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Strength and Toughness in Ceramic Systems [and Discussion]

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Strength and toughness in ceramic systems

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There has been a steady development and use of fracture mechanics, for describing the strength of brittle materials, ever since its inception by Griffith (1920). Materials considered include glass, ceramics, cement, brittle polymers, brittle metals, and a wide range of composite materials such as fibrous composites. The complexity of the fracture process generally increases as one passes along this list. A basic concept of fracture mechanics is a fracture surface energy or fracture toughness. Ideally this is a material constant but this is rarely true in practice. This paper summarizes the current state of understanding for ceramics and discusses a number of specific problem areas. This information should thus act as a signal to workers using fracture mechanics on cementitious materials. Problems considered include environmental sensitivity, statistical variations in strength, crack length effects, the concept of a flaw for porous materials, plastic effects, and transformation toughening.

1. INTRODUCTION

Fracture mechanics provides the basic framework for understanding the strength and toughness of ceramics. The tensile fracture strength of a ceramic σ_f can be understood in terms of the Griffith equation

$$\sigma_f = \frac{1}{Y}\left(\frac{2E\gamma_i}{C}\right)^{\frac{1}{2}} = \frac{K_{Ic}}{YC^{\frac{1}{2}}}, \tag{1}$$

where Y is a geometrical constant, E is the Young modulus, γ_i is an effective surface energy, C is a flaw size, and K_{Ic} is a stress intensity factor or fracture toughness. This equation implies that the surface energy or fracture toughness of the material is a constant, so that provided that the flaw size is known, the fracture strength can be estimated.

In the original experiment, Griffith (1920) produced thin slit-like cracks throughout the thickness of glass spheres and cylinders. The specimens were broken by the application of an internal pressure, with a compressive axial stress being applied as an additional variable for the cylindrical specimens. Griffith observed that the product $\sigma_f C^{\frac{1}{2}}$ was essentially constant in his experiments and furthermore that the effect of a compressive stress in the cylindrical specimens did not affect this observation. Griffith, in fact, tested only ten specimens and it is therefore, perhaps, not surprising that he did not discover some of the complicating factors that are significant in understanding the strength of ceramic materials under general conditions. He did, however, obviously recognize the importance of a number of key variables and, apart from the state of stress, he also mentioned the effects of the range of crack sizes used, the time taken to fracture the specimens, and the test environment.

Complicating factors affecting the strength of ceramics are manifested in two main ways. First, strength is generally time dependent in that the application of a tensile stress on a component causes a gradual diminution of its capability to withstand further stress without rupture. Second, there is a relatively large statistical variation in the strength of a batch of otherwise identical specimens. These factors can both be considered with reasonable success at an empirical level so that good prediction of mechanical performance may be made. Additionally there is an increasing awareness of the importance of various microstructural features and how these affect fracture. This paper is concerned with a review of some of the more important recent developments in understanding in these areas.

2. Subcritical crack growth

When a brittle ceramic specimen, with a large preformed crack, is fractured in tension, in vacuum or inert atmosphere, its behaviour follows classical expectations of the Griffith equation (1). The fracture surface energy is essentially constant, and specimens with similar-sized cracks fail at a similar force.

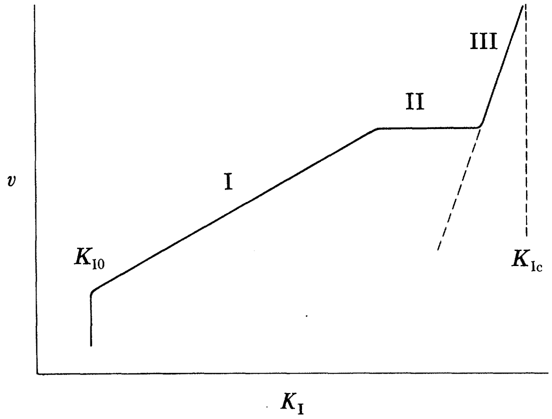

Figure 1. Idealized stress intensity factor–crack velocity (K/v) diagram for ceramics (logarithmic scales).

Under more aggressive conditions, for example wet environments for oxides, or at high temperatures for all ceramics, the situation is very different. Data relating crack velocity to stress intensity factor have been obtained for a wide range of ceramic materials by using standard fracture mechanics tests, particularly the double torsion test and the double cantilever beam test. The classical behaviour observed is shown in figure 1, where there are three well defined regions. Above a threshold stress intensity factor the crack velocity in region I is proportional to the nth power of the stress intensity factor. In region II the crack velocity is independent of stress intensity factor, and in region III the behaviour is similar to that in region I but with a significantly higher slope. Fracture finally occurs at the critical stress intensity factor K_{Ic}. The rate of crack growth in region I is reaction rate controlled, whereas in region II it depends on the diffusion of a corrosive species to the crack tip. In most situations the corrosive agent is water and region II occurs at higher crack velocities with increase in water content. Region III represents an inherent behaviour of the material and is the only stage observed when testing is done in vacuum.

