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The effect of processing variables on the mechanical and electrical properties of barium-titanate positive-temperature-coefficient-of-resistance ceramics

Part I *Additives and processing prior to sintering*

J. M. BLAMEY, T. V. PARRY
School of Engineering and Computer Science, University of Durham, Science Laboratories, South Road, Durham, DH1 3LE, UK

The effect of processing variables on the mechanical and electrical properties of barium-titanate positive-temperature-coefficient-of-resistance (PTCR) ceramics has been studied. In the first part of this investigation the effect of changes to processing prior to sintering have been compared. This has highlighted the importance of slow compaction rates and the presence of soft agglomerates in the preparation of strong compacts. The addition of a binder prior to milling has been found to improve the strength of the sintered material by up to 50% by encouraging the formation of smaller, less damaging, pores. Strength, measured by diametral compression of discs, was found to be highly dependent on the density of the ceramic. Typically, the presence of a 22% porosity leads to a 75% reduction in strength compared to samples containing only a 1% porosity. No systematic effect of grain size on strength was observed.

1. Introduction

Following the discovery of positive-temperature-coefficient-of-resistance (PTCR) effects in doped samples of barium titanate [1] and the subsequent deduction that this is due to a grain-boundary phenomenon [2], much work has concentrated on improving their electrical characteristics. They now find use in a wide range of applications including motor-protection devices, heating elements and temperature sensors. All of these involve heating and cooling of the material and thus they introduce thermal stresses, particularly when the material is subjected to mains voltages ($\sim 240\ V_{ac}$ in the UK). Improvements in the performance of these devices are generally measured in terms of enhanced electrical behaviour. However, repeated switching leads to the initiation and propagation of cracks due to thermal shock and fatigue, and improvements to the mechanical properties of the material are therefore also important. This is usually achieved by the careful control of both formulation and processing conditions. Much work has concentrated on the effects of chemical additions to produce desired electrical properties; interest in mechanical properties has lagged somewhat behind. As such, the service life of components made from these materials can be suspect if premature mechanical failures occur.

The conditions to which semiconducting barium-titanate devices are subjected often result in thermal stresses which may be large in magnitude. Poor thermal conductivity and a granular microstructure mean that these can be as a result of a number of conditions. Swift temperature changes, which may be induced in protection devices and heating elements under current surges, cause thermal stresses. These are tensile in nature at the component edges and compressive at the centre under heat-up. Stresses approaching 30 MPa may be produced from a rapid temperature change of 200 °C [3].

Large thermal gradients may also be present within a ceramic component due to poor thermal conductivity between grains. It has been shown that during heat-up the centre of a thermistor has often passed through the Curie temperature whereas the extremities of the component are 30 °C below this point. Because of the cubic–tetragonal crystallographic phase change which takes place at this temperature, and the associated volume changes, transformation stresses are set up.

Additionally, the PTCR effect is caused by grain-boundary activity with the centres of the grains considered to be conducting [2]. This leads to discontinuities and small mechanical stresses because of the differing heating rates of the grain centre, the grain boundary and the liquid phase. It has also been reported that thermal/mechanical stresses were the driving force for failure at soldered contacts of barium-titanate ceramics [4].

A number of important studies have also been made on preparation methodology. Nelson and Cook [5] investigated the optimum milling time and ball materials as well as the effects of contamination from processing. The advantages of wet as opposed to dry milling have also been investigated [6].

The preparation of ceramic compacts by die pressing has also been studied. Leiser and Whittlemore [7], found that large soft agglomerates containing less eccentric particles produced the strongest "green" pellets. Slower rates of compaction were also found to be advantageous, as confirmed by Youshaw and Halloran [8]. Thompson concluded that particle morphology was also important, with a platelet shape being preferable to spherical particles and sticky grains preferable to dry grains [9]. Fang and Hsieh [10] showed that, because of the higher compaction pressures that could be applied without cracking, wet powders produced less porous compacts than dry powders. The use of binders, or die lubricants, aid the pressing process in this way by wetting the powder [11]. However, their successful use depends on their ability to wet each grain. Ueyama *et al.* [12] have shown that the preparation of a dense pressing can lead to higher fired densities and strengths as well as a reduction in the sintering temperature required.

