JOURNAL OF MATERIALS SCIENCE 24 (1989) 698–702

Mechanical and dielectric failure of $BaTiO_3$ ceramics

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Both at room temperature and above the Curie temperature, Weibull plots for the mechanical and dielectric strengths of $BaTiO_3$ thick films sintered 1300° C to 1400° C showed good a correlation. The present results indicate that the microstructure plays a similar role in both mechanical and dielectric failures and firmly suggest that the fracture origins in both failures are analogous, possibly surface flaws associated with grain size. Specimens sintered at 1450° C showed a bend in the Weibull distribution for mechanical strength. This bimodal Weibull distribution was explained by the assumption that the geometric relation between the ratio of grain sizes to specimen thickness and stress gradient under a three-point bending condition affects the effective tensile stress of the tips of surface flaws.

1. Introduction

Brittle fracture generally limits the use of ceramic materials. Before ceramic materials are widely accepted for practical applications, many problems have to be solved. One of the most important is to improve their structural reliability [1].

In practice the reliability of ceramic materials is recognized only after their fracture strength test. The usual mechanical strength test requires a lot of test pieces to be subjected to failure, which would be inconvenient from the technological point of view.

Gogotsy *et al.* [2] reported that the critical stress needed to induce acoustic emission for reaction-sintered Si_3N_4 followed a similar Weibull distribution to its bend strength. They proposed that this phenomenon can be utilized to predict structure reliability by proof testing the specimens under a load of 70–80% of the average strength. However this method still requires a lot of test pieces, and the defects propagate during the test which will lead to degradation of specimens, making it difficult to judge if the specimens could be reutilized.

Mechanical failure is recognized to be a microstructure sensitive, and specifically large grains and pores are regarded as playing important roles as fracture origins [3]. The mechanical strength distribution and reliability of a material are usually estimated in terms of Weibull statistics [4].

Similarly, dielectric strength has also been shown to depend upon microstructure parameters such as grain size, porosity, etc. Furthermore, it has been proved mathematically that the Weibull modulus is independent of the selected number of specimens. Although bending strength decreases with an increase in span length and dielectric strength decreases with increasing electrode area, the Weibull parameter still remains the same in both cases [5, 6]. Hence a direct analogy between dielectric and mechanical strength distributions can be expected if the fracture origins for failure are similar in both cases. When the two sets of data follow a similar Weibull distribution, the cumulative failure probability of mechanical strength can be evaluated by analogy with the dielectric strength distribution without needing a large number of test pieces. This could become a new method for predicting the structural reliability of materials.

This has already been pointed out by Yamashita *et al.* [7] and confirmed partly for hot-pressed $BaTiO_3$ ceramics. The specimens they employed contained various kinds of additives and different microstructures. As they noted, the role of additives was not clarified and the different behaviours in Weibull distributions for mechanical and dielectric strengths of large-grained and fine-grained specimens with different porosities could not be rationally explained.

In the present study, $BaTiO_3$ thick films with uniform microstructure containing no additives, fabricated by a modified doctor blade method [8], were subjected to both failure tests to examine the verification of the above mentioned concept.

2. Weibull distribution

A statistical method commonly used to determine the strength of brittle materials is that proposed by Weibull [9]. The Weibull function is also known to statisticians as the Fisher–Tipper Type 3 distribution of smallest values or as the third asymptotic distribution of smallest values or as the third asymptotic distribution of smallest extreme value [10]. The Weibull statistics is based on the 'weakest link hypothesis" which means that the most serious flaw in the specimen will control the strength [11].

The tensile strength of a brittle material under uniform loading is found both theoretically and practically to follow the Weibull distribution, which is

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given by [9]

$$P_1 = 1 - \exp\{-V[(\sigma_f - \sigma_u)/\sigma_0]^m\} \qquad (1)$$

where P_1 is the cumulative failure probability for the stress, m is a parameter known as the Weibull modulus, V is the volume subject to tensile stress, σ_0 is a normalizing factor called the scaling parameter, and σ_u is a threshold stress below which the failure probability is zero. The Weibull modulus, which was previously considered to be an empirical constant, was given a physical meaning by Jayatilaka and Trustrum [12].