The important effects relating to time dependence of strength are generally concerned almost solely with region I in that the behaviour associated with other regions occurs during very short times. This has led to the emergence of the parameter n as all-important in determining the time dependent behaviour of ceramics.

For simple systems such as glass, where the effects of microstructure are eliminated, there is very good agreement between basic theory and experimental observation (Wiederhorn 1980). The theory is based on a stress enhanced chemical reaction between water and the highly stressed material near the crack tip. The basic rate equation from chemical reaction rate theory can be modified to reflect physical and chemical processes that occur at the crack tip. The theory is consistent with data for crack growth dependence on temperature, applied stress intensity factor, and the concentration of water in the environment.

3. Statistical variations in strength

The flaws from which fracture originates in normal engineering ceramics are small (typically 10–100 μm) and numerous. Fracture initiates from the largest effective flaw and therefore it is necessary to consider strength on a statistical basis. With reference to equation (1) statistical variations in strength can be discussed in terms of K_{Ic} and C (neglecting any errors of physical measurement, which are small). The determination of K_{Ic} from standard fracture mechanics tests requires the introduction of a large crack into the specimen that is much larger than the inherent flaw size. Data on the statistical variation of the critical stress intensity factor has been measured by Pankow & Finnie (1979) for polycrystalline alumina. Their results are shown in figure 2. The K_{Ic} data were generated from specimens with sharpened notches (radius 20 μm) and are compared with strength data for smooth beams broken in three-point bending. The scatter in K_{Ic} is four times less than the scatter in strength. This suggests that for large sharp cracks K_{Ic} may be essentially constant. This is intuitively reasonable because the crack is sampling a statistically large area of the specimen as it propagates. Therefore the scatter in strength must be due mainly to the variation, between specimens, in the largest flaw size.

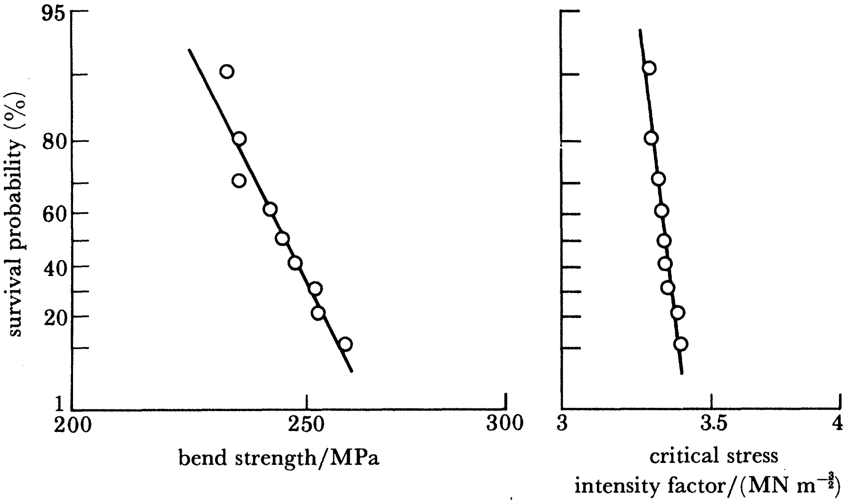

Figure 2. Statistical variations in strength and stress intensity factor for alumina (Pankow & Finnie 1979).

The statistical treatments used to describe the strength of ceramics are based on weakest link theory and on assumptions referred to in statistical theory as the Poisson postulates. The general theory of statistics of extremes is given in the book by Gumbel (1958) and the weakest link theory of strength, pioneered by Weibull (1951), is one aspect of this. In essence the problem is:

given a particular distribution of property values (for example strength), what is the minimum value expected for a particular number of samples? For example, one might be required to estimate the highest operating stress that could be applied to a component to give a failure rate of less than 1 in 10^6 from a number of observations of strength (typically, less than 100).

The theory assumes that the material can be divided into a number of small regions (which could be volume $\mathrm{d}V$ or area $\mathrm{d}A$ depending on whether volume or surface flaws are controlling) that act independently, each containing a flaw associated with a particular strength S. The strength of the whole is then determined by the strength of the weakest region, as in the links of a chain. The theory as applied to ceramics considers a function $g(S)$ such that the number of flaws per unit volume (or area) associated with a strength between S and $S+\mathrm{d}S$ is $g(S)\,\mathrm{d}S$. If $\mathrm{d}\varphi$ is the probability of failure of an element

$$\mathrm{d}\varphi(S) = \mathrm{d}V\int_0^s g(S)\,\mathrm{d}S, \tag{2}$$

with a survival probability $1-\mathrm{d}\varphi(S)$. In material of volume V there are $V/\mathrm{d}V$ volumes $\mathrm{d}V$. The probability $(1-\varphi)$ that no volume has a strength lower than S is the product of the separate probabilities, and

$$1-\varphi = (1-\mathrm{d}\varphi)^{V/\mathrm{d}V} = \left\{1-\mathrm{d}V\int_0^s g(S)\,\mathrm{d}S\right\}^{V/\mathrm{d}V}. \tag{3}$$

