additions on pore fraction is shown in Fig. 2. All materials contained an estimated 2% of inaccessible porosity, but the level was reasonably constant and is disregarded in the following discussions. The effectiveness of these additives in reducing porosity is roughly in line with additive particle size, with the larger d_{50} value zircon being least effective, and the finer zirconia and alumina powders most effective. This behaviour is in accord with that expected from standard treatments of the densities of binary and ternary mixtures of powders, where finer particles occupy the interstices between the larger to improve packing efficiency.[6] All the additive oxides improved the strength of the base material, with strength being a function of the amount of oxide added. Fig. 3 shows the effects on strength of additions of the alumina, zircon and zirconia, after sintering for at 1600 °C for 4 h. With alumina and zircon a maximum in strength was reached, by interpolation, at ~20% addition. The

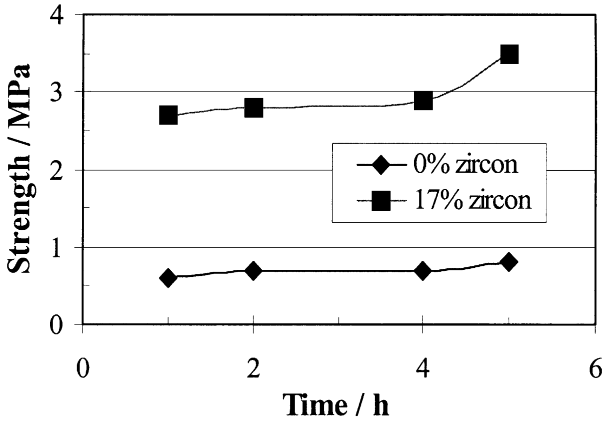

Fig. 1. Strength as a function of hold time.

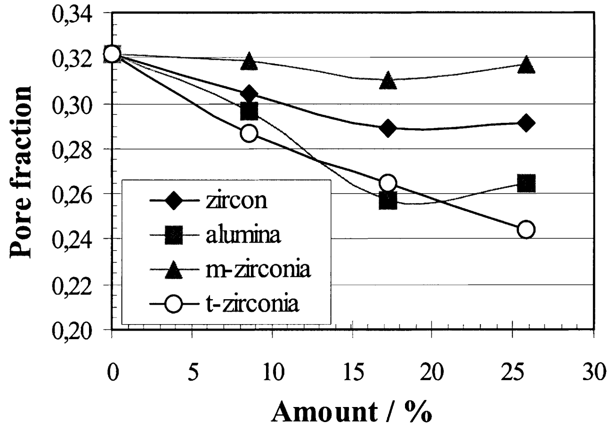

Fig. 2. Pore fraction as a function of amount of powder added.

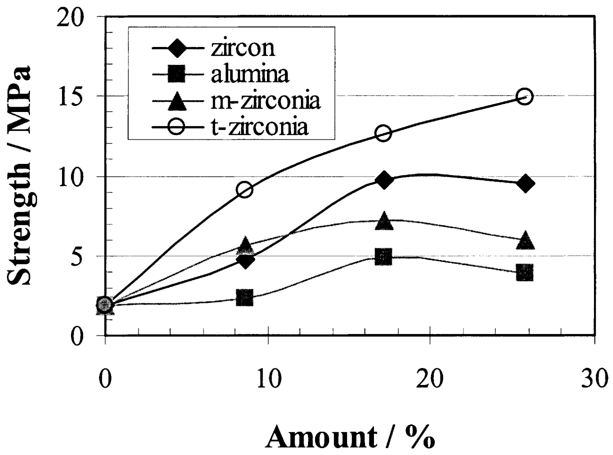

Fig. 3. Strength as a function of amount of powder.

influence of silica was not tested in detail, but a 17% addition was less effective in increasing strength of the base composition than the same level of alumina. It is also significant that the additions of fine monoclinic, and yttria stabilised tetragonal, zirconia powders also led to marked increases in strength: the tetragonal phase was particularly effective in this respect (Fig. 3). The additions of the very fine powders to the relatively coarse basic matrix also reduced the accessible (open) pore fraction. The temperature sensitivity of strength attainment with alumina and zircon additions after sintering for 4 h, as determined from a standard Arrhenius plot (Fig. 4), was 250 kJ mol^{-1}. This value is not amenable to precise interpretation but it would be consistent with a contribution of diffusion controlled processes to the development of interparticle bonding, possibly involving a small amount of liquid phase derived from the impurities in the clay mineral additions.

