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# Improved thermal shock resistant refractories from plasma-dissociated zircon

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Dissociated zircon (DZ), produced in a plasma furnace recombined and sintered to about 92% of the theoretical density in the range 1300 to 1500° C. The work-of-fracture of DZ increased from $20\,\mathrm{J\,m^{-2}}$ to $73\,\mathrm{J\,m^{-2}}$ with additions of 10 wt% monoclinic zirconia particles which had a mean diameter of about 13 μm. Thermal shock data showed that crack propagation in $\mathrm{DZ/ZrO_2}$ composites was stable.

## 1. Introduction

It has been shown that composites comprising a distribution of monoclinic zirconia particles of a suitable size in a ceramic matrix have improved mechanical properties relative to the matrix alone. Over-aged calcia partially stabilized zirconia alloys containing a precipitated phase of monoclinic $\mathrm{ZrO_2}$ had an increased work-of-fracture relative to the cubic stabilized matrix and also showed stable crack propagation in thermal shock tests [1]. Alumina–zirconia composites had a critical stress intensity factor about twice that of alumina alone [2]. In these materials the dispersed phase is tetragonal at the firing temperature and changes to the monoclinic form while cooling to room temperature. The transformation of the $\mathrm{ZrO_2}$ particles is accompanied by a 4% increase in volume which imposes a considerable tensile stress on the region of the matrix surrounding each particle. A volume process zone is postulated at the tip of a propagating crack in which the tensile stress field driving the crack interacts with the stress field around the particles. As a consequence of this interaction a dense network of microcracks is created within the process zone, or pre-existing microcracks extend at stresses less than the bulk fracture stress, which reduces the stored elastic energy and the Young's modulus in the neighbourhood of the tip of the main crack. The radius of the process zone is estimated to be about $\frac{1}{4}(K_{\mathrm{IC}}/\sigma)^2$ where $K_{\mathrm{IC}}$ is the critical stress intensity factor and $\sigma$ is the stress [2].

The zircon–zirconia system is well suited for the fabrication of such composites because the two phases are compatible in all proportions at temperatures up to 1676° C [3]. Normally zircon is not readily sinterable. Temperatures in the range 1600 to 1650° C are required to produce reasonably dense bodies. Even milled material has over 14% porosity when sintered at 1580° C [8]. 10 wt% clay is commonly added to commercial materials to act as a bond. This practice degrades the material by reducing its hot strength and rendering it susceptible to slag attack.

Dissociated zircon (DZ) produced in the plasma furnace is an attractive starting material with which to fabricate ceramics because it is extremely reactive. The furnace product consists mainly of spheroids, 25 to 250 μm diameter. The spheroids are two phase, i.e. amorphous silica and monoclinic $\mathrm{ZrO_2}$. A detailed account of the characterization of DZ has been published recently [4]. In this paper, the preparation of zircon and zircon/zirconia composite ceramics is described, along with their characterization with respect to strength, elastic modulus, fracture energy and thermal shock properties.

## 2. Experimental details

### 2.1. Materials

A supply of DZ was received from Associated Minerals Consolidated Ltd. The material was wetmilled with trichlorethane and zirconia grinding media to a mean particle size ~ 1 $\mu$m. After adding 4 wt% wax binder to the batch, it was granulated and formed into bars suitable for mechanical properties' testing by first die pressing and then isostatic pressing at about 170 MPa. The bars were fired at 1500° C for 5 h. Composite DZ/$ZrO_2$ test bars were made as described above except that monoclinic $ZrO_2$ particles (Magnesium Elektron, Mel-S) of mean diameter ~ 13 $\mu$m were added in various amounts to the granulated DZ powder. The $ZrO_2$ particles were dispersed by shaking for 15 min in a Glen Creston mill. A particular composite composition is designated by the wt% $ZrO_2$ added; thus DZ-5 is a composite containing 5 wt% $ZrO_2$.

