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Dependence of ceramic fracture properties on porosity

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A connected-grain model developed earlier to study the modulus of elasticity as a power-law of density was extended to study the dependence of the flexural strength of polycrystalline ceramics on porosity. Relations were derived for specific surface fracture energy, fracture toughness and flexural strength as power laws of $(1 - p)$, where p is porosity. Model validity was confirmed with data on α-alumina, UO_2, Si_3N_4, and the $YBa_2Cu_3O_{7-\delta}$ superconductor.

1. Introduction

The fracture of porous ceramics is a subject of considerable practical importance. The applications of porous devices such as gas sensors [1], heat exchangers [2], particulate filters [3], building materials [4], and refractories [5] require both high porosity and good strength. The strength of a porous material depends on pore distribution, pore morphology, and pore size, with high porosity generally leading to low strength. Therefore, to improve the fracture properties of porous ceramics, it is essential to understand the effect of porosity on fracture behaviour of these porous ceramics.

Ceramics have inherently random microstructures. The pores in these materials have random shapes, sizes, and distributions. Models proposed in the literature to describe the fracture behaviour of porous materials are either empirical or based on analytical treatment of geometrically regular pore shapes and idealized pore distributions: hence, they do not incorporate randomness of microstructure. The details of these models may be found in the review by Singh [6]. Here, only a brief summary of such earlier attempts is given.

Duckworth [7] proposed that the empirical relation between porosity, p, and flexural strength, $\sigma_f(p)$, is

$$\sigma_f(p) = \sigma_0 \exp(-bp), \qquad (1)$$

where σ_0 is the flexural strength of a pore-free material and b is an empirical constant. The value of b varies from 3–7 depending on the range of porosity. The applicability of Equation 1 at high porosity is limited and $\sigma_f(p = 1)$ is not zero. Dutta *et al.* [8] have proposed the following similar empirical relation to describe the dependence of strength on porosity

$$\sigma_f = \sigma_0(1 - p)^m \qquad (2)$$

where m is an exponent arising from a similar relation for elastic modulus. In their study, Dutta *et al.* [8] assumed that crack length is independent of porosity, and that specific fracture energy, γ, is proportional to the modulus of elasticity. When applied to the data on Si_3N_4, agreement between the model (Equation 2) and experimental data was somewhat limited.

On analytical grounds, Vardar *et al.* [9] developed a statistical model to predict the dependence of strength on the porosity of randomly distributed pores. Applying the Weibull approach, the authors concluded that strength depends on pore content, rather than on pore size. Recently, Krstic [10] proposed a similar model to describe the dependence of strength on porosity. Evans and Davidge [11], on the other hand, assumed that during fracture at low stress, a pore at the grain boundary extends along the first grain boundary to form a crack of length equal to the sum of the pore size, R, and the grain size G. Using Griffith's equation [12], they obtained

$$\sigma_f = \left[\frac{2\gamma E}{\pi(R + G)}\right]^{1/2} \qquad (3)$$

where γ is the specific surface energy and E is the modulus of elasticity. This equation was confirmed by experimental data on UO_2.

The analytical models described above are applicable to ceramics with low volume fractions of porosity, i.e. where pores are isolated. In practice, as discussed in an earlier paper [13], pores in highly porous materials are connected.

In view of the above discussion, there is a need for an analytical model that incorporates the random, connected-pore structure of ceramics. Such models have been attempted in efforts to explain charge and mass transport through the random-pore structures of rocks [14] by using both analytical and computational techniques. Based on these studies, a connected-grain model was proposed by Wagh *et al.* [13] to explain the dependence of elastic modulus on porosity. The connected-grain model of Wagh *et al.* [13] was extended here to predict the fracture behaviour of

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porous ceramics. In our model, a ceramic structure is characterized by the connectivity of grains and skewness of grain size distribution. Furthermore, the porosity dependence of modulus of elasticity, E, is given by $E(p) = E_0(1-p)^m$, where E_0 is the porosity of the pore free material, and m is dependent on the grain and pore size distribution. Our model has several important features: (a) it preserves the random nature of grain size and its distribution; (b) it relates the microstructure of the material, such as pore and grain size and their distribution, to the average properties of the material; and (c) it relates the ratio of physical properties of a porous material to the corresponding dense material with the porosity as a power law. Such relations are mathematically simple to handle and are known as scaling relations.

