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Strength and toughness of barium titanate ceramics

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The effect of processing variables on the mechanical and electrical properties of holmium-doped barium titanate ceramics with a positive temperature coefficient of resistance has been investigated. This paper contains details of the tests used to measure the mechanical properties of ceramics prepared using four compositional mixes. Two methods of measuring strength were used: diametral compression of disc samples and four-point bending of beam specimens. Fracture toughness was also evaluated using two methods: the failure of single edge-notched (SEN) beams under four-point loading and cracking from a surface indentation with a diamond pyramid indentor. Values of strength ranged from 18 to 82 MPa for the four materials when measured by the diametral compression test. This compared with a range of 35–79 MPa for the same materials tested in pure bending. Fracture toughness values ranged from 0.65 to 0.95 MPa $m^{1/2}$ for the SEN specimens and from 1 to 1.8 MPa $m^{1/2}$ using the indentation technique on the same samples.

1. Introduction

Barium titanate is currently used as both a dielectric and a positive temperature coefficient of resistance (PTCR) device material in its doped state. PTCR applications already include motor protection devices, heating elements and temperature sensors. All of these applications involve heating and cooling of the material and thus introduce thermal stresses. Mechanical as well as electrical properties must therefore be investigated in the development of successful devices.

This paper is concerned with the measurement of two important mechanical properties of ceramics in general and barium titanate in particular. These are tensile strength and fracture toughness. Tensile strength, in the form of modulus of rupture, is normally measured using prepared beams. These are loaded under three- or four-point bending. The problem with this test is that it requires a different sample geometry to that commonly used in PTCR devices. Apart from being costly and time-consuming, this can lead to other problems. Because of its inherently brittle nature, the strength of a ceramic is invariably controlled by the largest pore in the microstructure. This means that if the size and/or shape of the component is altered, the influence of the largest pore will also be subject to change [1]. Surface microcracks have also been observed following machining operations [2]. Results from this type of test, therefore, may need to be treated with some care.

It is for some of these reasons that the diametral compression test, using disc-shaped specimens, has been developed. In terms of sample preparation, it is ideal for testing pellets pressed in a simple cylindrical die, as little further sample preparation is required. The process has been in use in the pharmaceutical industry for a number of years for testing pill/capsule designs and results have been well documented [3]. It has also been in use for a number of years in the testing of concrete cylinders as it provides a convenient measurement of the strength of cores taken from structures [4]. A further advantage of this test is that it may allow the measurement of the strength of powder compacts prior to sintering. This would be useful in assessment of the performance of binders and die lubricants used in the production process.

The stress field produced by this form of loading is shown in Fig. 1. A constant tensile stress extends over approximately 70% of the diameter between the loading points of the disc [5]. This means that scatter in results is reduced and is certainly less than that reported for three-point bend tests.

The maximum tensile stress, assuming plane stress conditions, in a disc of diameter d and thickness t subjected to a load P has been shown to be [5]

$$\sigma = \frac{2P}{\pi dt} \quad (1)$$

The use of concave loading anvils, also shown in Fig. 1, has been demonstrated to inhibit failure at the loading surfaces by reducing contact stresses appreciably [6, 7].

Fracture toughness is defined as the resistance offered by a material to the extension of cracks within its structure. Inherently brittle materials show a low resistance to crack growth; hence this property usually specifies the limits of mechanical or thermal loading of many ceramics.

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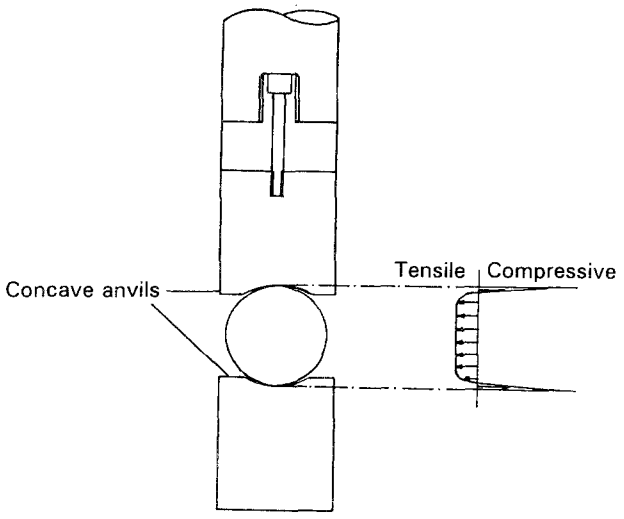

Figure 1 Stress field produced by diametral compression.