This investigation, concentrates on the effects on strength due to changes in the processing variables and production processes prior to sintering. The strength was established using diametral compression of discs and bend tests on relatively small beam samples. Electrical characteristics were limited to establishing resistance–temperature plots. Full details of the techniques employed have been described previously [13, 14].

2. Materials and methods

Ball milling was used for all mixing and processing. Agate balls of 10, 12 and 20 mm diameter were used in an ultra-high-molecular-weight polyethylene vessel, which reduced the particle sizes to the order of 10 μm. The binder was added prior to milling in sample groups 8 and 3a as a 2.5% solution of glucose and poly(vinyl alcohol) (PVA) in distilled water. Typically 150 ml of fluid was used for each 140 g charge of chemicals. All other groups had the binder added after milling.

The mixture was dried, granulated and sieved to extract powder of granule size 90–500 μm. Pressing of the powder into green pellets was performed using a range of cylindrical dies. Samples of 13 mm diameter and 2–3 mm thickness were used for diametral compression testing, with discs of 40 mm diameter and 4 mm thickness used for machining the beam specimens. The densities of the pressed powder compacts were in the region of 55% of theoretical density.

The green pellets were sintered in air in a tube furnace. The sintering profile used is shown in Fig. 1. The binder was burnt off at 500 °C and this temperature was maintained for 60 min to ensure the complete elimination of the binder. The temperature of the furnace was then raised to 1320 °C to allow the formation of the liquid phase and densification. During the firing process, contraction of the pellets took place with the samples typically attaining 85% of their theoretical density.

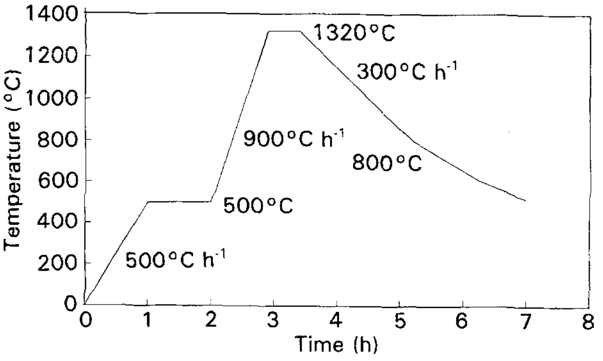

Figure 1 Sintering profile used for the preliminary and the main experiments.

2.1. Materials, preliminary investigation

A preliminary study was carried out on the simplified barium-titanate formulation shown in Table I. The effect of the main processing parameters was determined by adjustments to the variables set out in Table II.

Sample groups 5–8 were prepared from barium titanate produced in the laboratory and followed a similar preparation process. Initial wet milling of the barium carbonate and titanium dioxide was followed by reaction at 1100 °C, which was maintained for 2 h. This material was then milled with the other chemicals in the usual way.

2.2. Materials, main investigation

The formulations for the main part of this investigation were the same as those used for a more detailed study of mechanical properties reported recently [14]. For mixes 1, 3 and 4 barium titanate was obtained from TAM Chemicals as a high-purity grade (total impurities $\leq 0.05\%$ by mass), produced by the ignition of barium titanyl oxylate. Mix 2 contained material prepared in the laboratory from barium carbonate and titanium dioxide. Each mix was processed in batches of about 150 g, except for mix 3 which was prepared in a commercial-production facility. Details of the chemical additions are shown in Table III.

Small changes to the processing conditions of some of the sample groups were made as shown in Table IV.

2.3. Diametral 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, the smaller pellets which were initially investigated required more attention due to non-uniform shrinkage during the sintering process. The large faces of all of the pellets were ground flat to enable accurate density calculations to be made using the mass/volume method. These results were found to agree well with those obtained using a density bottle.

TABLE I Chemical compositions (mol %) of the mixes used in the preliminary investigation

Material	Mixes 1–4	Mixes 5–8
$BaTiO_3$	87.2	
$BaCO_3$		43.6
TiO_2		43.6
$CaTiO_3$	12.3	12.3
Ho_2O_3	0.40	0.40
$MnCO_3$	0.10	0.10

TABLE II Processing variables examined in the preliminary investigations

Sample group	Pressing pressure (MPa)	Milling time (h)	Binder used	Binder added during Milling
1	70	12	Yes	No
2	140	12	Yes	No
3	280	12	Yes	No
4	70	24	Yes	No
5	70	12	No	No
6	210	12	No	No
7	70	12	Yes	No
8	70	12	Yes	Yes

TABLE III Chemical compositions in (mol %) of the mixes used in the main investigation

Material	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

TABLE IV Changes in the processing conditions of some of the sample groups

Sample group	Change
3a	Binder added before the milling stage
3b	Binder added after the milling stage
4a	Pressed in the laboratory (~5 s)
4b	Pressed commercially (~0.5 s)
4c	As 4b with binder burnt off prior to green testing
4d	Prepared in a commercial facility

Density measurements were used to assess the porosity of the pressed and sintered pellets.