## 2.2. Measurements

Sintering studies were carried out on green bars of DZ in a conventional dilatometer in the range 1300 to 1500° C. Modulus of rupture (MOR) bars were diamond ground to 3 mm x 3 mm x 40 mm and broken in four-point bending over a span of of 29 mm. Six bars were used for each MOR measurement. Bars for fracture energy measurements were ground to 5 mm x 5 mm x 50 mm. The edge-notched beam test was used to obtain both the fracture energy (work-of-fracture, $\nu_{WOF}$) required to propagate a crack completely through a specimen and also the energy ($\nu_{NBT}$) required to initiate propagation of a crack. The notches were cut with a diamond blade (300 $\mu$m thick) to depths of 1, 2, 3 and 4 mm. Two bars were prepared for each notch depth. The work-of-fracture (WOF) was obtained from the notched bars broken over a span of 40 mm in three-point bending at room temperature. To reduce frictional effects during testing, specimen supports with roller bearings were used. The total work done in propagating a crack was obtained using an electronic integrator on an Instron testing apparatus at a cross-head speed of 0.05 mm min$^{-1}$. The data were processed by Turner's procedure [5]. To obtain $\nu_{NBT}$' the critical stress intensity factor was calculated from:

$$K_{IC} = \frac{3sP}{2bw^2}\sqrt{a}Y \qquad (1)$$

where $s$ is the span, $P$ is the breaking load, $b$ is the width and $w$ is the depth, $a$ is the notch depth and $Y$ is given by [6]:

$$Y = 1.96 - 2.75\,(a/w) + 13.66\,(a/w)^2 - 23.98\,(a/w)^3 + 25.22\,(a/w)^4. \qquad (2)$$

Using the known value of $K_{IC}$, $\nu_{NBT}$ was calculated from:

$$K_{IC} = (2\nu_{NBT}E_0)^{1/2}, \qquad (3)$$

where $E_0$ is the modulus of elasticity (MOE) which was estimated by loading bars (5 mm x 5 mm x 50 mm) in three-point bending and using the following equation:

$$E_0 = \frac{P}{\Delta}\left(\frac{s^3}{4bw^3}\right), \qquad (4)$$

where $\Delta$ is the beam deflection at fracture. The critical stress intensity factor was independent of notch depth.

The thermal shock behaviour of DZ and DZ/$ZrO_2$ materials was determined by measuring the strength retained in MOR test bars after they had been quenched into water at 20° C from progressively increasing temperatures in the manner described by Hasselman [7].

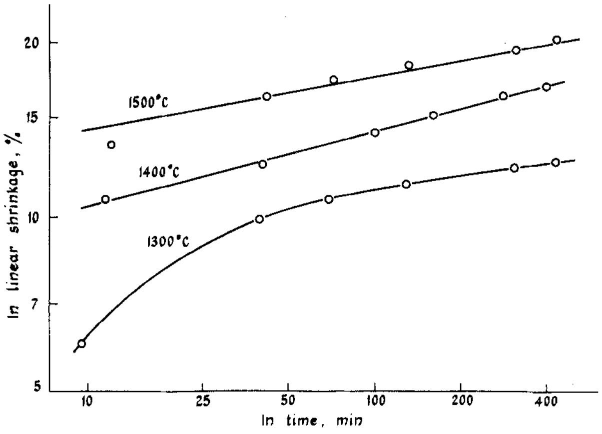

*Figure 1* Shrinkage of DZ as a function of time, at various temperatures.