For brittle materials, the relation $\sigma_u = 0$ is widely accepted as giving the closest fit. By putting $\sigma_u = 0$, Equation 1 can be written

$$y = \ln\ln[1/(1 - P_1)] = \ln(V/\sigma_0^m) + m \ln\sigma_f \qquad (2)$$

so that the plot of y against $\ln\sigma_f$ gives a straight line with slope m. The slope can, therefore, be estimated graphically by a least square or a maximum likelihood method [13].

Let us choose a sample size of n specimens and order the strength values so that

$$\sigma_1 \leqslant \sigma_2 \leqslant \cdots \sigma_i \cdots \leqslant \sigma_n \qquad (3)$$

Many estimators to calculate P for the ith strength are proposed [10]. The most popular estimator is expressed as

$$P_i = i/(n + 1) \qquad (4)$$

On the other hand, the Weibull distribution has also been used to estimate the scatter of dielectric breakdown strength [14]. Hence the probability of dielectric failure can be represented by an expression similar to that of mechanical failure as

$$P_2 = 1 - \exp\{-V'[(E_b - E_u)/E_0]^{m'}\} \qquad (5)$$

where E_0 and E_u are the scaling parameter and threshold field, respectively, and V' is the volume subject to dielectric stress.

Equations 1 and 5 can be rewritten as follows, dividing both strengths by their own average values $\bar{\sigma}_f$ and $\bar{E}_b$

$$\ln\ln[1 - /(1 - P_1)] = \ln V(\bar{\sigma}_f/\sigma_0)^m + m\ln(\sigma_f/\bar{\sigma}_f) \qquad (6)$$

$$\ln\ln[1 - /(1 - P_2)] = \ln V'(\bar{E}_b/E_0)^{m'} + m'\ln(E_b/\bar{E}_b) \qquad (7)$$

Using these equations, the experimental strength values could be plotted on a graph of the same scale and graphical comparison would become easier [7].

3. Experimental procedure

The modified doctor blade method was adopted in order to fabricate lots of homogeneous specimens thin enough for dielectric breakdown. Thick films of $BaTiO_3$ with 5 × 20 × 0.2 mm and 5 × 20 × 0.27 mm were fabricated following the previously reported procedure [8].

To control the microstructure of the specimens sintering temperatures were varied between 1300° C and 1500° C, while the sintering time was fixed at 3 h.