The loading anvils used for the diametral test were concave with radii of curvature of 6.25 mm. The diameter of the sintered pellets ranged from 10.5–11.2 mm, and this combination resulted in a ratio of about 1.18. This value has previously been used successfully to obtain accurate and repeatable results [15]. 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 which allowed determination of the onset of cracking. The specimens were examined after testing on a scanning electron microscope (Cambridge S600) to establish the point of crack initiation and to assess whether either transgranular or intergranular failure had occurred. Details of the testing procedure have been described previously [13, 14].

2.4. Unsintered compacts

Some pressed compacts of barium titanate were also investigated. The density was estimated and the diametral compressive strength measured using the same techniques. Loading anvils had a 7.5 mm radius of curvature to accommodate the as-pressed pellets which were larger prior to sintering.

2.5. Electrical measurements

Resistance–temperature plots were made to assess changes in the PTCR effect and the Curie temperature. The test apparatus was computer controlled with nine stations for samples housed in an insulated thermal cabinet. This allowed comparisons to be made between samples under nominally identical conditions. The rate of temperature increase during all experiments was 3 °C min^{-1}, and each temperature was maintained for 4 min^{-1} prior to each resistance measurement.

The pellets were of 5.1 mm diameter and 3–4 mm in thickness. The upper and lower faces of the discs were ground flat, polished and coated with an indium–gallium eutectic to provide the electrical contact. Samples from the commercial facility were cut to size prior to testing.

3. Results

3.1. Preliminary investigation

The levels of porosity shown by samples of barium titanate in the as-sintered condition are presented in Fig. 2 for the preliminary experiments. Once sintering had taken place, the porosity values decreased

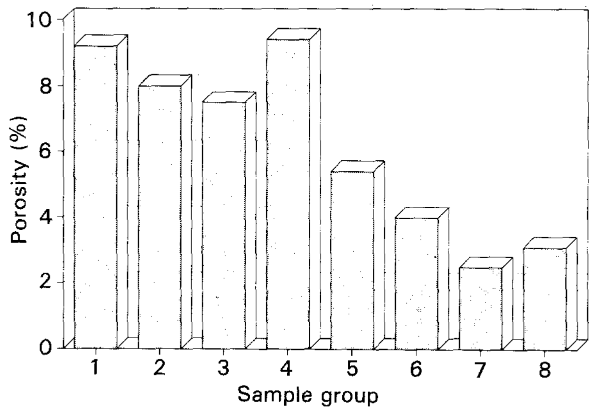

Figure 2 As-sintered porosity levels of the sample groups used in the preliminary experiments.

substantially with a large spread in values, ranging from 2–20%. It was noted that pellets pressed under higher pressures showed lower porosities both before and after sintering. However, the diametral compressive strength of samples decreased by 36–55% as the die pressure increased from 70–210 MPa, as illustrated in Fig. 3. Increasing the milling time from 12 to 24 h resulted in little change in either porosity or diametral compressive strength. Elimination of the binder prior to sintering resulted in an increase in porosity of 3% in the calcined material accompanied by a slight decrease in strength.

3.2. Main investigation

Porosities of the pellets of barium titanate prior to and following sintering are shown in Fig. 4. However, once sintering had taken place the porosity values decreased substantially. Again a large spread of as-sintered porosities was noted, with the largest values seen for mixes 3 and 4 (15–20%) and lowest for mix 2 ($\leq 3\%$). The addition of the binder prior to the second milling stage resulted in porosities up to ~30% lower. Material prepared on the production facility showed less porosity than that produced by the standard laboratory technique.