Irwin [8] pioneered the stress intensity approach to modern fracture mechanics following work by Westergaard [9]. It was noted that stresses and displacements in the vicinity of the tip of a sharp crack in an elastic body differ only from those in any other cracked component by the value of a single parameter, the stress intensity factor K. Dimensional analysis of a body containing a surface crack of length a, subjected to a stress σ, under mode I loading, shows that

$$K = \psi\sigma(\pi a)^{1/2} \quad (2)$$

where ψ is a dimensionless constant which is dependent on loading geometry and crack configuration [10]. It is normally obtained by numerical analysis or analytical means and solutions for a number of common geometries have been documented [11]. For brittle materials, fracture occurs when the stress in the close vicinity of the crack tip reaches a critical value for bond rupture to occur. Corresponding to this condition, there will also be a critical value of the stress intensity factor K_{IC}:

$$K_{IC} = \psi\sigma_f(\pi a_c)^{1/2} \quad (3)$$

where σ_f is the failure stress of a component containing a (surface) defect of length a_c. Measurement of K_I for fast fracture has confirmed that K_{IC} is a material parameter when fracture occurs exclusively by mode I under plane strain conditions. Therefore by measuring the failure loads of samples of known defect characteristics, it is possible to calculate this critical value as the fracture toughness.

The use of a bend test on a pre-cracked beam has been in use for many years and has been shown to provide acceptable results without requiring extensive sample preparation [12]. The fracture toughness is calculated by considering the bending moment diagram of the beam arrangement:

$$K_{IC} = \frac{\psi P a_l (\pi a)^{1/2}}{bd^2} \quad (4)$$

where a_l is the moment arm of a simply supported beam of width b and thickness d subjected to a load P at the mid-span. However, the need for a technique to measure fracture toughness which requires minimal sample preparation has also been recognized. The use of a sharp indentor as an alternative means of measuring fracture toughness has been demonstrated [13]. It was discovered that the cracks originating from the corners of a Vickers indent increased in length with increasing load. Lawn and Swain [14] observed that the radius of the cracked region increased with $(\text{load})^{0.67}$ and the crack length was dependent on the indentor profile and the roughness of the material surface. Evans and Charles [15] prepared a formula for "half-penny" cracks (Fig. 2a):

$$\left(\frac{K_{IC}\phi}{Ha^{1/2}}\right)\left(\frac{H}{E\phi}\right)^{0.4} = 0.129\left(\frac{c}{a}\right)^{-1.5} \quad (5)$$

where H is the hardness, E is Young's modulus and ϕ is a shape factor. Niihara *et al.* [16] modified this formula for Palmqvist cracks (Fig. 2b). Lankford [17] has modified the Evans and Charles formula following extensive experimentation. However, the results obtained from the two equations for the toughness values of ceramics are similar and the original formula was chosen for this study.

The advantage of this technique is that any shape of sample may be used provided that it is thicker and wider than twice the extent of the cracking. The sample surface should also be flat to enable accurate measurement of crack lengths.

2. Experimental procedure

2.1. Materials

The basic material for the production of PTCR devices is barium titanate, which for this investigation was produced from four mixes. In mixes 1, 3 and 4 this was obtained from TAM Chemicals as a high-purity grade (total impurities < 0.05 wt %), produced by the ignition of barium titanyl oxylate. Mix 2 contained material prepared in the laboratory from barium carbonate and titanium dioxide.

To this a number of other elements were added, such as holmium as a dopant, to give the PTCR effect. The materials were produced in batches of about 150 g, except for mix 3 which was prepared in a commercial production facility in a quantity of 25 kg. The detailed additions are shown in Table I.