This reduces to, as $V/\mathrm{d}V \rightarrow \infty$,

$$1-\varphi = \exp\left\{-V\int_0^s g(S)\,\mathrm{d}S\right\}. \tag{4}$$

The theory of the statistics of extremes considers three kinds of asymptotic function for $g(S)$: the first two refer to variates that are unlimited in extreme values; for distributions that are bounded at one extreme the so-called asymptotic function of the third kind holds. So, this third function is of most relevance to the strength of engineering ceramics, which must have a tensile strength not less than 0. Analysis shows that the simplest function for $g(S)$, relevant to a lower limit S_u, is given by

$$\int_0^s g(S) = \left(\frac{S-S_\mathrm{u}}{S_0}\right)^m, \tag{5}$$

where S_0 is a 'scale' parameter and m the 'shape' parameter. This will be recognized as the well-known Weibull distribution; m is usually known as the Weibull modulus and increases with decreasing variability in strength.

Weibull statistics are widely applied to the strength of ceramics, and for many data there is good agreement between experimental results and the above function. Often, the lower limit of strength S_u is taken as zero and thus, rearranging equations (4) and (5) gives a proportionality between survival probability $P_\mathrm{s} = 1-\varphi$ as

$$\ln\ln\,(1/P_\mathrm{s}) \propto m\ln S. \tag{6}$$

Typical data fitting this relation are shown in figure 3. The prediction of stress levels for high survival probabilities is possible but this should be treated with some caution because extrapolations way beyond the experimental data are involved and there is little evidence to indicate that the predictions are accurate.

An additional attraction of Weibull statistics is that, for materials that are consistent with the theory, it is possible to predict effects on strength of the state of stress (for example, uniaxial, biaxial), the distribution of stress, and the specimen size. Here, however, we are concerned more with the average rather than extreme values of strength. Both these effects are a manifestation of the fact that the greater the volume of material under stress, or the greater the number of flaws perpendicular to the tensile stress, the higher the chance of finding a large flaw.

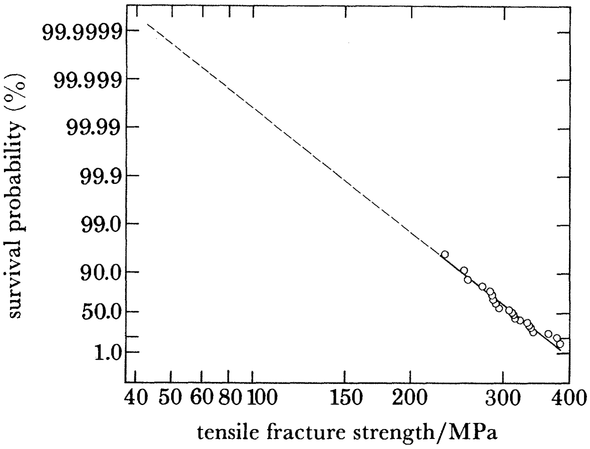

FIGURE 3. Statistical data for the tensile strength of REFEL silicon carbide according to equation (6) (Davidge 1979).

4. DESIGN PROCEDURES FOR CERAMICS

Although the experimental data that can be obtained on the time dependence of strength and the statistical variations in strength are based partly on empirical relations, they can be used for engineering design purposes (Davidge 1979).

Useful design procedures are now developed such as the strength–probability–time (s.p.t.) diagram (Davidge *et al.* 1973) and the proof stress diagram (Wiederhorn 1974), and these are being used increasingly for the routine evaluation of engineering ceramic components. Examples are shown in figures 4 and 5 for a vitreous bonded alumina ceramic as used for grinding wheels The s.p.t. diagram shows that under use at the maximum recommended operating speeds (with the maximum stress one quarter of the mean bursting strength of the wheel) the probability of survival is extremely high. With the additional safeguard of a proof test (which is common practice in the industry), the proof test diagram indicates what level of proof test ratio (proof stress: maximum operating stress) is required to guarantee a specific minimum lifetime for the grinding wheel. This is only one specific example of an engineering approach to the use of ceramics and there are many others.

5. MICROSTRUCTURAL EFFECTS

In this section we mention a number of microstructural effects that are relevant to the understanding, at a more fundamental level, of the mechanical properties of ceramics.

(*a*) *Changes in fracture toughness with crack length*

Data for the critical stress intensity factor are obtained generally from specimens with large preformed cracks, but there are complications at flaw sizes comparable in size to microstructural features. The surface energy for a grain size crack should approximate to the cleavage or grain boundary surface energy (γ_0), which is usually at least an order of magnitude less than the effective surface energy for macroscopic fracture (γ_i). Further propagation of the crack beyond a grain size dimension has a greater surface energy requirement and this may be a simple step function, or more complicated as indicated in figure 6, where it is envisaged that γ rises to γ_i