Fig. 5 shows the results of the diametral compression tests on the green pellets. Addition of the binder prior to the milling stage (sample group 4a) led to a ~50% increase in strength. The samples prepared on the production facility showed much higher strengths, which may be due to the presence of die lubricant. The effect of the binder on strength was investigated by burning of the binder at 500 °C and then cooling the samples prior to testing. This led to a decrease in strength of 80% and the samples became extremely difficult to handle without causing premature failure.

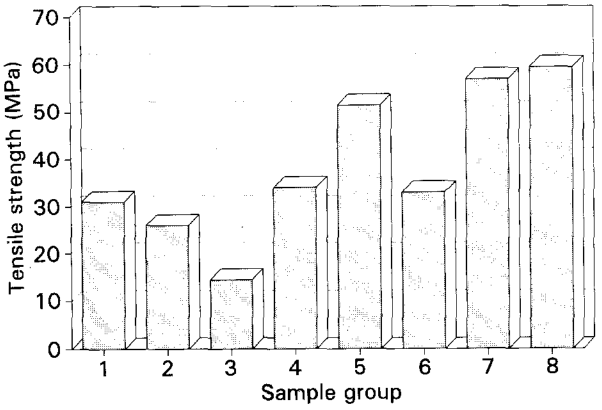

Figure 3 Tensile strength measured by diametral compression of the sample groups used in the preliminary experiments.

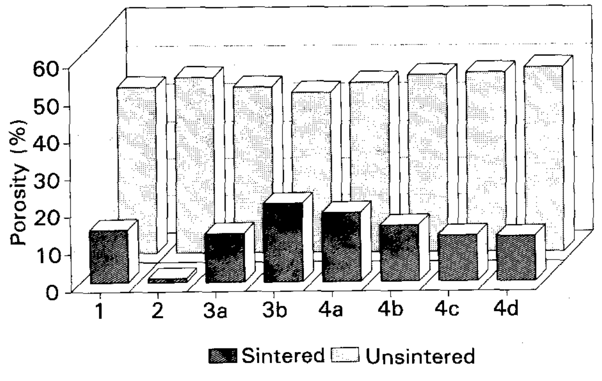

Figure 4 Porosity levels prior to and after sintering of the sample groups used in the main experiments.

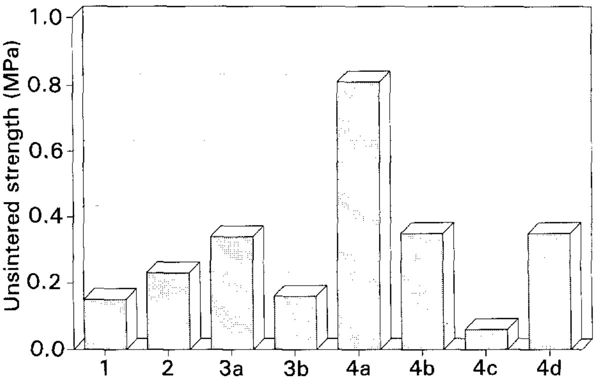

Figure 5 Diametral compressive strength of the green sample groups used in the main experiments.

The largest values of strength measured by diametral compression and four-point bending for the sintered pellets were for mix 2 (Fig. 6). This material also had the lowest porosity. The commercial pressing and sintering processes were shown to be beneficial in producing stronger pellets. Addition of the binder prior to milling led to a 100% increase in strength over those in which the binder was added at the normal time. Further work was conducted on pressing pressure with mix 4 (Fig. 7). It was found that the porosity of the green samples decreased with increasing pressure, down to 38% at pressures of 1000 MPa. However, cracks were visible to the naked eye in compacts pressed at pressures in excess of 200 MPa.

3.3. Electrical properties

The resistance–temperature plots for the four mixes are shown in Fig. 8. These were all sintered in flowing air. Mix 1 showed the largest resistance change, over three decades, with a switching temperature of 145 °C. Mix 2 showed the smallest resistivity change as well as the shallowest gradient, with a switching temperature at about 150 °C. As expected mixes 3 and 4 showed very similar characteristics, with mix 4 exhibiting a slightly larger PTCR effect. Switching temperatures were higher than for the other mixes at ~180 °C.