It is to be expected that porosity in a sintered material will have an influence on strength, and the empirical Eq. (3) often provides a satisfactory fit to data for sintered materials:

$$S = S_o \exp[-b.p] \tag{3}$$

where S_o is the strength at full density, b is a numerical constant with values for alumina[7] in the region of 4, and p is pore fraction. Data for pore fraction-strength relationships are shown in Fig. 5. The extrapolated strength at zero accessible porosity (S_o) is ~190 MPa, which can be considered reasonable for a dense but relatively coarse-grained material. The constant b (~15) for the additions of alumina is, however, much larger than expected from earlier work with fine grain sintered aluminas.[8] This implies an associated increase in the value of S_o with alumina additions, and which would be the expected consequence of the sintering, and bonding, obtained with a very fine powder. Thus it appears that the function of the fine alumina powder is two-fold: to reduce porosity in the sintered material by filling interstices between larger particles with small particles, and to provide an additional improvement in the intrinsic strength of the matrix. With the additions of zircon and the two types of zirconia powder the plots show a large discontinuity, in that for a very small reduction in porosity, corresponding to very low levels of addition, there are much larger increases in strength. Thereafter with decreasing porosity the plots become approximately linear. However, in these three cases the projected S_o value are impossibly large (>1 GPa), indicating that other major factors are influencing strength.

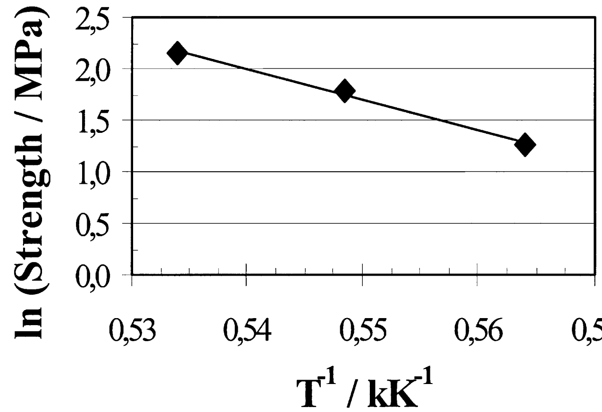

Fig. 4. Temperature sensitivity of strength.

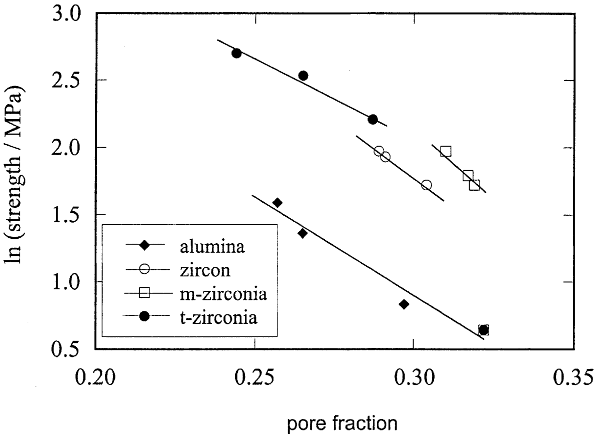

Fig. 5. Strength as a function of pore fraction.

The dissociation of zircon, as expressed by Eq. (4):

$$ZrSiO_4 = ZrO_2 + SiO_2 \tag{4}$$

is influenced by particle size and purity. It is generally believed to occur at around 1670 °C, but has been observed to begin at temperatures as low as 1285 °C[8] in impure systems. The formation of mullite by reaction of the SiO_2 with alumina is also possible, and is likely to favour zircon dissociation by reaction (5):[9–13]

$$2ZrSiO_4 + 3Al_2O_3 = 2ZrO_2 + 3Al_2O_3.2SiO_2. \tag{5}$$

It would be difficult to establish with confidence the presence of this additional mullite, because of the much large proportion of mullite powder used in the preparation of the materials: detailed high resolution transmission electron microscopy would be required. Silica is a possible intermediate, or product, of the zircon decomposition, but additions of silica to the basic formulation did not produce any marked improvement in strength, indicating that it is the ZrO_2, which is primarily responsible for the large increases seen. The presence of monoclinic and tetragonal zirconia in material prepared with zircon could clearly be shown by XRD, as seen in Fig. 6. This establishes beyond doubt that decomposition of the zircon is occurring at the sintering temperatures of ~1500 °C used. It is significant that additions of the fine zirconia powders also led to increases in strength: the tetragonal phase was particularly effective in this respect (Fig. 5) possibly in part because it was also the most effective in reducing porosity.

