Letters

Grinding-induced tempering of ceramics containing metastable tetragonal zirconia

The object of this communication is to provide a simplified fracture mechanics analysis of the strengthening of surface-ground ceramics containing metastable tetragonal zirconia. It is shown that the strength increase is critically related to the ratio of the size of grains, or of flaws induced by grinding, to the depth of the zone in which the metastable tetragonal zirconia transforms to monoclinic on grinding.

There has recently been considerable interest in the phenomena of strengthening ceramics by grinding. Normally under such conditions the strength of most brittle ceramics is reduced. This is because grinding introduces flaws into the surface from which catastrophic fractures may initiate. However, the reverse applies in ceramics containing a mechanically dispersed phase or precipitate of tetragonal zirconia particles of a critical size such that they are metastable at room temperature. In these materials the severe localized tensile stresses introduced during grinding are sufficient to promote the transformation of the zirconia close to the surface. The transformation from the tetragonal to the monoclinic form of zirconia involves both volumetric and shear strains and introduces a state of biaxial compression at the surface. This transformation is normally inhibited by the combined effects of stabilizing material, constraining effect of the matrix and grain size or precipitate size of the metastable tetragonal zirconia [1].

Previous work by Pascoe and Garvie [2] showed that the monoclinic content of a surface-ground calcia-partially stabilized zirconia material decreased rapidly with depth when the surface was carefully removed by polishing (Fig. 1). They also found that the strength of machined bars decreased with the depth of surface removed or, in other words, with the amount of monoclinic phase at the surface (Fig. 2). Subsequent work by Garvie *et al.* [3] has shown that the strength-controlling flaws of both calcia- and magnesia-partially stabilized zirconia alloys are of dimensions comparable to the grain size.

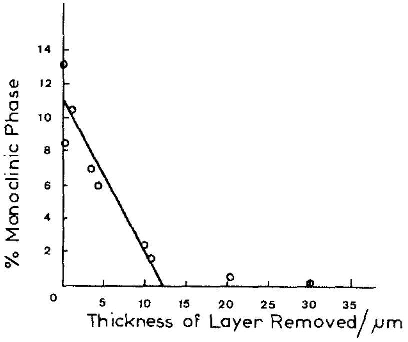

Figure 1 Variation of apparent monoclinic content measured at the surface, of a calcia-stabilized zirconia alloy, with the thickness of the layer removed (after Pascoe and Garvie [2]).

An estimate of the compressive stresses introduced by the transformation of grains of tetragonal to monoclinic zirconia in a matrix, is [4]

$$\sigma_c = \frac{\Delta V}{3V} f_t \Bigg/ \left[\frac{(1+\nu_1)(1-f_t)}{2E_1} + \frac{(1-2\nu_2)f_t}{E_2}\right] \qquad (1)$$

where $\Delta V/V$ is the volumetric expansion associated with the phase change, f_t is the volume fraction of transformed material, and ν_1, E_1 and ν_2, E_2 are the Poisson's ratio and Young's modulus of the matrix and transformed materials, respectively. The above expression ignores the influence of shear strains associated with the transformation. For materials with similar elastic modulii, Poisson's ratios, and low volume fractions of transformable material, Equation 1 simplifies to,

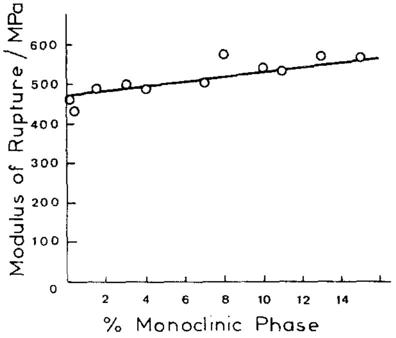

Figure 2 Dependence of flexural strength of monoclinic content of a calvia stabilized circonia alloy (after Pascoe and Garvie [2]).

0022–2461/80/061577–03$02.30 © *1980 Chapman and Hall Ltd.*

$$\sigma_c = \frac{\Delta V}{3V} f_t \frac{\langle 2E \rangle}{[1 + \langle \nu \rangle + f_t]}, \qquad (2)$$

where $\langle E \rangle$ and $\langle \nu \rangle$ are the mean values of the modulus and the Poisson's ratio of the matrix and transformable material. As pointed out recently by Suezawa and Ishioka [5] this value of σ_c is probably too high by 10 to 20% because of the influence of the free surface. Typical values for a 5% volume fraction of transformed monoclinic zirconia in a cubic zirconia matrix, involving a 4% volumetric expansion, would produce compressive stresses of the order of -225 MPa at the surface.