TABLE I Mechanical properties of zircon refractories

| | DZ | DZ-10 | Clay-bonded zircon |
|---|---|---|---|
| Modulus of rupture (MPa) | 145 ± 15 | 149 ± 6 | 21.9 |
| Modulus of elasticity (GPa) | 185 | 188 | 55.6 |
| $\gamma_{WOF}$ (J m$^{-2}$) | 19.8 | 73.1 | 20.9 |
| $\gamma_{NBT}$ (J m$^{-2}$) | 13.0 | 22.2 | 20.8 |
| $K_{IC}$ (MPa m$^{1/2}$) | 2.2 | 2.9 | 1.5 |
| $R''''$ (m) | $1.1 \times 10^{-4}$ | | $24.1 \times 10^{-4}$ |
| $R_{st}$ (m$^{1/2}$ ° C$^{-1}$) | | 3.6 | 3.5 |
| Porosity (%) | 8.1 | 8.0 | 21 |
| Thermal expansion (° C$^{-1}$)* | $5.6 \times 10^{-6}$ | $5.6 \times 10^{-6}$ | $5.6 \times 10^{-6}$ |

*The thermal expansion data were taken from [9] and assumed to be the same for all the materials listed in Table I.

## 3. Results and discussion

### 3.1. Sintering

Sintering data for DZ are presented in Fig. 1. It was necessary to correct for the sintering that occurred during heat-up for each isothermal run. An effective sintering time to be added to the observed times for each temperature was estimated by an iterative procedure using the following equation [15]:

$$\tau = \frac{RT^2}{\beta Q}, \tag{5}$$

where $\tau$ is the effective sintering time, $T$ is the sintering temperature (K), $\beta$ is the heating rate and $Q$ is the activation energy for sintering. The procedure is to make a reasonable guess for $Q$ and then calculate $\tau$. This process is repeated until parallel linear log shrinkage versus log time plots are obtained, one for each temperature. When $Q = 490\,\text{kJ m}^{-1}$, linear log–log plots were obtained for the 1400 and 1500° C isotherms but they were not parallel. No value of $Q$ yielded a linear plot for the 1300° C isotherm. Possibly these discrepancies were due to the recombination reaction proceeding during the course of sintering. Such a reaction would violate the assumption of Equation 5 that there is a unique sintering mechanism.

### 3.2. Mechanical properties

It will be seen that DZ-10 had the best thermal shock properties in terms of retained strength at any particular quenching temperature. The mechanical properties and also the apparent porosity of this composite are listed in Table I along with similar data for DZ and a commercial zircon refractory. Data for the latter refractory were obtained from the literature [9]. The commercial material has a porosity of 21% which is reflected in its low MOR (22 MPa) and MOE (56 GPa). The porosity of DZ was only 8% whilst MOR and MOE were 145 MPa and 185 GPa, respectively. The increased mechanical properties of DZ relative to the commercial material may not be due simply to the lower porosity of DZ. For many materials the relationship between strength and porosity is approximately expressed by [10]:

$$S = S_0 e^{-\delta P} \tag{6}$$

where $S$ is the strength at some porosity, $P$, $S_0$ is the strength of the fully dense material and $\delta$ is a constant. A typical value of $\delta$ for ceramic oxides is ~6.5 [11]. From Equation 6, the calculated value of $S_0$ for DZ is nearly three times that of the commercial product. The WOF of both materials ($\gamma_{WOF}$) was about the same, 21 J m$^{-2}$. The fracture energy to initiate crack propagation ($\gamma_{NBT}$) was equal to $\gamma_{WOF}$ for the commercial zircon but only amounted to about 13 J m$^{-2}$ for DZ. The critical stress intensity factor ($K_{IC}$) of DZ at 2.2 MPa m$^{1/2}$ was significantly larger than the value for the commercial material (1.5 MPa m$^{1/2}$).

The MOR of DZ-10 was 150 MPa which is marginally higher than DZ; the difference is not statistically significant. The porosity and MOE of the composite were about the same as DZ. The work-of-fracture of DZ-10 increased markedly to ~73 J m$^{-2}$; $\nu_{NBT}$ had approximately the same value as the clay-bonded zircon.