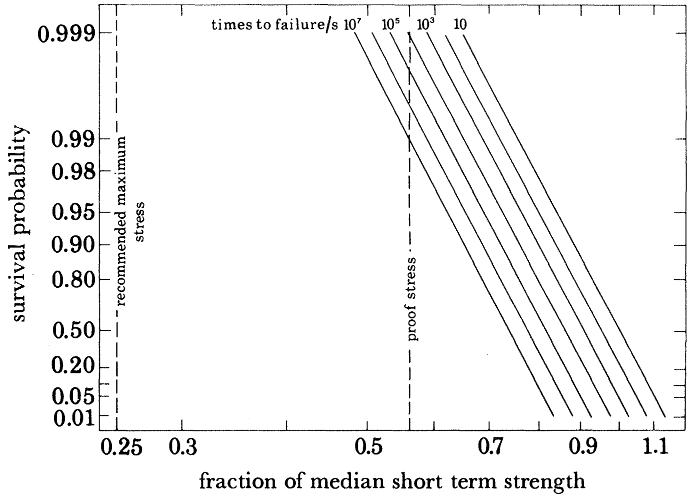

FIGURE 4. Strength–probability–time diagram for vitreous bonded alumina ceramic (McLaren *et al.* 1978).

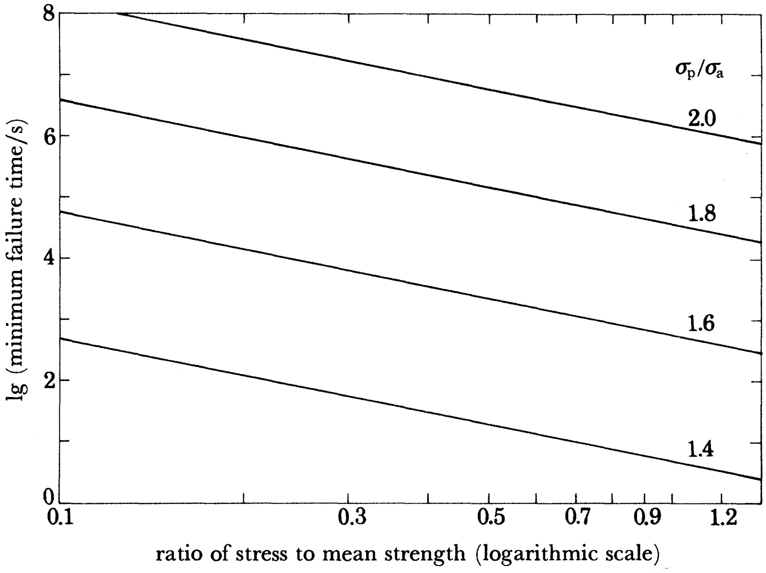

FIGURE 5. Proof test failure diagram for vitreous bonded alumina.

over a length of a few grain dimensions. Strength is controlled by the maximum value of γ/C and in figure 6 the value at points P, Q and R, for the three curves drawn. Fracture may thus be preceded by a period of subcritical crack growth based on microstructural considerations. (This is in addition to the environmental stress corrosion effects discussed above.) Thus for inherent flaws it is conceptually difficult to discuss strength in terms of an independent crack size and stress intensity factor in that these two parameters interact strongly.

A serious consequence of this effect relates to the different engineering design behaviour of large cracks, as used to generate engineering design data, and small cracks from which the fracture originates in normal specimens. Values of n obtained from K/v diagrams should thus be treated with some caution, and it is often preferable to use data for n obtained from strain rate dependence of strength or delayed fracture measurements, which relate to the behaviour of the inherent flaws. For example, in alumina it has been found that the value of n obtained from strain rate variations is approximately one half that obtained from double torsion tests (Davidge *et al.* 1973). The K/v data from macroscopic cracks would thus lead to a highly optimistic performance of components.

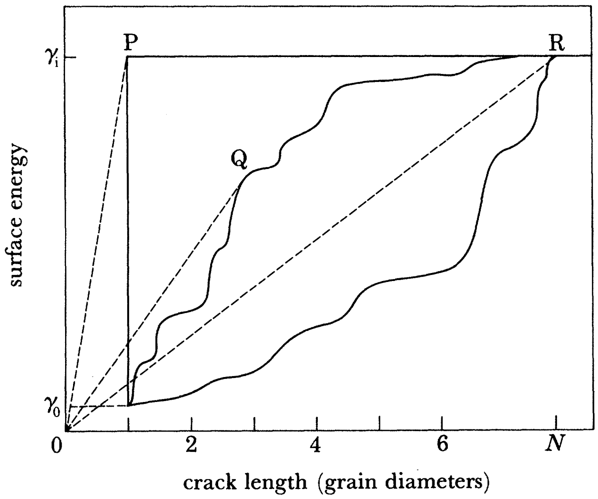

FIGURE 6. Variation of effective surface energy with crack length.