Ball-milling was used for the mixing process. Agate balls of 10, 12 and 20 mm diameters were used in a

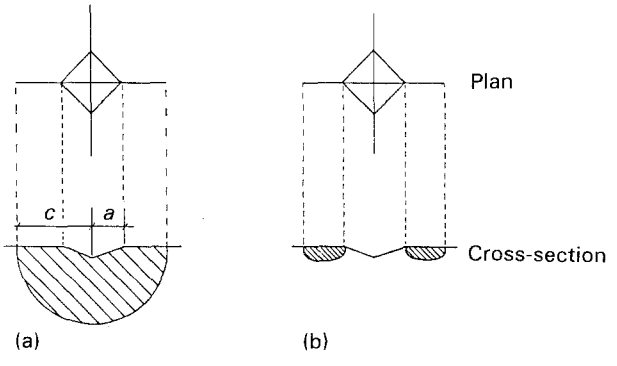

Figure 2 (a) "Half-penny" and (b) "Palmqvist" cracks under a Vickers indentor.

TABLE I Chemical compositions of mixes used in this investigation

Material	Composition (mol %)			
	Mix 1	Mix 2	Mix 3	Mix 4
$BaTiO_3$	99.0	–	80.2	80.2
$BaCO_3$	–	49.5	–	–
TiO_2	0.50	50.0	1.73	1.73
$CaTiO_3$	–	–	13.9	13.9
Ho_2O_3	0.20	0.20	0.30	0.30
Si_3N_4	0.30	0.30	–	–
SiO_2	–	–	0.70	0.70
Al_2O_3	–	–	0.40	0.40
$MnCO_3$	–	–	0.10	0.10

rotating UHMW polyethylene vessel, which reduced the particle sizes to the order of 10 μm. The binder was added at this stage in the laboratory as a 2.50% solution of a glucose–poly(vinyl alcohol) (PVA) mixture in distilled water. Typically 150 ml of fluid was used for 140 g of chemicals.

The mixture was dried, granulated and sieved to extract the portion of powder of granule size 90–500 μm. Pressing of the powder into "green" pellets was then performed using a range of cylindrical dies. Samples of 13 mm diameter and 2–3 mm thickness were used to provide sufficient material for diametral compression testing, with discs of 40 mm diameter and 4 mm thickness used for the preparation of beam specimens. Loads of 1.0 and 8.0 tonne were used for the two sizes of die, resulting in compaction pressures of 78 and 66 MPa, respectively. The densities of the pressed powder compacts were in the region of 55% of the theoretical density.

The green pellets were sintered in air in a tube furnace. The standard sintering profile is shown in Fig. 3. The binder was burnt off at 500 °C, this temperature being maintained for 60 min to ensure complete elimination of the binder. The temperature of the furnace was then raised to 1320 °C to allow formation of the liquid phase and densification of the pellets. During the firing process contraction of the pellets took place, resulting in them attaining typically 85% of their maximum density.

Mix 2, which was prepared from laboratory-prepared barium titanate, followed a similar process. Initial wet milling of the barium carbonate and titanium dioxide was followed by a reaction at 1100 °C, a temperature which was maintained for 2 h. This material was then milled with the other chemicals in the usual way.

2.2. Diametral compression testing

Sample preparation involved making sure that the loading surfaces were parallel and free from large defects. With the 13 mm pellets little polishing was necessary; however, smaller pellets which were initially investigated required more attention due to non-uniform shrinkage during the sintering process [18]. The large faces of all of the pellets were ground flat, however, to enable accurate density calculations to be made. These were made using the mass/volume method. The results compared well with those obtained using a density bottle. Density measurements were used to assess the overall porosity of the pellets.

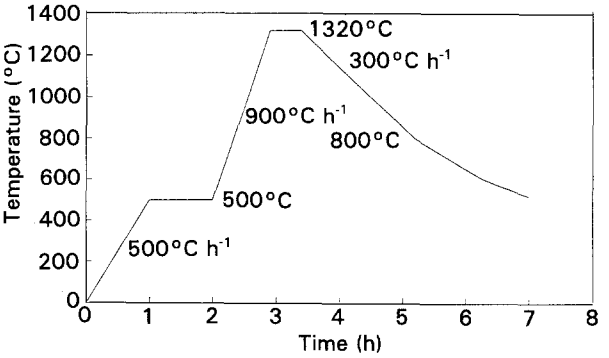

Figure 3 Barium titanate sintering profile.