### 3.3. Thermal shock resistance

Thermal shock data for DZ are given in Fig. 2. The critical temperature difference, $\Delta T_c$, at which unstable crack propagation occurs is about 300° C as shown by the discontinuous change in strength when the test bars were heated to 320° C and quenched into water at room temperature. Com-

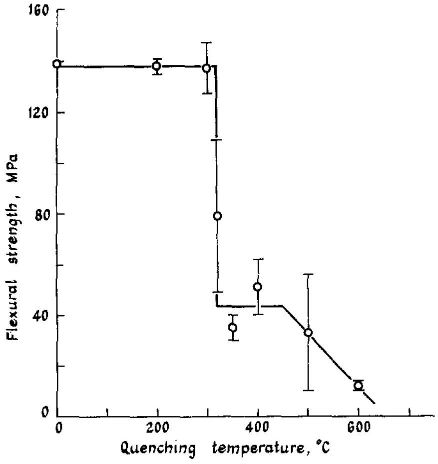

*Figure 2* Thermal shock resistance of DZ.

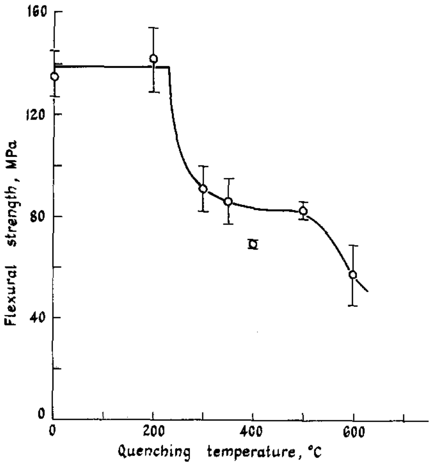

*Figure 3* Thermal shock resistance of DZ-5.

posite DZ-5 has about the same initial strength as DZ and possibly displayed stable crack propagation alhtough there was a marked decrease in strength in the range 250 to 350° C (Fig. 3). Composites DZ-10, -20 and -30 showed stable crack propagation, the decrease in strength with increasing severity of thermal shock being almost a linear function of the quenching temperature (Fig. 4). These materials are very thermal shock resistant; at a quenching temperature of 600° C, the retained strength of DZ-10 is about 74% of its initial value. The lower initial strengths of DZ-20 and 30 are probably due to linking-up of microcracks which would have a higher density in these materials owing to the higher concentration of $ZrO_2$ particles. On the basis of the properties measured in this work, DZ-10 had close to the optimum concentration of $ZrO_2$ particles of diameter, 13 $\mu$m.

Fig. 5 shows fractographs of DZ and DZ-10 taken with the scanning electron microscope. The fracture surface of DZ-10 (Fig. 5b) is much rougher than that of DZ (Fig. 5a) and is consistent with the higher WOF of the former compared with the latter. The fact that there is a tensile stress field in the matrix material around the $ZrO_2$ particles implies that any crack traversing the composite will tend to cut through the particles, rather than pass around them [12]. Evidence for this phenomenon is shown in the micrograph of thermally shocked DZ-10 shown in Fig. 6. This figure also shows that cracks greater than 500 $\mu$m have been created by thermal shock, yet the material has suffered only a modest loss of its original strength.

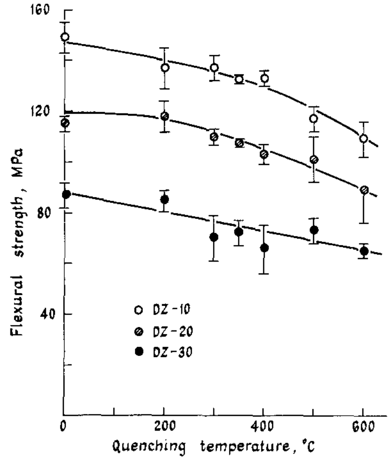

*Figure 4* Thermal shock resistance of DZ-10, -20 and -30.

Virkar and Johnson [13] have commented that alternating tensile compressive stress fields in $ZrO_2$–Zr composites may be responsible for the enhanced fracture energy observed in that system. Similar quasi-periodic stress fields exist in DZ/$ZrO_2$ composites and may be responsible for the rough fracture surface.