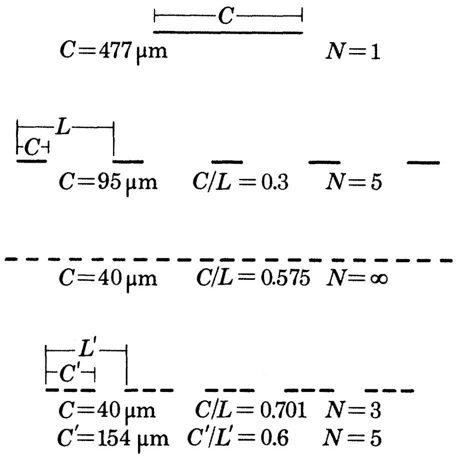

FIGURE 7. Various linear arrays of microcracks that would all propagate at the same stress (Okada & Sines 1983).

(*b*) *Effects of crack density*

A further complication arises from the density of inherent cracks. The theory assumes that these flaws do not mutually interact. However, when the crack spacing is similar to the crack size this is not true. Okada & Sines (1983) have identified a relatively high density of active microcracks in polycrystalline alumina and a number of close but small microcracks can coalesce and lead to failure. Figure 7 shows three such arrays of cracks that could all propagate in a short time at the same stress as the single large crack at the top of the figure. Note that this has serious consequences for non-destructive testing techniques. The nil-observation of flaws above a particular size in a sample could lead to an optimistic prediction for strength if fracture was initiated from closely-spaced smaller flaws. An additional problem is that the times to failure under delayed fracture conditions for the various crack arrays vary by an order of magnitude.

Related effects are expected to be significant in porous materials. For porosity values larger than 5–10 %, the porosity in ceramics is of the open, connected type. In highly porous materials the pores, which act as flaws, are all interconnected and the entire specimen can be regarded as being permeated by a single large flaw.

(c) *Zirconia toughening of ceramics*

The presence of cracks in ceramics is not always detrimental to their mechanical properties and, for zirconia toughening, the presence of a high density of very fine cracks can be positively beneficial.

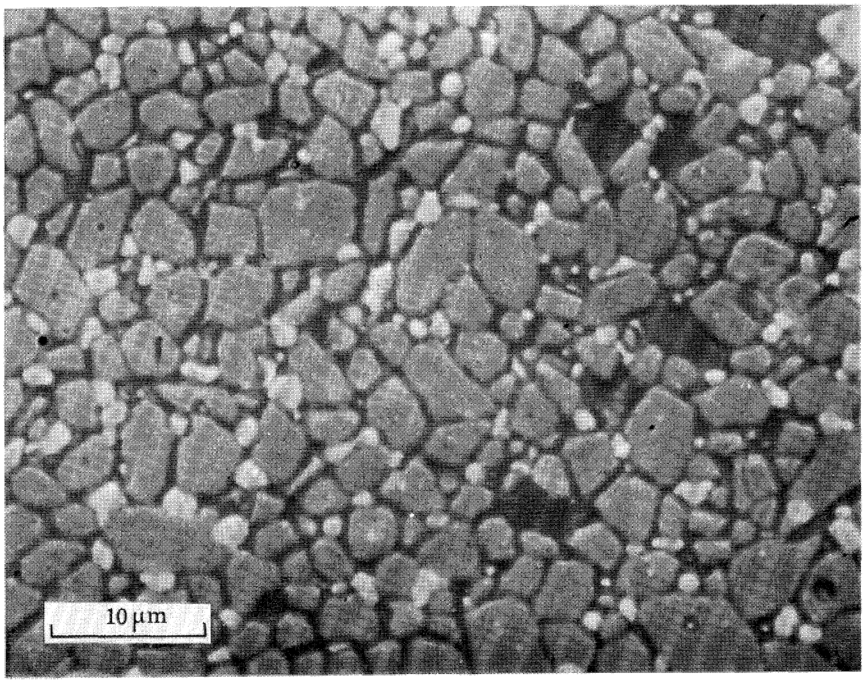

FIGURE 8. Optical micrograph of alumina toughened with 20 % tetragonal zirconia.

Zirconia exists in several crystallographic forms. Normally, amounts of stabilizing oxides such as MgO, CaO or Y_2O_3 are incorporated to stabilize the cubic phase. Pure zirconia, however, exists in a tetragonal crystallographic form at temperatures above 1000 °C but in a monoclinic form at lower temperatures. The transformation, from one phase to the other on cooling, which is of a martensitic type, produces large volume increases (*ca.* 5 %) and high shear strains. When tetragonal zirconia is incorporated as a second phase into a host matrix, two different effects can occur depending upon whether the zirconia is retained as the tetragonal phase or has transformed to the monoclinic phase in the ceramic as fabricated. In the first case one can get toughening plus strengthening, in the second one can find toughening but commonly without strengthening.

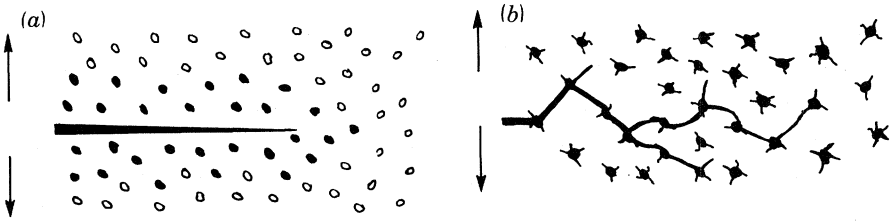

FIGURE 9. Toughening mechanisms for zirconia toughened ceramics. (*a*) Tetragonal zirconia particles (open areas) transform to monoclinic zirconia (black areas) in the vicinity of the crack tip. (*b*) Monoclinic zirconia particles with associated microcracks lead to deflexion and bifurcation of the main crack.