The loading anvils used for the diametral test were concave with a radius of curvature of 6.25 mm. The diameter of the sintered pellets ranged from 10.5 to 11.2 mm, and this combination resulted in a ratio of approximately 1.2. This value has previously been used successfully to obtain accurate and repeatable results [6, 7]. An Instron 1000 testing machine provided the loading through a 5 kN load cell at a speed of 2 mm min^{-1}. An X–Y plotter was used to produce load–deflection curves from which the load at the onset of cracking could be estimated. The specimens were examined after testing on a scanning electron microscope (Cambridge S600) to establish the point of crack initiation, and to assess whether transgranular or intergranular failure had taken place.

2.3. Four-point bend tests

The larger pellets, 34 mm in diameter and 4 mm thick after sintering, were sectioned using a rotating diamond saw to produce four beams, approximately 40mm × 4mm × 4mm from each disc. The faces of the beams were ground with 240 and 600 grit paper and then lapped with 6 μm alumina paste. A cloth polishing wheel was then used to finish the surfaces which were to act as the loading contacts. Four beams from each disc were used for flexural strength testing. The remainder of the beams were notched to a depth of approximately 1.4 mm (40% of the depth) to enable fracture toughness to be measured. A diamond-coated saw of 0.75 mm width was used to produce notches at the mid-point of each beam. Pre-cracking was not carried out on these specimens, as previous investigations had concluded that the act of machining was sufficient to form small cracks along the machined edge [19]. Scanning electron microscopy and the use of a toolmaker's microscope confirmed this for both barium titanate and model beams of polymethylmethacrylate (PMMA). A red dye was used to highlight the extent of any machining-induced cracks.

A Lloyd 6000R testing machine was used to apply loading. The frame was modified by the addition of linear bearings to provide increased lateral stability in compression. Any shear forces at the contacts could have greatly affected the results. The arrangement for

beam testing is shown in Fig. 4. Four-point bending was used as it eliminates shear forces and provides a large area subjected to the maximum tensile stress. The loading platform was able to rotate so that equal forces were applied to the upper contacts. The steel cylinders used to provide contact with the beam were coated with PTFE tape to minimize friction.

2.4. Indentation tests

A Vickers diamond indentor mounted in the Lloyd 6000R machine acted as the crack initiator. The maximum load applied was noted and the radial cracks formed under loading were decorated with a red dye and measured with the scanning electron microscope. Fracture toughness was then calculated from Equation 5. The Lloyd machine was used in preference to the standard Vickers testing machine as load, rate of loading and time under load could easily be altered via computer control. Preliminary testing revealed the suitability of 0.10 mm min^{-1} as the loading rate. All specimens were mounted in polyester resin and polished to produce a supported flat ceramic surface.

3. Results

3.1. Porosity

The porosity of the "green" pellets of all of the mixes, presented in Fig. 5, was similar and ranged between 45 and 47%. However, following sintering there was a larger variation. Mix 2, prepared in the laboratory, had a porosity of 1.5%, whilst those sintered from the other mixes showed up to 19% porosity.

3.2. Tensile strength

The results of four-point bend tests and the diametral compression specimens, illustrated in Fig. 6, showed some differences. For a dense material such as mix 2, the results of each test were comparable. However, as the porosity increased, the results from the two methods diverged. For mix 4 the strength measured from beam specimens was three times that from discs. Diametral compression tended to suggest lower strengths in all cases. There was a wide range of strengths measured for the mixes. Mix 1 showed the lowest mechanical strength with mix 2 producing the strongest samples.

3.3. Fracture toughness

The values of fracture toughness for each material, presented in Fig. 7, were more similar than their strengths. The results from the notched beams were almost identical for mixes 2, 3 and 4 at 0.95 MPa $m^{1/2}$, with Mix 1 showing a value of 0.65 MPa $m^{1/2}$. The indentation test returned results which were consistently higher than those from the beams. However, the difference appeared to be larger for the more porous materials, and this meant that for mix 4 fracture toughness values as high as 2.0 MPa $m^{1/2}$ were obtained using Equation 5. The scatter in results from the indentation method of measuring fracture toughness was greater than for the notched beam tests at 15% and was similar for all mixes.