We extend the model of Wagh *et al.* [13] to study fracture parameters, e.g. specific surface fracture energy, fracture toughness, and flexural strength, and their dependence on porosity. In Section 2, the model is briefly described and the porosity dependence of specific fracture energy is derived. In Section 3 the result is applied to Griffith's theory of fracture [12], and explicit porosity dependence of the flexural strength is obtained. The model predictions are compared with experimental data in Section 4.

2. Dependence of specific surface energy of ceramics on porosity

A polycrystalline ceramic structure may be considered as a three-dimensional continuous network of grains. As in a mathematically tractable model, grains can be represented by solid cylinders of material where their length is of the order of the average grain size. Thus, a ceramic microstructure may be represented by a continuous network of solid cylinders with pore channels in between. Materials-related transport phenomena, such as mechanical, thermal, electric, and magnetic properties, may be studied by considering the materials chains, whereas the pore-related properties, such as fluid permeability, may be studied by considering the pore channels.

The random size distribution of grains can be represented by the variation in the cross-section of the solid cylinders along the length of the chains of cylinders. The analytical simulation to obtain the variation of the size of grains is performed by shrinking the radii of randomly chosen cylinders by a fraction x at a time. This process is repeated until the average size of a cylinder is reduced to the average grain size in the ceramic under consideration. A detailed description of the procedure is given in [13]. In this paper, we present only the highlights of the derivation of a one-dimensional model.

We assume that initially, the microstructure consists of cylinders whose size is equal to the largest grain size, r_0, in the material. The random reduction, say for the ith cylinder, reduces its radius from r_i to xr_i. This means that the area of the cross-section of the cylinder would be reduced by a factor of x^2. The probability, $\Phi(n)$, that any particular cylinder will shrink n times is given by the binomial distribution

$$\Phi(n) = \left[\frac{M!}{(M-n)!n!}\right]\frac{1}{(N!)^n}\left[\frac{(N-1)}{N}\right]^{M-n} \tag{4}$$

where N is the total number of cylinders and M is the total number of times the shrinking operation is performed. The average of the cross-sectional area $\langle A\rangle$ of the ith cylinder is given by

$$\begin{aligned}\langle A\rangle &= \pi\langle r_i^2\rangle \\ &= \pi r_0^2\sum_{n=0}^{M} x^{2n}\Phi(n)\end{aligned} \tag{5}$$

where r_0 is the radius of the unshrunk cylinder. The summation of the right-hand side of Equation 5 yields

$$\langle A\rangle = \pi r_0^2\left[\frac{(N+x^2-1)}{N}\right]^M \tag{6}$$

Similarly, the average volume of the ith cylinder of length l is

$$\begin{aligned}\langle V\rangle &= \pi\langle r^2\rangle l \\ &= \pi l r_0^2\sum_{n=0}^{M} x^{2n}\Phi(n) \\ &= V_0\left[\frac{(N+x^2-1)}{N}\right]^M\end{aligned} \tag{7}$$

where, $V_0 = \pi r_0^2 l$ is the volume fraction of an unshrunk cylinder. Because $N\langle V\rangle/N_0V_0$ is the volume fraction of the material, we have from Equation 7

$$\frac{\langle V\rangle}{V_0} = \left[\frac{(N+x^2-1)}{N}\right]^M = (1-p) \tag{8}$$

Similarly, from Equations 6 and 8

$$\langle A\rangle = A_0(1-p) \tag{9}$$

where $A_0 = \pi r_0^2$ is the area of the cross-section of an unshrunk cylinder. Equation 9 relates the average area of the cross-section of the cylinders to the porosity of the material.

The analytical treatment presented here is limited to a one-dimensional model. However, computer simulations carried out by Wong *et al.* [14] show that these relations are the same for a three dimensional network of cylinders. Therefore, these relations may be used to obtain porosity dependence of various physical properties of polycrystalline ceramics.