4. Discussion

In general, the strengths of samples prepared from commercially available barium titanate were only 50% of those made of material prepared in the laboratory. It was also evident that porosity in the samples prepared from commercial titanate was much higher. The use of higher pressing pressures to form samples with lower porosity also produced problems. Radial cracks were evident at pressures in excess of

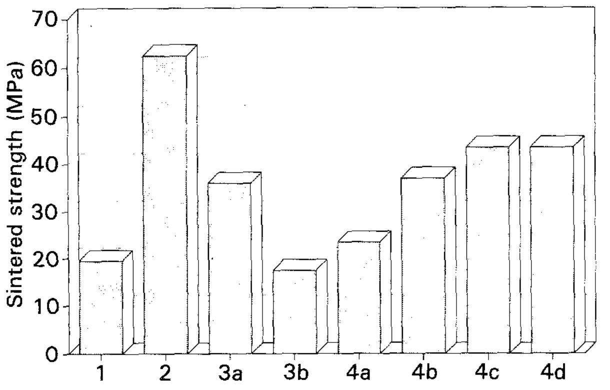

Figure 6 Diametral compressive strength of the as-sintered sample groups used in the main experiments.

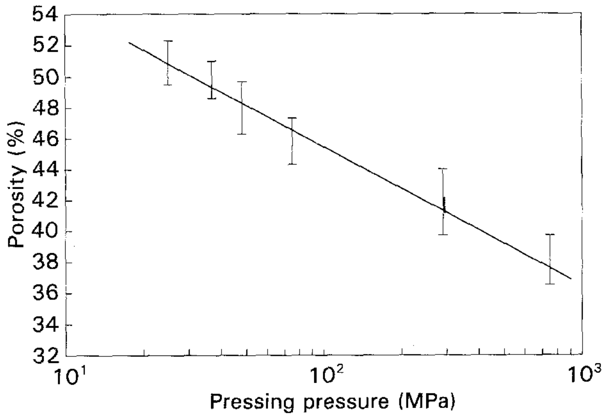

Figure 7 Plot of as-pressed porosity against pressing pressure for mix 4.

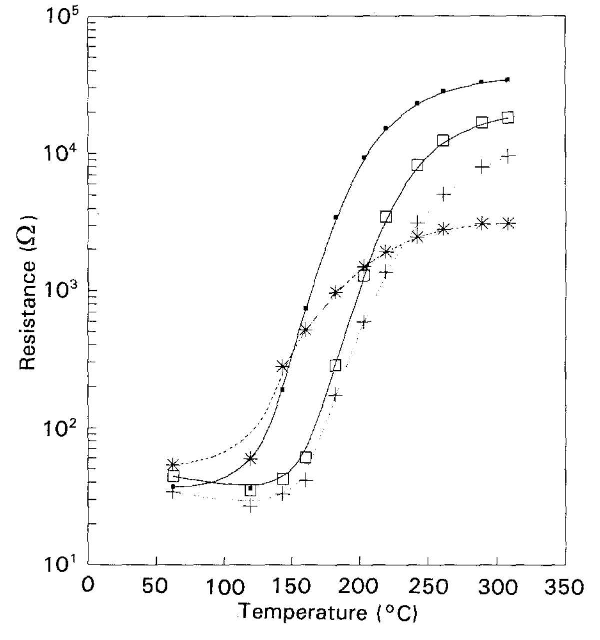

Figure 8 Resistance–temperature plots for samples of mixes 1–4 sintered in air: (■) mix 1, (✱) mix 2, (+) mix 3, (□) mix 4.

200 MPa, which is consistent with observations by Youshaw and Halloran [8]. This led to premature failure, initiating at these stress concentrators; this did not 'heal' during sintering. Very low pressures (≤ 70 MPa) resulted in pellets which had so little strength in the green state that handling was very difficult. Successful pressing depends on powder-agglomerate size and hardness, and on the characteristics and speed of the die. The process should compress the agglomerates, breaking them into small grains that conform to each other, instead of crushing the material into a fine and highly porous powder. Softer agglomerates tend to be preferable and tend to break into a range of sizes, thus providing better packing. The importance of a die lubricant was also apparent, as shown by a 100% increase in green strength. By adding the binder prior to milling, a more even coating of each grain was accomplished and the strength of the green samples increased by over 150%. The use of slow compaction, as opposed to shock compaction, led to only a small decrease in porosity but to a 120% increase in strength. The use of a high compaction rate can lead to regions of crushed material as well as sites of loosely bonded material and damaging pores. A slower rate allows for reorganisation of material, air being more successfully dispelled, as well as reduced crushing. Mixes 1 and 2 were observed to contain harder agglomerates (possibly due to the absence of lead and calcium titanates) and the effect of this was to increase green porosity and reduce strength.

