with zinc oxide. If P^{+5} ions replace Zn^{+2} ions on normal lattice sites, the equilibrium reaction is given by the relation

$$P_2O_5 \rightleftarrows 2P(Zn)^{\bullet\bullet\bullet} + 2ZnO + \tfrac{3}{2}O_2 + 6\theta, \qquad (1)$$

where $P(Zn)^{\bullet\bullet\bullet}$ is a P^{+5} ion substituting for a Zn^{+2} ion on normal lattice sites. The extra semi-free electrons will change the concentration of interstitial zinc ions $Zn_i^{\bullet\bullet}$ at the equilibrium relation [4]

$$ZnO \rightleftarrows Zn_i^{\bullet\bullet} + \tfrac{1}{2}O_2 + 2\theta\,, \qquad (2)$$

in the direction of decreasing concentration of interstitial zinc ions. This disagrees with the explanation in which material transport of zinc oxide is controlled by the interstitial zinc ions [5–8]. If P^{-3} ions substitute for oxygen ions on normal lattice sites, in order to maintain electrical neutrality, oxygen vacancies must be created. Consequently, oxygen diffusion might be enhanced by the addition of H_3PO_4, but this is not yet established clearly. Further work on the role of H_3PO_4 in the sintering of ZnO is being carried out.

References

1. W. KOMATSU, M. MIYAMOTO, S. FUJITA, and Y. MORIYOSHI, *Yogyo Kyokai Shi* **76** (1968) 407.
2. H. SCHÄFFER and H. MAYWALD, *Z. Phys. Chem.* **B244** (1970) 289.
3. F. L. KATOMACK and F. A. HUNMMEL, *J. Electrochem. Soc.* **105** (1958) 132.
4. K. HAUFFE and J. BLOCK, *Z. Phys. Chem.* **196** (1950) 438.
5. T. J. GRAY, *J. Amer. Ceram. Soc.* **37** (1954) 534.
6. V. J. LEE and G. PARRAVANO, *J. Appl. Phys.* **30** (1959) 1735.
7. W. KOMATSU, Y. MORIYOSHI and N. SETO, *Yogyo Kyokai Shi*, **77** (1969) 347.
8. Y. MORIYOSHI and W. KOMATSU, *J. Amer. Ceram Soc.* **53** (1970) 671.

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Comments on "fracture measurements on cement paste"

Higgins and Bailey show in their interesting paper [1], that the apparent fracture toughness for paste, mortar and concrete in the ordinary three-point bending test depends on the beam depth. They also in general terms discuss a model explaining this effect, a so called "tied crack model". By this they imply that there exists a residual attractive force between the two faces of a newly formed crack.

Similar thoughts are presented in [2]. The main idea of the model proposed in that paper is to choose the variation of stress σ with crack width w so that

$$\int_0^{w_1} \sigma dw = G_c \qquad (1)$$

w_1 representing the crack width where the stress has fallen to zero. This means that the energy

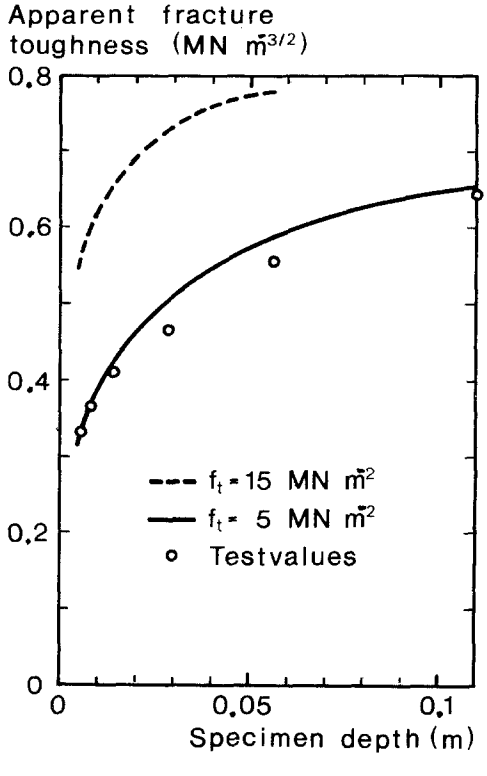

Figure 1 Test results of K'_{IC} versus specimen depth [1] compared to theoretical curves according to the model proposed in [2].

absorbed per new-formed unit crack area is the same as in the ordinary energy balance approach.