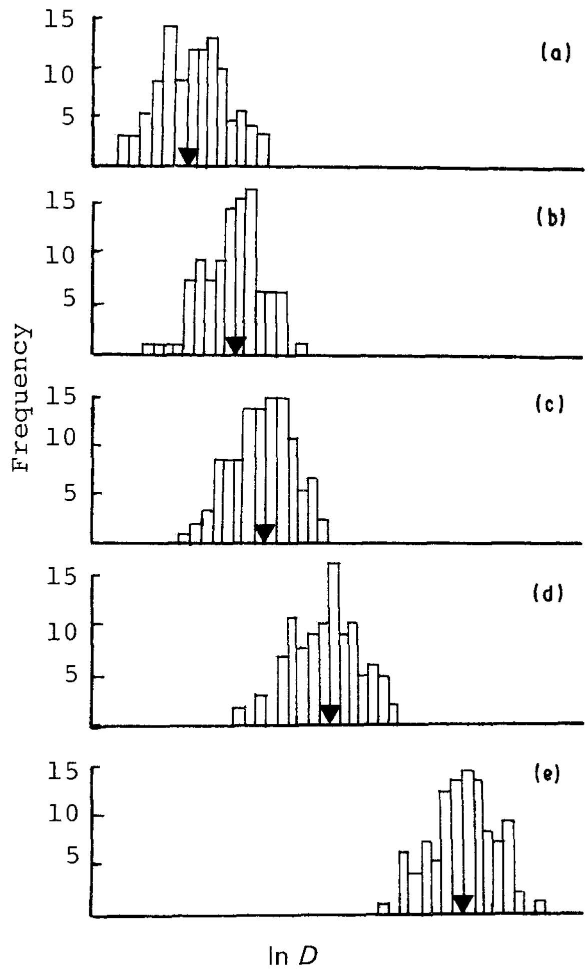

Figure 1 Logarithmic grain size distributions in $BaTiO_3$ thick film for each sintering temperature (D is the mean grain size). (a) $\bar{D}$ = 3.35 μm (1300° C) (b) $\bar{D}$ = 5.18 μm (1350° C) (c) $\bar{D}$ = 7.26 μm (1400° C) (d) $\bar{D}$ = 15.0 μm (1450° C) (e) $\bar{D}$ = 68.7 μm (1500° C).

Scanning electron microscope observations on gold-sputtered specimens were performed to measure the grain size distributions. Each grain shape was transformed to a circle without altering the area and its diameter was taken to be the grain size. Logarithmic grain size distribution was then calculated for about 100 grains in each sample.

The three-point flexure method was used to measure the bending strength which is expressed as

$$\sigma = (3PL)/(2bd^2) \qquad (8)$$

where P, L, b, and d mean applied weight, span length (12 mm), width of the specimen (5 mm) and thickness (200 and 270 μm) respectively. After the mechanical strength test, the dielectric breakdown measurement was carried out with the same samples, so that extrinsic microstructural defects might not be induced from a structure deformative process such as grinding and polishing etc.

For the dielectric breakdown test, silver paste was attached to both sides of the film as the electrodes. The d.c. voltage was applied to a specimen placed in the silicone oil (to protect the surface discharge) and increased at the rate of 50 V sec^{-1}. The breakdown voltage was determined by measuring the abrupt increase in current and breakdown field and regarded as the dielectric strength (E_b).

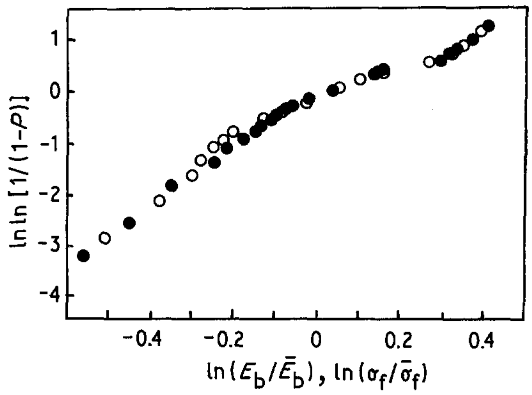

Figure 2 Weibull plots of the data of mechanical and dielectric strengths measured at room temperature for the specimens of $BaTiO_3$ sintered at 1350° C (200 μm). (○ mechanical strength ($\bar{\sigma}_f$ = 21.1 N mm^{-2}), ● dielectric strength ($\bar{E}_b$ = 45.5 kV cm^{-1})).

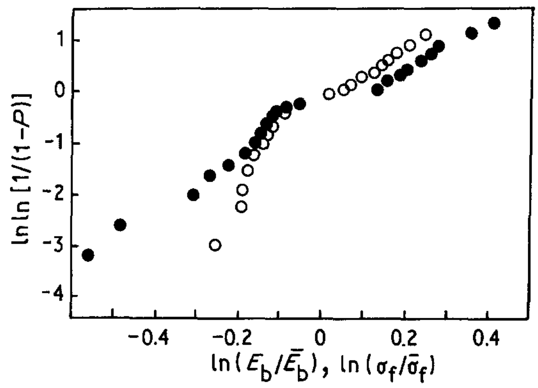

Figure 3 Weibull plots of the data of mechanical and dielectric strengths measured at room temperature for the specimens of $BaTiO_3$ sintered at 1450° C (200 μm). (○ mechanical strength ($\bar{\sigma}_f$ = 19.7 N mm^{-2}), ● dielectric strength ($\bar{E}_b$ = 30.2 kV cm^{-1})).

4. Results

4.1. Failure at room temperature

First, measurements were carried out at room temperature. Both mechanical and dielectric strengths were estimated by the Weibull statistics (Equations 5 and 6).