The essential feature of the toughening plus strengthening mechanism is that the zirconia particle size must be kept very fine, typically 1 μm or less. The elastic constraint of the matrix material may be great enough to suppress the phase transformation when the material is cooled to ambient temperatures after fabrication. In material with the optimum microstructure, figure 8, the transformation is triggered by the application of stress. In regions near the tips of the cracks, the magnified tensile stresses can reduce the constraint of the matrix on the particle so that the transformation occurs. The result is that a partly compensating compressive stress is set up just ahead of the crack tip, which makes crack propagation much more difficult, thus increasing both toughness and strength. Normally the transformed particles are restricted to a zone *ca.* 10 μm wide adjacent to the crack face. Toughness and strength are increased by about a factor of 2 with absolute values depending on the inherent properties of the matrix material. The basis of this mechanism is sketched in figure 9.

For the straightforward toughening (but not strengthening) mechanism the zirconia particles have already transformed in the material in its state as fired. The transformation and volume increase are associated with the generation of a network of localized cracks radiating from the transformed particles. The essential feature here is that any major crack is continually deflected and bifurcated on approaching the toughening particles, which leads to the increase in toughness, as indicated in figure 9. This mechanism is particularly significant for bestowing dramatic improvements in thermal shock resistance.

(*d*) *Effects of microstructural and chemical changes at high temperature*

In the discussion so far the only changes occurring in the material involve the subcritical growth of microcracks up to the point of catastrophic failure. Whereas this situation is obtained for low-to-moderate temperatures, it is much more complicated at higher temperatures where additional effects can occur involving microstructural or chemical changes to the material. There are a number of important effects including:

(*a*) localized plastic flow, which can induce crack healing or the generation of creep induced voids;

(*b*) chemical changes, particularly oxidation, which again can produce crack healing but also the generation of new defects;

(*c*) microstructural changes such as grain growth, phase changes or surface evaporation. Any of these changes may be either deleterious or advantageous with respect to strength.

The important consequence is that the original flaw population present at ambient temperature cannot necessarily be regarded as relevant in controlling the mechanical response of a material to stress at high temperatures. This means that the valuable techniques mentioned above such as proof testing or non-destructive testing have limited validity for high temperature performance prediction. This is because the ranking of the strength of a set of components is different at low temperature compared with high temperature. A dramatic example of this for hot pressed silicon nitride is shown in figure 10. Data for two sets of specimens are compared at 25 °C and 1200 °C, before and after proof testing at 25 °C. In the data at 25 °C the strength of the proof-tested specimens is highly truncated, and in agreement with theory, indicating the value of the proof test. On the other hand, similar data for specimens tested at 1200 °C, which had first been heated for 30 min at 1200 °C, show virtually identical strength distributions irrespective of proof-testing. This indicates strongly that the original flaws are not relevant in controlling strength under high temperature conditions.

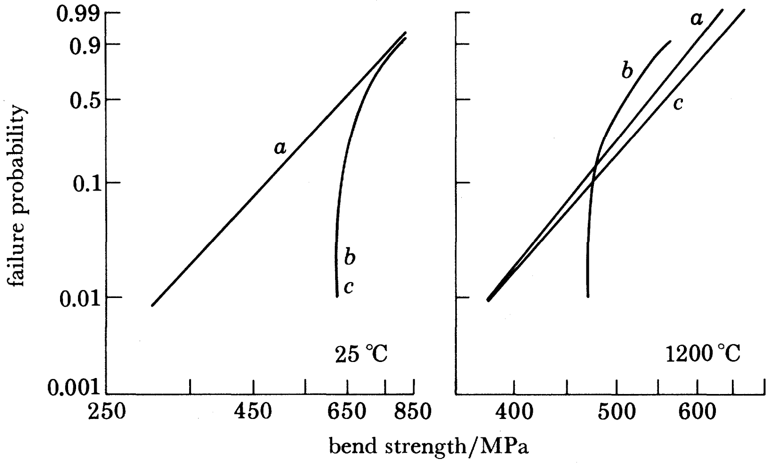

Figure 10. Effects of proof testing at 25 °C on the strength of silicon nitride tested at 25 °C, and after 30 min at 1200 °C. (*a*) Samples not proof tested. (*b*) Theoretically predicted curve after proof testing. (*c*) Proof tested samples.

One thus has a daunting list of possibilities for potential high temperature effects that control strength and it is not surprising that performance prediction techniques under these conditions are still in their infancy. This is however clearly a priority area for research if the reliability of structural components for high temperature applications is to be derived with any confidence.