Using this model and the finite element method it can be shown [3] that the apparent fracture toughness value K'_{IC} for paste, determined from the ordinary linear-elastic three-point bending formula, depends on the beam depth as shown in Fig. 1.

In this figure the upper dashed curve is related to a tensile strength f_t of $15\,MN\,m^{-2}$ and a "limiting" fracture toughness K_{IC} of $0.8\,MN\,m^{-3/2}$ as proposed by Higgins and Bailey. Their direct tensile test-results can however be criticised, simply because they get a ratio between tensile and bending strength of about 1. As bending tests are so much easier to perform, let us take these values as basis of the further discussion. The values from the flexural tests of Higgins and Bailey, with beams with a depth of 14 mm, lie between 10 and $15\,MN\,m^{-2}$. With these small beams the ratio between bending and tensile strength is expected to be between 2 and 3, see [2], indicating a f_t-value of about $5\,MN\,m^{-2}$. Putting $f_t = 5\,MN\,m^{-2}$ and as before $K_{IC} = 0.8\,MN\,m^{-3/2}$ into our model, gives the lower continuous curve in Fig. 1. The small circles in the figure are values according to the tests of Higgins and Bailey.

References

1. D. D. HIGGINS, J. E. BAILEY, *J. Mater. Sci.* **11** (1976) 1995.
2. A. HILLERBORG, M. MODEER, P.-E PETERSSON, *Cement and Concrete Research* **6** (1976) 773.
3. M. MODEER, "Theoretical Apparent Fracture Toughness Values for Brittle Materials in Three-point Bending", (Division of Building Technology, Lund Institute of Technology, Sweden, 1977).

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Reply to "Comments on 'fracture measurements on cement paste'"

Modéer points out that in a recent paper by Hillerborg, Modéer and Petersson [1], a tied crack model is discussed for the fracture toughness of concrete similar to that proposed by us to explain our fracture experiments on cement paste [2]. We would emphasize that our model was also supported by direct experimental observation of stable microcracks reported elsewhere [3].

Modéer encounters difficulties in fitting our experimental results precisely to his theoretical calculations and in consequence casts doubt on our tensile testing results. He takes a value of $5\,MN\,m^{-2}$ for the tensile strength of a material on which we had measured strengths of up to $12.5\,MN\,m^{-2}$ in direct tensile tests. While acknowledging the difficulties of direct tensile testing, we must point out that considerable care was exercized in developing the testing rig; furthermore, we are not aware of any experimental errors that result in directly measured values of tensile strength which are ***higher*** than the true values.

Modéer also states that we "get a ratio between tensile and bending strength of about 1". In fact, as stated in our paper [1], the maximum measured strength in bending was $19\,MN\,m^{-2}$ and in direct tension, $12.5\,MN\,m^{-2}$, a ratio of 1.5 : 1. Differences between tensile and bend strength can be attributed to several sources. Firstly, it is difficult to perform direct tensile tests without introducing some extraneous bending moments [4]. Secondly, a much larger volume is normally stressed in direct tensile tests so that the probability of a large flaw being present is greater than in the equivalent bend test. Finally, a difference can also be attributed to non-elastic effects as suggested in [1] and [5]. In practice all these effects may contribute to make the measured bending strength greater than the measured tensile strength.