It is important to note that conditions within the process zone are not necessarily the same as those outside it. The microcracks need only be latent in the bulk of the material. The microcracks can be developed within the process zone by the action of the stress field, associated with the propagating main crack, interacting with the tensile fields around the $ZrO_2$ particles. Latent microcracks imply that there need be no sacrifice of the initial mechanical properties of the matrix material to achieve stable crack propagation.

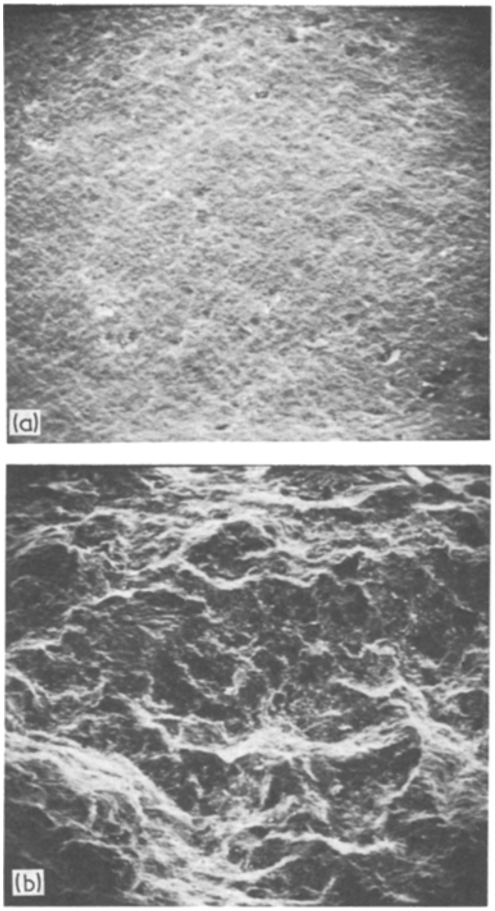

*Figure 5* SEM micrographs of the fracture surface of DZ and DZ-10: (a) zircon, (b) zircon/zirconia composite.

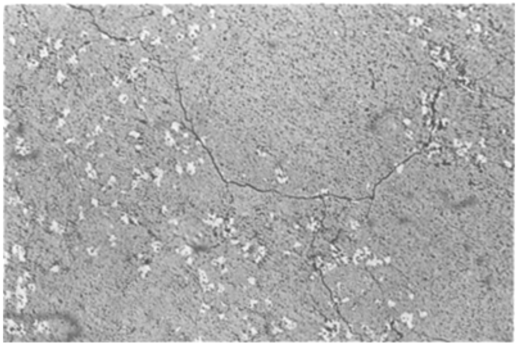

*Figure 6* Optical micrograph of DZ-10 thermally shocked from 660° C, × 162.

## 4. Implications for future refractories research

Larsen *et al.* [14] distinguish two kinds of thermal shock parameters, namely a thermal shock damage resistance parameter, $R''''$ and a thermal shock resistance factor, $R_{st}$ defined in turn below:

$$R'''' = \frac{\gamma_{NBT} E_0}{\sigma^2} \tag{7}$$

and

$$R_{st} = \frac{\gamma_{WOF}}{\sqrt{(\alpha^2 E_0)}} \tag{8}$$

where $\alpha$ is the thermal expansion. The factor $R''''$ applies to materials which undergo a catastrophic loss of strength at some critical value of the temperature difference, $\Delta T_c$. Accordingly, the fracture energy to be used in Equation 7 is the energy required to initiate the propagation of cracks. Equation 7 has been used successfully to classify a variety of ceramics in terms of their thermal shock resistance. The higher the value of $R''''$ the higher will be the strength retained after the material has been subjected to the critical temperature difference, $\Delta T_c$. To date the only way refractories' manufacturers have of increasing the value of $R''''$ for their products is by sacrificing the strength of the material. This is accomplished by using large grain sizes and/or introducing appreciable porosity into the refractory. This is reflected in the high value of $R''''$ for the clay-bonded zircon which also has 21% porosity. DZ has much higher values of strength and elastic modulus but would probably not be a useful material *per se* because its $R''''$ value is only ~ 1/20 of that of the commercial material. If DZ had porosity comparable with that found in commercial refractories it probably would have sufficiently improved thermal shock resistance to make useful products.