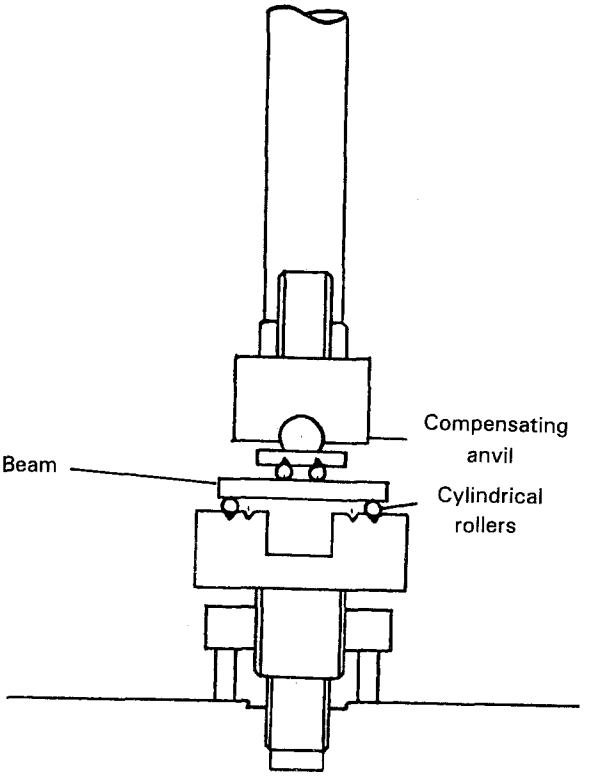

Figure 4 Beam testing arrangement.

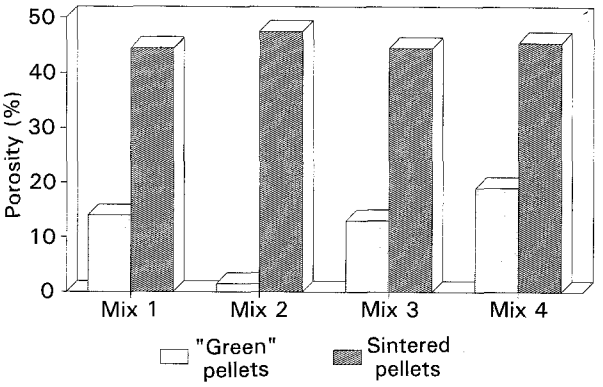

Figure 5 Porosity values of pellets prior to and after sintering.

4. Discussion

Failure in brittle materials can be controlled by crack growth from pores. It is for this reason that the porosity of ceramic components should be monitored. However, from any of these measurements the actual size of pores and the sharpness of cracks cannot be determined unless destructive testing occurs. Critical defect sizes can be estimated from the maximum tensile stress and fracture toughness tests. Assuming $\psi = 1$, these were of the order of 40–60 μm. This is much larger than the grain sizes of any of these materials, which ranged from 0.5 to 10 μm. Thus, failure is not simply being initiated from grain boundaries and defects significantly larger than the mean grain size must be present in these samples. These are

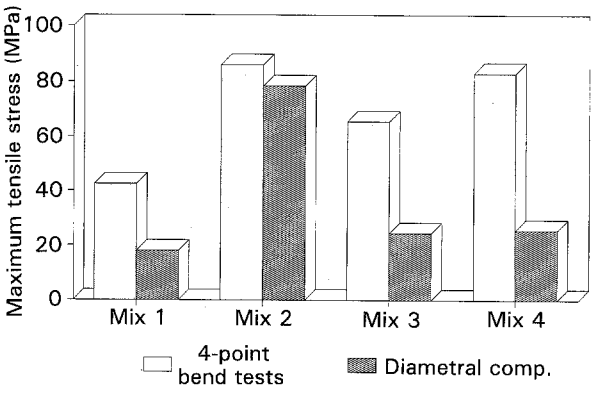

Figure 6 Maximum tensile strength measured from diametral compression and four-point loading.