As described in our earlier article [13], each grain in a polycrystalline ceramic consists of a lattice structure in which the bonds between atoms are represented by elastic springs. The number of springs at a given cross-section is proportional to the area of cross-section. Based on this, it was shown [13] that the average spring constant $\langle k\rangle$ of the entire material is given by

$$\begin{aligned}\langle k\rangle &\propto \langle r^{-2}\rangle \\ &\propto (1-p)^m\end{aligned} \tag{10}$$

and because, $E \propto \langle k\rangle$, it can be shown that

$$E = E_0(1-p)^m \tag{11}$$

where E_0 is the elastic modulus of a pore-free material and m, a function of the shrinking parameter x increases when x decreases and vice versa. In one dimension [13], m is equal to $-1/x^2$. In three dimensions, its value is given in thermodynamic limits [13] by

$$m = \frac{\ln(x^2)}{(1 - x^2)}. \quad (12)$$

Using Equation 11, we proceed to study the porosity dependence of specific surface energy, i.e. the energy spent in generating new fracture surfaces which is measured as energy per unit area of the new surfaces. When the material is loaded, energy may be stored in the grains as elastic strain energy. This energy is relieved as the specific surface energy when fracture is initiated and new surfaces are formed. Energy may also be consumed at the crack tip by dislocation motion [15], by micropores [16], and by cleavage-step formation [17, 18]. A summary of various fracture modes that consume energy during fracture is given in the review by Singh [6].

During fracture under stress, the materials chains are stretched and the elastic strain energy is stored in each cylinder. By definition, the elastic strain energy density, u is given by

$$u = \int_0^{\varepsilon_f} \sigma \mathrm{d}\varepsilon \quad (13)$$

where σ is the tensile stress, ε the strain, and ε_f the strain at fracture. Because ceramics are non-ductile materials, we may assume $\sigma = E\varepsilon$. Equation 13 then leads to $u \propto E$. Using this information in conjunction with Equation 11 results in

$$u = u_0(1 - p)^m \quad (14)$$

where u_0 is the energy density in the pore-free material. Therefore, the elastic strain energy in a volume, V, is given by

$$uV = U_0(1 - p)^{m+1}$$

where U_0 is the elastic strain energy in a dense material. Because the specific surface energy, γ, is the energy given by

$$\gamma = \frac{U}{\text{area}} = \gamma_0(1 - p)^{m+1} \quad (15)$$

the elastic strain energy will vary with porosity as $(1 - p)^{m+1}$. In Equation 15, γ_0 is the specific surface energy of the fully dense material.

3. Applications to Griffith's theory

The expression for surface energy developed in the previous section will be used here to obtain the dependence of fracture strength and toughness on porosity and grain size, based on Griffith's theory of fracture [12]. Fracture of a polycrystalline ceramic is caused by inherent flaws [19]. In polycrystalline ceramics there exists a statistical distribution of grain size. As discussed in the previous section, due to the shrinking procedure, a small pore exists adjacent to a large grain so that the sum of the grain and pore sizes remains equal to the original grain size (cylinder size) of the model. The original grain size can be taken as the largest grain size, G_0, in the microstructure, which is also equal to the largest pore size R_0, and may be considered a constant of the given material. Based on the analysis by Evans and Davidge [11] for pore-initiated failure, the critical flaw size, c is equal to this sum. Therefore

$$c \simeq (G + R) = G_0 \quad (16)$$

and, based on Griffith's equation (Equation 3), fracture stress, σ_f, is given by

$$\sigma_f = \left(\frac{2\gamma E}{\pi G_0}\right) \quad (17)$$

Thus, the critical flaw size is equal to the largest grain size, G_0. Because G_0 is a constant, the flexural strength, σ_f, depends on porosity only through its dependence on modulus of elasticity and the specific fracture energy. Substitution for γ and E from Equations 15 and 11 in Equation 17 leads to

$$\sigma_f = \sigma_0(1 - p)^t \quad (18)$$

where $t = m + 0.5$ and $\sigma_0 = (2\gamma_0 E_0/\pi G_0)^{1/2}$. The dependence of flexural strength on porosity is given by Equation 18. Similarly, we can write the porosity dependence of the fracture toughness as

$$K_{IC} = (2\gamma E)^{1/2} = K_{ICO}(1 - P)^{m+0.5} \quad (19)$$

where $K_{ICO} = (2\gamma_0 E_0)^{1/2}$. Thus, the formula for flexural strength and fracture toughness have the same exponent.

In the low-porosity limit, Equation 18 reduces to the Duckworth relation given by Equation 1. This suggests that the empirical parameter, b, used by Duckworth is the same as the exponent t in the present model in the low-porosity limit. The Duckworth relation also exists for elastic modulus given by $E = E_0 \exp(-ap)$, where a is an empirical constant. In the low-porosity limit, a can be shown to be equal to m in Equation 11. From Equation 18 this means that the empirical parameters b and a in the Duckworth relations for flexural strength and modulus of elasticity differ by a value of 0.5. It is also noteworthy that the exponent t in Equation 18 is higher by a value of 0.5 than the exponent empirically predicted for flexural strength by Dutta *et al.* [8], who predict the same exponent for both flexural strength and elastic modulus. The inferences arising from Equation 18 will be verified with experimental data on various polycrystalline ceramics in the next section.