DZ-10 shows stable crack propagation and the factor $R_{st}$ can be used as an index of its thermal shock resistance. The values of $R_{st}$ for DZ-10 and the commercial product are about the same. Products made from DZ-10 would be expected to have the same sort of spalling resistance as the commercial zircon, but with a much higher hot strength and resistance to slag attack. The high value of $R_{st}$ for DZ-10 arises from its large work-of-fracture.

Larsen *et al.* [14] determined $\gamma_{WOF}$ and $\gamma_{NBT}$ for 38 commercial high alumina refractories. In every case $\gamma_{WOF}$ was much larger than $\gamma_{NBT}$. These workers believe this condition may be essential for spalling resistance in refractories and attributed it to the coarse-grained, porous microstructure of the commercial materials. The fact that a high ratio of $\gamma_{WOF}$ to $\gamma_{NBT}$ has been achieved in relatively dense and strong DZ/$ZrO_2$ composites suggests that addition of a dispersed phase of monoclinic $ZrO_2$ is a powerful method of improving the spalling resistance of refractories without degrading their mechanical and chemical properties.

## 5. Conclusions

(1) DZ powders are sinterable and can be used to fabricate relatively dense and strong materials.

(2) Addition of 10 wt% monoclinic $ZrO_2$ particles to DZ causes a large increase in the work-of-fracture.

(3) Crack propagation in DZ/$ZrO_2$ composite materials during thermal shock was stable.

(4) The value of the thermal shock resistance parameter, $R_{st}$, for a relatively dense and strong DZ/$ZrO_2$ composite with 10 wt% $ZrO_2$ was the same as that for a porous commercial zircon.

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## References

1. R. C. GARVIE and P. S. NICHOLSON, *J. Amer. Ceram. Soc.* **55** (1972) 152.
2. R. F. PABST, J. STEEB and N. CLAUSSEN, "Fracture Mechanics of Ceramics" (Pennsylvania State University, 1977).
3. W. C. BUTTERMAN and W. R. FOSTER, *Amer. Mineral.* **52** (1967) 880.
4. A. M. EVANS and J. P. N. WILLIAMSON, *J. Mater. Sci.* **12** (1977) 779.
5. C. TURNER, *Mat. Sci. Eng.* **11** (1973) 275.
6. A. G. EVANS and T. G. LANGDON, *Prog. Mater. Sci.* **21** (1976) 171.
7. D. P. H. HASSELMAN, *J. Amer. Ceram. Soc.* **53** (1970) 490.
8. E. G. ORLOVA, E. D. POSOKHOVA and G. E. KARAS, *Ogneup.* 8 (1975) 39.
9. R. N. ENDERFIELD, B. C. HOCKING and M. G. OXLADE, *Refract. J.* September/October (1975) 10.
10. E. RYSHKEWITCH, *J. Amer. Ceram. Soc.* **36** (1953) 65.
11. W. DUCKWORTH, *ibid* **36** (1953) 68.
12. R. W. DAVIDGE and T. J. GREEN, *J. Mater. Sci.* **3** (1968) 629.
13. A. V. VIRKAR and D. L. JOHNSON, *J. Amer. Ceram. Soc.* **60** (1977) 514.
14. D. R. LARSEN, J. A. COPPOLA, D. P. H. HASSELMAN and R. C. BRADT, *J. Amer. Ceram. Soc.* **57** (1974) 417.
15. M. J. BANNISTER, private communication.

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