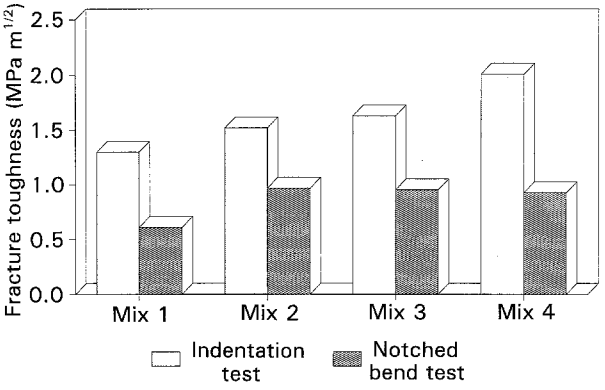

Figure 7 Fracture toughness values measured using single edge-notched beams and the Vickers indentation cracking technique.

thought to be present in the "green" samples and the sintering process and the production of the liquid phase is not sufficient to close these cracks completely. Infiltration of pressed compacts with a pigmented resin followed by polishing has been used to delineate such defects with some success.

Diametral compression proved to be a successful technique for evaluating tensile strength, with results being consistent within each sample group. However, differences in magnitude between these results and those obtained through four-point bending did occur.

Considerable sample preparation was required in the preparation of the beams, which involve polishing and lapping of the surfaces. This will act to remove any stress concentrators caused by the actions of sintering and machining. The diametral tests can be susceptible to non-uniform loading and shearing loads may be set up at the loading contacts. This can be made worse by the small dimensional changes which occur during sintering, resulting in local failure under loading and a potential site for crack propagation.

With the size of samples used in this study, the diametral test applies the maximum tensile stress to the sample over a much larger area than the beam test. This increases the probability of larger pores being present which can propagate at lower values of maximum tensile stress. A previous investigation [7] has shown that these defects are more likely to occur within the bulk of the sample than be located at the surface, and they are therefore more likely to be detected by the diametral compression test. Further weight is added to this argument if the results from mix 2 are considered. This had the lowest porosity and also showed the smallest difference between the two test methods.

However, using the diametral compression technique does not guarantee that the largest pore will necessarily act as the failure initiation site. There is a large volume of material not undergoing appreciable tensile loading. The application of barium titanate as a PTCR device means that the entire structure will be under stress. To investigate this further, discs of mix 1, which had a porosity of about 15%, were loaded to 50% of the average failure load (corresponding to a value of 9.8 MPa), over eight equally separated diameters. This was sufficient to cause failure in $\sim$40% of the samples. Although this may have been partly due to crack propagation following repeated testing, it indicates that the diametral compression technique can also yield overestimates of tensile strength with porous materials.

The diamond pyramid indentation test gave values of fracture toughness ranging between 50 and 100% higher than the notched beams tests. These results made use of the empirical formula derived by Evans and Charles [15]. This was derived from tests on silicon carbide and alumina ceramics which had porosities of less than 3% and fracture toughness values at least twice that of barium titanate. However, a number of other possible explanations exist. The current literature gives no indication as to the degree of penetration which can be tolerated without altering the results. The barium titanate samples showed crack length/thickness ratios of 0.20–0.35 in this investigation. The effect of the lower surface (and the resin in which the samples had to be mounted) may act as a barrier to further propagation and so lead to higher toughness values with this method of testing.

During early stages of this work it was noted that no cracks were visible at loads below 90 N for the titanate samples. The fact that barium titanate required a measurable load to initiate cracks from the corners of the indent, which is a stress concentrator, only means that the load required to drive the crack is only about 55% of the value used in the calculations. Fracture toughness is related to $H_V^{0.6}$ and hence $(\text{load})^{0.6}$. This means that the reduction in fracture toughness would be about 40%, which would correspond with the results from the notched beam tests.

5. Conclusions

Diametral compression has been shown to give consistent measurements of tensile strength within each sample group when concave loading anvils are used. The values were, however, consistently lower than those obtained from bend tests.

The use of a diamond pyramid indentor to measure fracture toughness was investigated and comparisons made with notched beam tests. The technique yielded results using the Evans and Charles formula which were consistently higher than expected. Values of up

to 2.1 MPa $m^{1/2}$ for the indentation test and 1.3 MPa $m^{1/2}$ for the bend tests were measured for mix 4, which compares with values of ~4 MPa $m^{1/2}$ for alumina. During indentation it was noted that for this material little cracking was evident at loads less than 90 N, a previously unreported phenomenon for ceramics.

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