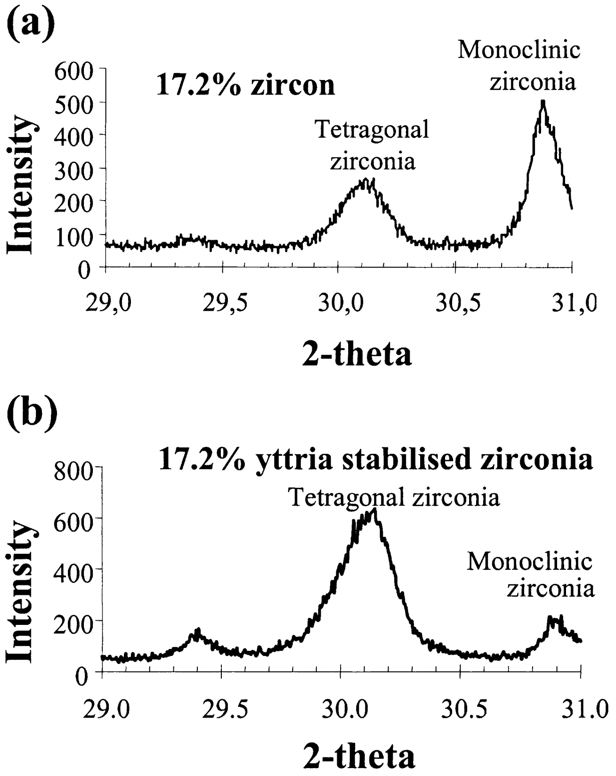

Fig. 6. XRD patterns of materials prepared with (a) zircon and (b) yttria stabilised zirconia.

It is clear that the addition of a very fine powder to the moderately coarse powders providing the base refractory composition increases the strength of the material. The most probable explanation for the effect of the alumina is that it is largely the simple consequence of a reduction in porosity resulting from improved efficiency in powder particle packing. And because nm dimension alumina powders are readily sinterable at temperatures in the region of 1600 °C, some direct bonding by the alumina particles of the larger alumina and mullite particles also occurs, resulting in a further increase in strength. The zirconia, through an attempted (or realised) tetragonal to monoclinic transformation on cooling from fabrication temperature, provides transformation toughening and microcrack, strengthening mechanisms.[14] Both types of zirconia powder, the monoclinic and the partially stabilised tetragonal, are effective because the monoclinic is transformed to tetragonal during sintering.

The effectiveness of tetragonal zirconia in strengthening other oxide materials, in the alumina-zirconia composites for example, is very well documented. The absolute values of strength attained in the extremely porous refractories being examined here are not great: the highest value for the partially stabilised zirconia was only 12.6 MPa, but this is a factor of ~7 higher than that of the base material containing no fine powder additions, and a factor of ~3 better than that obtained with the same addition (17%) of alumina. For zircon the factor is ~5. This indicates that one important function of the zircon in the initial refractory blend is to be a source of tetragonal zirconia, but as with the alumina there are likely to be a number of different mechanisms by which the fine zircon powder can increase strength. There will be the reduction in porosity by filling interstices between larger grains; Fig. 7 illustrates the pore filling effect by showing the reduction in the volume of pores of size ~3 μm by the addition of 17.2% of the submicron zirconia powder. A third and independent effect, though one less easy to quantify will be that of similarly increasing the intrinsic strength of the finer grain matrix through improved interparticle bonding, caused by fast solid state or liquid phase sintering of the fine powder and its reaction products.

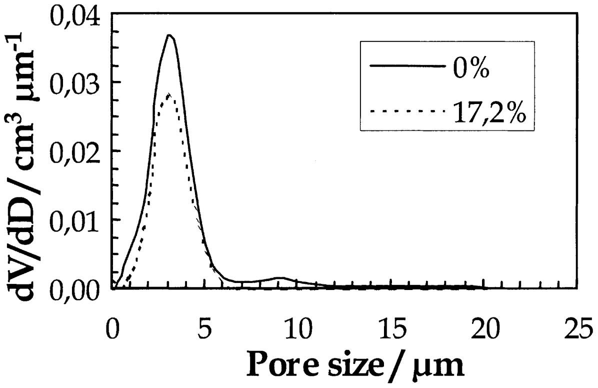

Fig. 7. Pore size distribution.

4. Conclusions

The incorporation of ~17% of submicron zircon powder in a relatively coarse grained aluminosilicate refractory leads to a fivefold improvement in room temperature mechanical strength. The influence of zircon on strength is suggested to be the consequence of three factors: a small (~10%) reduction of porosity in the sintered material through filling of interparticle voids; an improvement of interparticle bond strength through the sintering of the very fine particles; the strengthening of the fine grain matrix phase by zirconia transformation toughening mechanisms, using the zirconia released through high temperature decomposition of the zircon. These effects are also shown by fine monoclinic and partially stabilised tetragonal zirconia powders, most markedly by the tetragonal zirconia, which improves strength by a factor of ~7. Additions of submicron alumina also provide improvements in strength, though to a lesser degree. The factors in this case appear to be a ~15% reduction in porosity, and a faster sintering of the fine powder leading to improved bonding of the matrix phase.

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