6. RELEVANCE TO CEMENT

Cement is traditionally regarded as a brittle material that is very weak in tension. Cement and concrete structures are designed so that the material is used predominantly in compression, with the aid of steel reinforcement or pre-stressing where appropriate. The great bulk of the literature on the mechanical properties of cement is concerned, therefore, with behaviour under compressive stresses (for a recent review see Sereda *et al.* 1980). The information summarized in the current paper is therefore of peripheral interest to the traditional uses of cement and concrete.

The recent development of macro-defect-free (MDF) cement with greatly enhanced mechanical properties (for example bend strengths of 200 MPa) shows that cement can now be considered for a range of applications, hitherto impracticable, where the material can be used under significant tensile stresses. A straightforward application of fracture mechanics and the Griffith equation (1) indicates that the MDF cements have increased values (about twice) for the Young modulus and surface energy and, of major significance, a greatly reduced (by about an order of magnitude) flaw size (Birchall *et al.* 1981, 1982). The detailed explanation must be more complex because the fracture toughness of cement is not a material constant and is significantly affected by specimen geometry and test conditions (Bailey & Higgins 1981; Alford *et al.* 1982).

In conclusion, based on the state of the art for ceramics, a number of comments are listed below that might be considered when applying fracture mechanics to the tensile behaviour of cements. It is hoped that these will stimulate improved understanding for cements.

(1) The application of fracture mechanics to cements is more complex than for ceramics.

(2) A statistical scatter in the strength of cements is expected; Weibull statistics can probably be applied.

(3) Subcritical crack growth under stress is expected for cements.

(4) The properties of cements (in the absence of stress) will change with time in sympathy with microstructural developments.

(5) Significant variation in the fracture toughness of cement with crack length should be expected.

(6) Some measure of crack healing could occur through microstructural changes.

(7) The concept of a flaw size in a very porous material like cement is complex and will make interpretation of strength difficult.

(8) The deliberate introduction of a fine dispersion of cracks, for example by the growth of fine particles during ageing, could lead to useful enhancements in properties through highly localized microcracking.

(9) Design data for engineering application of new cements require development. These could be based on the same principles as those for ceramics, but behaviour is likely to be more complicated.

(10) A considerable amount of research effort is required on the fracture mechanics of cement to improve understanding and stimulate engineering uses for the material.

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Discussion

H. F. W. Taylor (*University of Aberdeen, U.K.*). In the first mechanism of zirconia toughening that Dr Davidge mentioned, how rapid must the transformation be for it to be effective? One can think of several possible expansive processes in a cement paste, but I wonder if any of them would occur quickly enough.

R. W. Davidge. In the first toughening mechanism the transformation takes place through a martensitic reaction; this very rapid response is essential, otherwise at high strain rates the crack could propagate before the benefits of toughening have been obtained. The possible expansive processes in cement would not be of the above type, but there could be benefits through the second type of toughening mechanism involving a fine dispersion of microcracks.

J. E. Bailey (*University of Surrey, U.K.*). Dr Davidge drew attention to subcritical crack growth problems in fracture mechanics. It is perhaps relevant to point out that rather tortuous subcritical crack growth has been observed in notched three-point bend tests on cement paste, indicating that stress concentrations are reduced and that cracks, however sharp, are effectively blunted by the cement microstructure.

R. W. Davidge. Professor Bailey's observations indicate that the fracture toughness of cement should increase quite markedly with increase in crack length. Toughness values measured from fracture mechanics type specimens with large preformed notches are thus probably not applicable to the initial propagation of the inherent flaws.

M. S. T. Price (*UKAEA, AEE, Winfrith, Dorset, U.K.*). One point that Dr Davidge has not had time to mention is that there is a problem with an inherently granular material of relating the results of strength measurement on test specimens to the bulk behaviour. The problem is rendered more difficult if non-uniform stress conditions are used.

A material that I would suggest has important analogies with cement is polycrystalline graphite. It is granular and extensively flawed. The main reason for pointing to the behaviour of graphite is the considerable study of the material for structural uses in nuclear and aerospace application. See for example a review such as 'Fracture in graphite' by M. S. T. Price, presented at The Sixth London International Carbon and Graphite Conference, Society of Chemical Industry, London, 20–24 September 1982.

The way forward must take due account of microstructure and take advantage of the power of finite element computational techniques.

R. W. Davidge. For ceramics, it is relatively straightforward to use the principles of fracture mechanics and statistical variations in strength to relate the strengths of specimens with different sizes or stress distributions. Whether such principles can be applied to cement materials will depend on much more detailed information about their basic fracture behaviour.

J. Skalny (*Martin Marietta Laboratories, Baltimore, Maryland, U.S.A.*). Are there any other materials that could be used to replace zirconia (ZrO_2) in toughening ceramics? What are the chances of using this toughening mechanism for a porous material like hydrated cement?