Fig. 2 shows the Weibull plots of the data for mechanical strength and dielectric strength obtained for the specimens sintered at 1350° C. The Weibull plots of the data for each strength showed good linearity. These linearities mean that the scattering of both data are well expressed by the Weibull distribution function and both failures obey the weakest link hypothesis.

From comparison between the two plots, it is seen that the distribution shapes of both strengths are very close to each other. This trend indicates that microstructure has a similar role in both failures, though the decisive factor for fracture is not well known.

In these specimens the Weibull modulus (m) of mechanical strength can be substituted for that of dielectric strength. Furthermore, the distribution of mechanical strength can be estimated by the distribution function determined from the dielectric strength measurements if the average mechanical strength is known beforehand. Compared with the Weibull modulus, average mechanical strength could be determined from a relatively small number of test pieces.

On the other hand, the Weibull plots for the specimens sintered at 1450° C and 1500° C revealed different distribution shapes between mechanical and dielectric strengths (Fig. 3). The Weibull plot of dielectric strength showed good linearity but that for mechanical strength showed a bend in the line. Both plots showed a good coincidence in a high strength region but differed in a low strength region.

From these results, the Weibull moduli were calculated by a least squares method and are summarized in Fig. 4. The error bar means the range that contains 80% data points. These plots showed good correlations quantitatively for the specimens sintered at 1300° C, 1350° C and 1400° C, but not at 1450° C and 1500° C.

The similarity of Weibull moduli of two failure tests indicates that the effective microstructural factor for two failures are analogous to each other; that is the weak spot distributions responsible for both failures are similar. This result would firmly suggest that the fracture origins in both failures are similar in small-grained specimens but not in large-grained specimens.

4.2. Failure above the Curie temperature

It was thought that the above result was due to the analogy of both failure origins. It has been accepted that weak spot distribution should account for the observed scatter of fracture strength. Similar results would be obtained if the same weak spot distribution specimens were examined, even if the intrinsic strength changes.

It has been shown by Pohanka *et al.* [14] that the strength of $BaTiO_3$ above the Curie temperature (T_c) was greater than that at room temperature. They say that the difference in strength is attributed to the

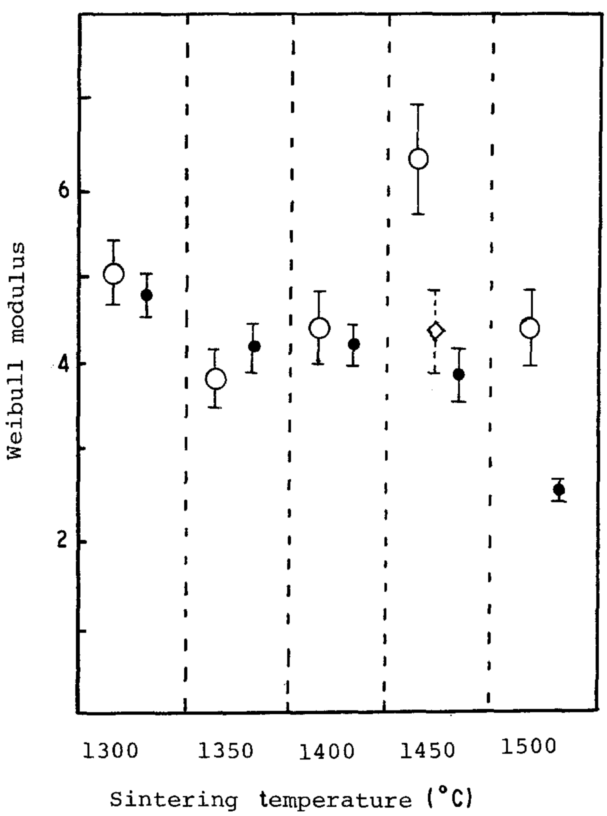

Figure 4 Weibull moduli of mechanical and dielectric strength distribution plotted against sintering temperature. (○ mechanical strength, ● dielectric strength.) (◇ for 1450° C was calculated from the high mechanical strength region.)