As a first approximation we might consider the compressive stress field beneath the ground surface to decrease linearly with depth, that is with the amount of transformed monoclinic (Fig. 1). Such a stress distribution is very similar to that found in chemically tempered glasses. The stress distribution through such a plate of thickness $2d$ is given by

$$\begin{aligned} \sigma(x) &= -\sigma_c(1 - x/\delta) \quad 0 \leqslant x \leqslant \delta \\ \sigma(x) &= -\sigma_c(1 - 2d/\delta + x/\delta) \quad 2d - \delta \leqslant x \leqslant 2d \\ \sigma(x) &= +\sigma_c(\delta/2d) \quad \delta \leqslant x \leqslant 2d - \delta \qquad (3) \end{aligned}$$

where δ is the thickness of the transformed zone.

The stress intensity factor of a crack at the surface of a material with a transformed compressive stress field loaded in bending is,

$$K_I = K_\beta + K_C \qquad (4)$$

where K_β is the stress intensity factor due to bending and K_C is that due to the compressive stress field. The former stress intensity factor is given by

$$K_\beta = Y\sigma_\beta(\pi c)^{1/2} \qquad (5)$$

where σ_β is the outer fibre stress, Y a modifying factor depending upon flaw geometry and c is the crack depth. Following Lawn and Marshall [6] the stress intensity factor due to the compressive stress field given by Equation 3 is,

$$K_C = Y\sigma_c(\pi c)^{1/2} M\left(\frac{c}{\delta}, \frac{\delta}{d}\right), \qquad (6)$$

where $M(c/\delta, \delta/d)$ is an additional modifying factor that is dependent upon the ratios of both the crack length and plate thickness to the compressive layer thickness. It is given by

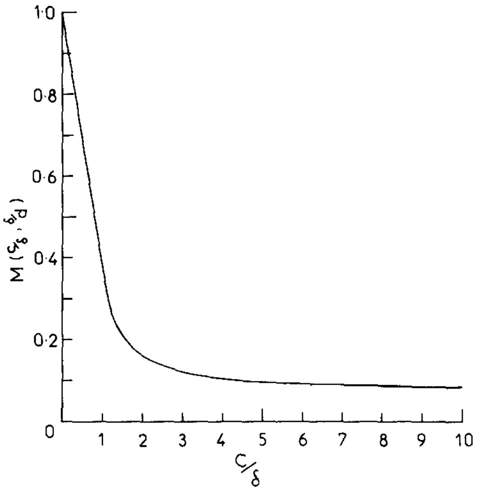

Figure 3 Variation of $M(c/\delta, \delta/d)$ with normalized crack length, according to Equation 7.

$$\begin{aligned} M\left(\frac{c}{\delta}, \frac{\delta}{d}\right) &= \left(1 - \frac{2c}{\pi\delta}\right) \quad 0 \leqslant c \leqslant \delta \\ &= \left(1 + \frac{\delta}{2d}\right)\left(\frac{2}{\pi}\right)\sin^{-1}\left(\frac{\delta}{c}\right) \\ &-\left(\frac{2c}{\pi\delta}\right)\left[1 - \left(1 - \frac{\delta}{2c}\right)^{1/2} - \frac{\delta}{2d}\right] \quad \delta \leqslant c \leqslant 2d - \delta. \qquad (7) \end{aligned}$$

The variation of $M(c/\delta, \delta/d)$ with normalized crack length for the particular case of $\delta/d = 1/50$, is shown in Fig. 3. Upon substituting for K_β and K_C in Equation 4 and letting $K_I = K_{IC}$, that is the critical conditions for crack propagation, and rearranging the terms, we have for the breaking stress,

$$= \frac{K_{IC}}{Y(\pi c)^{1/2}} + M\left(\frac{c}{\delta}, \frac{\delta}{d}\right) f_t \frac{\Delta V}{3V} \frac{\langle 2E \rangle}{[1 + \langle \nu \rangle + f_t]}. \qquad (8)$$