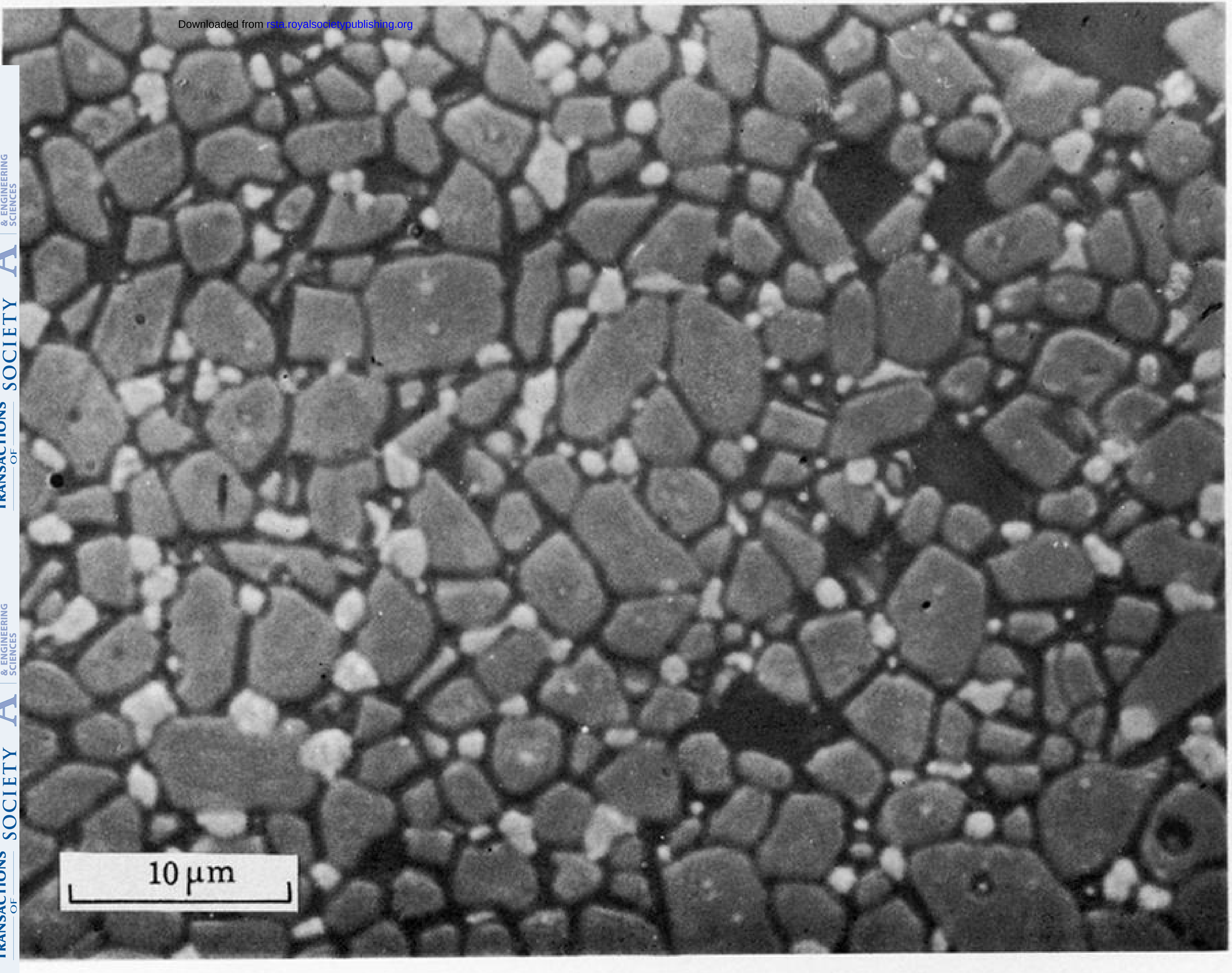
R. W. Davidge. The only other material found to toughen ceramics, as observed with zirconia, is the chemically related but much more expensive HfO_2. (My replies to Dr Alford's comments are also relevant.)

N. McN. Alford (*I.C.I., Runcorn, Cheshire, U.K.*). Dr Davidge suggested that the incorporation of reactive particles might be a means of toughening cement. In zirconia-toughened ceramics it is still not clear whether microcrack formation causes toughening as Dr Davidge suggested, or whether the martensitic transformation itself dissipates strain energy. I would suggest that the benefits of incorporation of reactive particles would merely cause a reduction in strength and modulus, and benefits to toughness would be minimal if any.

R. W. Davidge. I agree that incorporation of reactive particles into cement could cause deterioration of several mechanical properties. However, I believe that a fine dispersion of particles to produce localized cracking of dimensions rather less than the inherent flaws could in principle give useful improvements in toughness. It would clearly be useful to check these ideas experimentally.

C. D. Pomeroy (*Cement and Concrete Association, Wexham Springs, Slough, U.K.*). Cement hydrates comprise many different components, which will have different toughnesses. How does this affect the application of fracture mechanics and the production of crack growth? Would crack arrest by tougher components significantly influence the fracture mechanism?

R. W. Davidge. It is not so much the individual toughness of the component phases of concrete that affect fracture behaviour, but the various complex ways in which the components react with each other. Of particular importance are differences in thermal expansion behaviour and n elastic properties.



IGURE 8. Optical micrograph of alumina toughened with 20% tetragonal zirconia.