4. Comparison of theory with experiments

Figure 1 shows the plots of experimental data on flexural strength as a function of porosity for α-alumina [20], Si_3N_4 [19], $YBa_2Cu_3O_{7-\delta}$ superconductor [21], and β-alumina [22] and least squares fits of Equation 18 with the experimental data are also shown in the figure. The exponents t obtained from the fits for these

TABLE I Comparison of exponent in Equation 18, $\sigma_f = \sigma_0(1 - p)^t$, obtained from fracture data and calculated from modulus of elasticity

Materials	Porosity range	m from Eq. 11	Exponent t	
			From Fig. 1 fracture data	Calculated from $t = m + 0.5$
α-alumina	0.05–0.54	2.14	2.54	2.64
Si_3N_4	0.26–0.6	2.41	2.98	2.92
UO_2	0.02–0.09	3.02	3.52	3.52
$YBa_2Cu_3O_{7-\delta}$	0.05–0.26	2.43	3.07	2.93
β-alumina	0.02–0.37	4.09	5.59	4.59

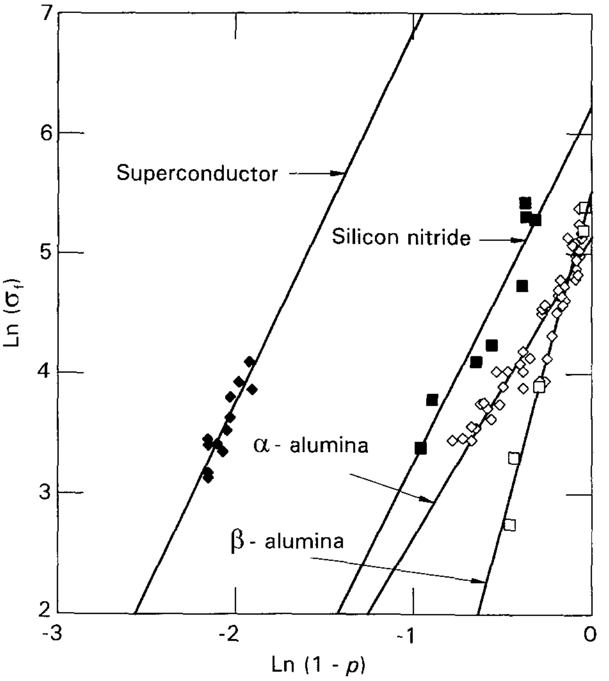

Figure 1 Porosity dependence of flexural strength, σ_f, for various ceramic materials fitted with Equation 18, $\sigma_f = \sigma_0(1 - p)^t$.

materials (Fig. 1) are tabulated in Table I. In addition, the values of t for UO_2 with low porosity are also shown in the table which also includes the values of t ($= m + 0.5$) obtained from the elasticity data for these materials. It can be seen from Table I that the values of t agree quite well with $m + 0.5$ for α-alumina, Si_3N_4, UO_2, and $YBa_2Cu_3O_{7-\delta}$ superconductor, confirming the validity of Equation 18.

α-alumina in this study had a relatively fine microstructure. Gutshall and Gross [23] have shown that in a fine-grained alumina, the major mode of fracture is intergranular. The formalism derived here is valid for intergranular fracture; hence, the agreement between the elasticity data and the fracture data is not surprising.

The results on Si_3N_4 and $YBa_2Cu_3O_{7-\delta}$ show a similar trend. The values of the exponents t obtained from fracture data and calculated from elasticity data agree quite well, fully confirming the validity of the model. Furthermore, Rice *et al.* [19] found that the fracture toughness and fracture energy of Si_3N_4 do not depend on pore size but on the amount of porosity which is consistent with Equation 18.

The formalism suggested here, can also be applied to low-porosity data on UO_2. Igata and Domito [24] measured the elastic modulus and flexural strength of UO_2 and express their data as the Duckworth relations shown in Equation 20a and b.

$$E = E_0 \exp(-3.025p) \quad (20a)$$

and

$$\sigma_f = \sigma_0 \exp(-3.525p) \quad (20b)$$

In Equation 20a, the exponent 3.025 for elastic modulus represents m in the present model, whereas the exponent 3.525 in Equation 20b, the flexural strength equation, represents t. These two exponents differ by 0.5, in agreement with the result from our model.