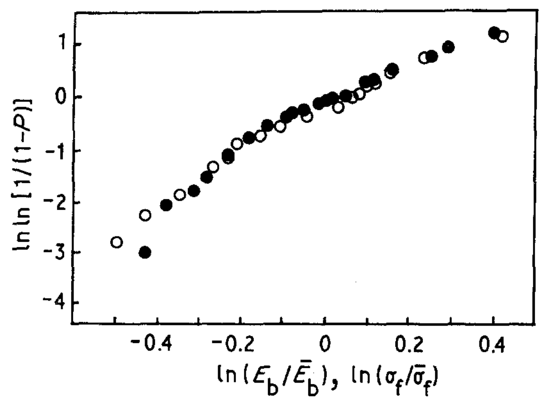

Figure 5 Weibull plots of the data of mechanical and dielectric strengths measured above T_c for the specimens of $BaTiO_3$ sintered at 1350° C (200 μm). (○ mechanical strength ($\bar{\sigma}_f$ = 23.7 N mm^{-2}). ● dielectric strength ($\bar{E}_b$ = 53.0 kV cm^{-1}).

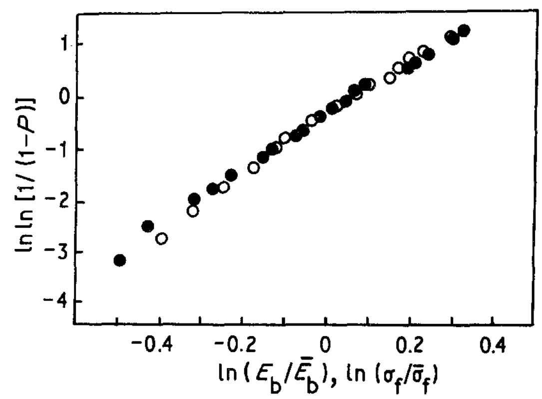

Figure 7 Weibull plots of the data of mechanical and dielectric strengths measured at room temperature for the specimens of $BaTiO_3$ sintered at 1450° C (270 μm). (○ mechanical strength ($\bar{\sigma}_f$ = 37.8 N mm^{-2}), ● dielectric strength ($\bar{E}_b$ = 44.7 kV cm^{-1})).

internal stress induced as cubic to tetragonal phase transformation. Above T_c where the internal stress is absent, the observed strength is higher when the critical flaw size is constant.

Specimens warmed up above T_c without changing the weak spot distribution shape would give rise to changes in average mechanical and dielectric strengths. In the present study, this was experimentally confirmed as shown in Figs 5 and 6. Average strengths for both mechanical and dielectric failures are seen to be higher above T_c than at room temperature. It is also to be noted that the sets of the Weibull plots show similar tendencies to those observed at room temperature.

4.3. Thickness dependence of failure

It was a rather strange phenomenon that only the specimens sintered at 1450° C and 1500° C showed bends in Weibull plots of mechanical strength, though the grain size distribution shapes were similar to those for the specimens sintered at lower temperatures. Then we examined whether the ratio of the average grain size to the specimen thickness was responsible for the observed phenomenon, a stress distribution under a three-point bending condition is not uniform throughout a test piece and this would have a large effect on a large-grained specimen.

Fig. 7 shows the result of the examination. The Weibull plot for the mechanical strength of the 270 μm specimen sintered at 1450° Ca showed good linearity unlike Figs 3 and 6.

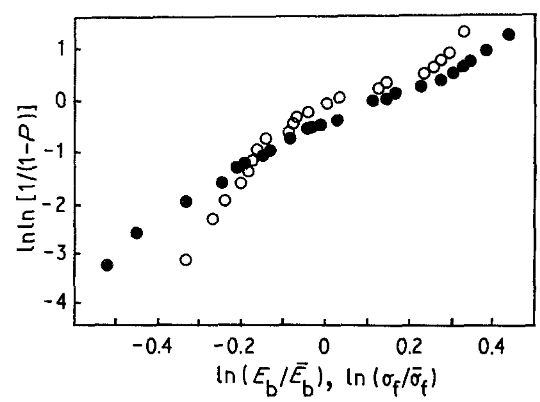

Figure 6 Weibull plots of the data of mechanical and dielectric strengths measured above T_c for the specimens of $BaTiO_3$ sintered at 1450° C (200 μm). (○ mechanical strength ($\bar{\sigma}_f$ = 26.0 N mm^{-2}). ● dielectric strength ($\bar{E}_b$ = 35.2 kV cm^{-1})).