Shrinkage was greater in pellets pressed at lower pressures during sintering, resulting in lower final porosity levels. This can be explained in terms of the pressing process. If the ceramic powder behaved as a fluid (hydrostatically) the axial and radial forces during pressing would be equal. In reality this situation is only approached by wet pressing or the addition of lubricants or binders, but the radial force is only at best ~30% of the axial force. This leads to greater porosity and shrinkage in the radial direction following sintering. Shrinkage in the axial and radial directions is presented in Table V that the for samples of each mix pressed at 70 MPa from which it can be seen that samples which attain the highest fired densities have similar shrinkage in both directions.

It can clearly be seen that the densification reactions in mix 2 appear much stronger than for the other mixes. Additionally, the time spent above a certain temperature during sintering appears to be important to the densification process, as shown by the lower porosities of samples prepared in the production furnace.

There was a 20% increase in strength when a binder was used. The binder appears to assist in the formation of an open-pore network which allows the liquid phase to flow easily through the microstructure. With no binder present the green samples tended to contain discrete pores which the liquid phase was unable to fill, leading to more damaging pores. It was noted that when no binder was used the scatter of diametral compressive strengths was greatest.

Transgranular failure was found to be more common in the barium-titanate samples indicating that the liquid phase was not the weakest link. Grain size was fairly consistently in the range 5–20 μm, but the commercial titanate contained pores up to 40 μm in

TABLE V Porosity and shrinkage levels of each formulation used in the main investigation

Mix	Pressed porosity (%)	Radial shrinkage (%)	Axial shrinkage (%)	Fired porosity (%)
1	43.7	16.2	8.2	87.4
2	47.8	19.2	19.2	99.0
3	44.6	14.8	12.4	87.0
4	45.6	14.8	8.9	82.3

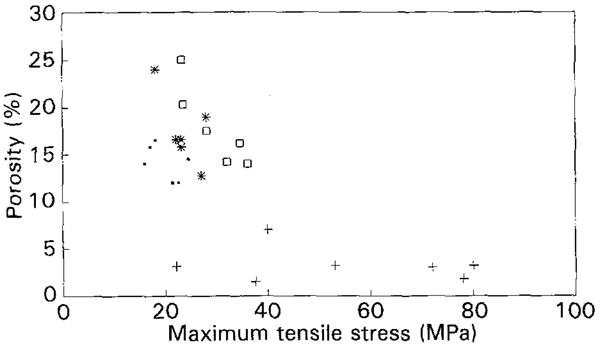

Figure 9 Plot of porosity against diametral compressive strength for all sample groups used in the main experiments: (■) mix 1, (+) mix 2, (∗) mix 3, and (□) mix 4.

diameter and cracks up to 50 μm in width. Calculations of the critical defect size for the diametral compression samples was in the region of 200–400 μm for the commercially available material and 40 μm for laboratory-prepared titanate. Therefore, alterations in the preparation of samples to reduce the grain sizes to less than 5 μm would not achieve any strength increase. This could be one of the reasons why increasing the milling time made no difference to sample strength.

Measuring strength by diametral compression proved successful with both green and sintered pellets, with consistent results obtained for all of the sample mixes. To investigate the dependence of strength on porosity these two parameters have been plotted against each other in Fig. 9. As expected, a strong correlation was found with lower porosity levels associated with the higher strengths. As porosity increased to 22% the strength dropped to only 25% of the strength value at low porosity ($\leq$ 1%). This correlation was expected because of the close similarity between measured fracture-toughness values of mixes 2, 3 and 4 [14].

5. Conclusion

The pressing stage of the preparation of barium-titanate ceramic components has a large effect on the strength of the product. The process should ideally be slow and with a maximum pressure of 200 MPa. Binders, die lubricants and a humid atmosphere can all be employed to improve the strengths of compacts by softening the agglomerates, which improves their handleability.

Shrinkage of pellets following sintering was seen to be greater in the radial direction, owing to the reduced pressures applied to this face under compaction. However, the material which attained almost 100% density showed similar shrinkage in both axial and radial directions.

The strength of sintered ceramics has been shown to be highly porosity dependent. Porosities of 22% reduced failure strengths to only 25% of the values at low porosity levels.

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