In the case of β-alumina, the agreement between t and $m + 0.5$ is not good. This is believed to be related to the presence of a glassy second phase on the grain boundary. Evans *et al.* [22] have shown that during sintering of β-alumina, as a result of purity related problems, sodium aluminate is formed. Because of this, β-alumina may contain glass as a grain-boundary phase. The model presented here is based on the assumptions that the material under consideration consists of distinct grains, and that the mode of fracture treated here is intergranular. The glassy phase does not have a distinct grain structure, and fracture may occur through the glassy phase. Thus, the present model is not adequate for β-alumina that contains a glassy phase.

5. Conclusion

This work is part of an overall attempt to develop a connected-grain model to explain porosity dependence of various transport properties of ceramics, including mechanical, fracture, thermal, and electrical properties. In this paper, we have attempted to model fracture properties of ceramics, which have discrete grain structures, and for which consistent data are available. The model, however, must be generalized for materials where a glassy phase is present. This will be considered in future work.

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References

1. G. FISHER, *Ceram. Bull.* **65** (1986) 622.
2. J. METCHOLSKY Jr, *ibid.* **68** (1989) 367.

3. M. R. GHATE, K. E. MARKEL Jr, L. A. JARR and S. J. BOSSART (eds), "Proceedings of the 7th Annual Gasification and Gas Stream Cleanup Systems Contractors' Review Meeting", Vol. 1, US DOE/METC-87/6079 (DE 87006495) (US DOE, Washington, 1987).
4. J. G. ACKERS, B. F. M. BOSNJAKOVIC and L. STRACHEE, *Radiat. Prot. Dosim.* **7** (1984) 413.
5. I. L. KALNIN, *Ceram. Bull.* **46** (1967) 1174.
6. J. P. SINGH, *Adv. Ceram. Mater.* **3** (1988) 18.
7. W. DUCKWORTH, *J. Amer. Ceram. Soc.* **36** (1953) 68.
8. S. K. DUTTA, A. K. MUKHOPADHYAY and D. CHAKRABORTY, *ibid.* **71** (1988) 942.
9. O. VARDAR, I. FINNIE, D. R. BISWAS and R. M. FULRATH, *Int. J. Fract.* **13** (1977) 215.
10. V. D. KRSTIC, *Theor. Appl. Fract. Mech.* **10** (1988) 24.
11. A. G. EVANS and R. W. DAVIDGE, *J. Nucl. Mater.* **33** (1969) 249.
12. A. A. GRIFFITH, *Phil. Trans. R. Soc. Lond.* **A 221** (1920) 163.
13. A. S. WAGH, R. B. POEPPEL and J. P. SINGH, *J. Mater. Sci.* **26** (1991) 3862.
14. P. WONG, J. KOPLIK and J. P. TOMANIC, *Phys. Rev. B* **30** (1984) 6606.
15. F. F. LANGE, *Phil. Mag.* **16** (1968) 711.
16. E. M. PASSMORE, R. M. SPRIGGS and T. VASILOS, *J. Amer. Ceram. Soc.* **48** (1965) 1.
17. F. F. LANGE and K. A. D. LAMBE, *Phil. Mag.* **18** (1969) 129.
18. M. H. LEWIS, *ibid.* **13** (1967) 1123.
19. R. W. RICE, K. R. McKINNEY, C. CM. WU, S. W. FREIMAN and W. J. M. DONOUGH, *J. Mater. Sci.* **20** (1985) 1392.
20. R. L. KOBLE and W. D. KINGERY, *J. Amer. Ceram. Soc.* **29** (1956) 377.
21. J. P. SINGH, H. J. LEU, R. B. POEPPEL, E. VAN VOORHEES, G. T. GOUDEY, K. WINSLEY and D. SHI, *J. Appl. Phys.* **66** (1989) 3154.
22. J. R. G. EVANS, R. STEVANS and S. R. TAN, *Br. Ceram. Trans. J.* **83** (1984) 43.
23. P. L. GUTSHALL and G. E. GROSS, *Engng Fract. Mech.* **1** (1969) 463.
24. N. IAGATA and K. DOMITO, *J. Nucl. Mater.* **45** (1972/73) 317.

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