5. Discussion

Mechanical and dielectric strength distributions for small-grained specimens sintered below 1400° C showed good correlations both at room temperature and above the Curie temperature. Considering that microstructural parameters seriously affect the strength distribution, the results obtained would suggest that the starting points for both failures and their distributions are the same. The identity of the fracture origins for both failures may be expected from previous work on various kinds of cermic materials.

Mechanical strengths calculated on the basis of an ideal structure are several orders of magnitude greater than those commonly achieved in ceramic materials [15]. The accepted explanation for this discrepancy is that the usual ceramic materials contain defects which raise the local stress up to the theoretical strength value under a relatively small applied stress. Surface flaws, grain–boundary gaps, pores and voids would behave as stress concentrating defects in brittle ceramics. In a bending test the effective applied stress gives the highest tension to the opposite surface of the specimen, so that surface flaws including grain boundaries and pores near the surface would govern the mechanical strength distribution.

In the case of dielectric breakdown in ceramics, it has also been accepted that breakdown starts from the microstructural defect. Beauchamp pointed out that dielectric breakdown in MgO had a tendency to occur at grain boundaries and often at three grain pockets [16]. Heiman *et al.* [17] calculated the electric field enhancement due to hemispherical protuberance at the polysilicon–poly-oxide interface.

The specimens in the present study must have contained a considerable amount of surface flaws and the silver-paste electrode would have penetrated into the concave part of the surface. The electric field in the vicinity of the tip of electrode is inversely proportional to the radius of curvature of the tip which should be determined by the flaw shape, and hence field concentration to concave portions of surface flaws would lead to dielectric breakdown.

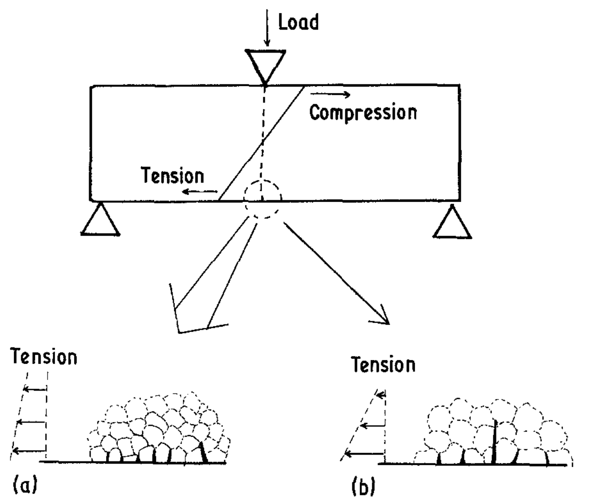

Figure 8 Schematic of the relation between surface flaw size and tensile stress in the vicinity of the lower surface in a three-point flexure test; (a) Small-grained specimen (b) Large-grained specimen.

The electric field concentration to surface flaws seems to be an analogous phenomenon to the stress concentration to surface flaws in a bending test, and thus a similar role of surface flaws in both mechanical failure and dielectric breakdown must have given rise to similar Weibull distributions.

Figs 4, 6 and 7 all show the Weibull plots for the specimens sintered at 1450° C. From these figures the following experimental facts can be extracted: (1) only thick specimens showed a good statistical correlation between mechanical and dielectric failures (Fig. 7), (2) Weibull moduli for dielectric strength are all analogous ($\simeq 4.0$) regardless of the specimen thickness, and (3) bends in Weibull plots for mechanical strength appear in thin specimens (figs 4 and 6), while Weibull moduli in high-strength regions are $\simeq 4.0$, which is similar to that of a thick specimen.