Returning to Modéer's difficulty in obtaining a precise correlation between his tied crack model and our experimental results we would suggest that a minor justifiable change in the assumptions may be sufficient to reconcile theory and experiment. Modéer assumes that when a crack opens there is a stress σ across the newly formed crack faces which varies with crack separation w, as shown in Fig. 1a. In our paper we suggest a similar stress and attribute it to fibres or other particles bridging the gap (see Fig. 13 of [2]). For such a

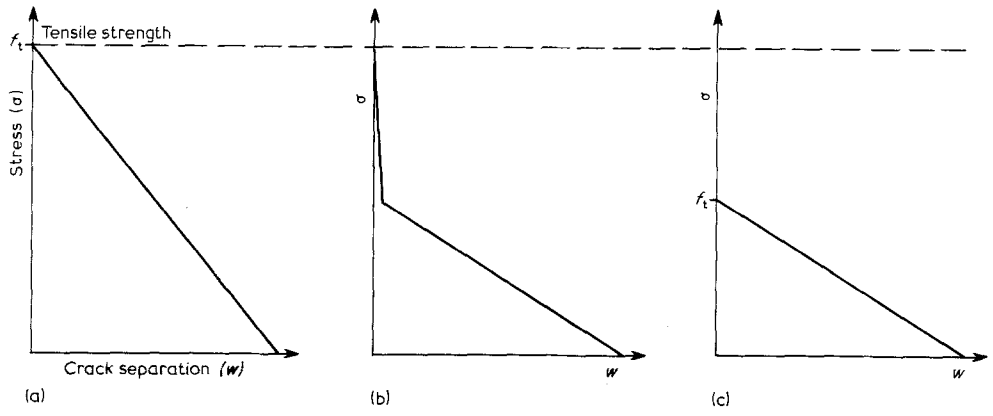

Figure 1 Possible stress–separation relationships for a tied crack.

failure mechanism it is reasonable to suggest that a relatively large force is required to start the fibres or particles slipping and thereafter a smaller "frictional" force resists the subsequent slipping, i.e. a stress–separation relationship of the form shown in Fig. 1b. Since "fracture mechanics" is principally concerned with the area under this curve, i.e. the work required to propagate the crack, we can approximate Fig. 1b with 1c, in which the stress parameter f_t is no longer the strength of the material, but is some lower arbitrary stress. This interpretation suggests that the good fit obtained by putting $f_t = 5\,\mathrm{MN\,m^{-2}}$ is no longer inconsistent with the fact that direct tensile strengths of up to $12.5\,\mathrm{MN\,m^{-2}}$ were experimentally measured.

References

1. A. HILLERBORG, M. MODÉER, P. E. PETERSSON, *Cement and Concrete Research* **6** (1976) 773.
2. D. D. HIGGINS and J. E. BAILEY, *J. Mater. Sci.* **11** (1976) 1995.
3. D. D. HIGGINS and J. E. BAILEY, Conference on Hydraulic Cement Pastes, Sheffield (Cement and Concrete Assoc., Slough, 1976) p. 283.
4. C. W. MARSCHALL and A. RUDNICK in "Fracture Mechanics of Ceramics" Vol. I, edited by R.C. Bradt, D. P. H. Hasselman and F. F. Lange, (New York, Plenum Press, 1974).
5. J. AVESTON, R. A. MERCER and J. K. SILLWOOD, Conference on Composites Standards, Testing and Design, National Physical Laboratory (IPC Science and Technology Press, Guildford, 1974) p. 93.

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Thermal shock resistance of silicon nitride

Silicon nitride (Si_3N_4), silicon carbide (SiC), sialon and aluminium nitride (AlN) have been recognized as leading candidates for high-temperature gas turbine materials [1–9]. Of all the ceramic components in gas turbines, rotor and stator blades have to receive and withstand the most severe mechanical and thermal stresses. Fully densified Si_3N_4 and SiC would be limited materials because of the requirement that components should possess high strength at operating temperatures.

Recent developments have produced a hot-pressed high-strength Si_3N_4 with 5 wt% yttrium oxide (Y_2O_3) and 2 wt% aluminium oxide (Al_2O_3) by applying a new sintering method, the grain-boundary crystallization (GBC) method [9].

A major factor determining the importance of ceramics is their usefulness at high temperatures. Since this often involves rapid heating and cooling of the material, good thermal shock resistance is advantageous. Thermal shock tests currently in use are essentially of two types: determination of the minimum shock to nucleate cracking, and determination of the amount of damage sustained