It is readily evident that the breaking strength should increase linearly with the volume fraction of transformed material, other factors remaining constant. This feature has been observed by Pascoe and Garvie (Fig. 2); the solid line in Fig. 2 being that predicted by Equation 8 upon substituting the known values of $M(c/\delta, \delta/d)$, c, $\langle E \rangle$, etc. Another very significant factor is that the increase in the breaking strength is strongly dependent upon the ratio of the initial flaw size to the thickness of the transformed zone for $c/\delta < 3$. Typically, in ceramics the strength is controlled by the grain size, provided the grain size is comparable to the flaws introduced during grinding. Hence the strengthening effect would be greatest when the grain size is much smaller than the transformed zone. However, a limitation in obtaining the optimum strengthening by reducing the grain size would come from the necessity of grinding to initiate the transformation. The depth of the machining flaws introduced into the surface (as well as the depth of the transformed zone) will depend on the severity of grinding.

Other factors that need to be considered are the volume fraction of transformable material and the compensating tensile stresses within the bulk of the material. If the volume of the transformable material is too large, agglomeration may occur and introduce significant microcracking. This phenomena would thereby alter the ratio of the initial flaw size to the depth of the transformed zone and hence reduce the strengthening effect. The tensile stress developed within the material, as indicated by Equation 3, depends very much on the thickness of the material and the magnitude of the surface compressive field. In addition, the severe stress gradients near the edge of the specimen may well significantly modify the static fatigue in corrosive environments from that of annealed materials. Previous studies by Hagan *et al.* [7] showed that a similar phenomena occurred in thermally tempered materials. In conclusion this work suggests that the optimum strengthening of ground ceramics containing metastable tetragonal zirconia may be obtained by reducing the ratio of the grain size or surface flaw size to the depth of the transformed zone.

Since writing this article, Claussen and Petzow [8] have presented further experimental evidence to support the above. They found in a hot-pressed alumina/metastable tetragonal zirconia system that the modulus of rupture could be doubled by grinding-induced tempering.

Acknowledgements

The author wishes to thank M. J. Bannister, R. C. Garvie and N. A. McKinnon for informative discussions and comments on the manuscript.

References

1. R. C. GARVIE, R. H. J. HANNINK and R. T. PASCOE, *Nature* **258** (1975) 703.
2. R. T. PASCOE and R. C. GARVIE, "Ceramic Microstructures 1976", edited by R. M. Fulrath and J. A. Pask (Westview Press, Boulder, 1977).
3. R. C. GARVIE, R. H. J. HANNINK and C. URBANI, Proceedings of the 4th CIMTEC meeting, St Vincent, Italy, May (1979).
4. M. V. SWAIN, to be published.
5. M. SUEZAWA and S. ISHIOKA, *Mat. Sci. Eng.* **37** (1979) 282.
6. B. R. LAWN and D. B. MARSHALL, *Phys. Chem. Glasses* **18** (1977) 7.
7. J. T. HAGAN, M. V. SWAIN and J. E. FIELD, *J. Mater. Sci.* **13** (1978) 189.
8. N. CLAUSSEN and G. PETZOW, Proceedings of the 4th CIMTEC, St Vincent, Italy, May (1979).

Received 28 September
and accepted 19 October 1979

M. V. SWAIN
CSIRO,
Division of Materials Science,
Melbourne,
Australia

Alkali resistance of fibres in cement

To efficiently use Portland cement as a construction material it is generally reinforced with various types of fibres. Widely used reinforcements are steel wires and asbestos. Other reinforcements recently tried as substitutes were polypropylene [1], carbon [2, 3], glass fibres [4, 5] and other organic fibres [1, 6].

Apart from compatibility and abrasion resistance due to mixing, fibre reinforced cement has to withstand the alkaline attack during hydration and, subsequently, under moist conditions. Portland Cement has a pH value of 12 to 13.

Commercially available A and E glass fibres lose their strength rapidly in an alkaline medium as a result of chemical attack [7]. Alkali-resistant glass fibres, with high zirconia content (CEM–FIL) developed recently, have been studied as a reinforcement over the last few years [8–10].

Two other fibres, basalt and jute, are available in abundance and from cheap sources – the former from a mineral rock and the latter from a vegetable source. Basalt rock is melted around

0022–2461/80/061579–06$02.60/0 © *1980 Chapman and Hall Ltd.*