Bimodal Weibull distribution with bends seen in Figs 4 and 6 are referred to as "composite Weibull distributions" and are considered to show that there are two causes for their mechanical failure. Since all the Weibull moduli for dielectric strength and those for mechanical strength in high-strength region of thin specimens (Figs 4 and 6) and whole region of thick specimen (Fig. 7) are all analogous ($\simeq 4.0$), there must exist a particular cause for mechanical failure in the low-strength regions of the thin specimens.

As mentioned before, the stress distribution under a three-point bending condition is not uniform throughout a test piece, that is, the stress gradient exists. In the small-grained specimen, tensile stress applied to the surface flaws whose sizes must be comparable to grain sizes [18] is considered to be constant regardless of their size (Fig 8a), judging from the observations that Weibull distributions were of a single mode for all the specimens sintered below 1400° C (Fig. 4). However, in the case of a large-grained specimen, the stress gradient must have a large effect on how the tensile stress is effectively applied to the tips of surface flaws (Fig. 8b). For example, even at the largest surface flaws, which often become the origin of brittle fracture, the effective tensile stress may be smaller than that at smaller surface flaws due to the stress gradient. In such a case the flaw intensity may become of a bimodal distribution, though the flaw size distribution stays as a single mode, as assumed from the idea of statistics of extremes [19]. This is considered to be the reason why only thin specimens with large grain sizes show bimodal Weibull distributions of mechanical strength (Figs 4 and 6).

For a thick specimen with large grains (Fig. 7) a geometric relation between the ratio of grain size (surface flaw size) to thickness and for a smaller-grained thin specimen may have given rise to a single-mode Weibull distribution of mechanical strength.

Since electric field may not have a gradient corresponding to that of mechanical stress, the Weibull distribution of dielectric strength was observed to be of a single mode in all cases reflecting only the flaw size distribution.

References

1. A. S. EVANS, *Mater. Sci. Engng* **17** (1985) 3.
2. G. A. GOGOTSI, A. V. DROZOV and A. N. NEGOVSKII, *Proc. Ultrason. Int.* **83** (1983) 69.
3. R. W. DAVIDGE and G. TAPPIN, *Proc. Brit. Ceram. Soc.* **15** (1970) 47.
4. S. M. WIEDERHORN and E. R. FULLER, *Mater. Sci. Engng* **71** (1985) 169.
5. H. ABE and M. KAWAI, *Ceram. Jpn* **17** (1982) 44.
6. K. H. WEBER and H. S. ENDICOTT, *AIEE Trans.* **76** (1957) 393.
7. K. YAMASHITA, K. KOUMOTO and H. YANAGIDA, *J. Amer. Ceram. Soc.* **67** (1984) C-31.
8. M. NAGAI and H. YANAGIDA, *Yogyo-Kyokai-Shi.* **84** (1970) 157.
9. W. WEIBULL, *J. Appl. Mech.* **18** (1951) 293.
10. B. BERGMAN, *J. Mater. Sci. Lett.* **3** (1984) 689.
11. F. T. PIERCE, *J. Text. Inst.* **17** (1926) 355.
12. A. De. S. JAYATILAKA and K. TRUSTRUM, *J. Mater. Sci.* **12** (1977) 1426.
13. K. TRUSTURUM and A. De. S. JYATILAKA, *ibid.* **14** (1979) 1080.
14. R. C. POHANKA, R. W. RICE and B. E. WALKER, *J. Amer. Ceram. Soc.* **59** (1976) 71.
15. S. M. WIEDERHORN, *Ann. Rev. Mater. Sci.* **14** (1984) 373.
16. E. K. BEAUCHAMP, *J. Amer. Ceram. Soc.* **54** (1971) 484.
17. P. A. HEIMAN, S. P. MURARKA and T. T. SHENG, *J. Appl. Phys.* **53** (1982) 6240.
18. H. P. KIRCHNER and R. M. GRUVER, *J. Amer. Ceram. Soc.* **53** (1970) 232.
19. E. J. GUMBEL, "Statistics of Extremes" (Columbia University Press, Columbia, 1958).

Received 27 October 1987
and accepted 25 February 1988