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Improved Compaction in Multilayer Capacitor Fabrication

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Abstract

The most common defects found in multi-layer ceramic capacitors are derived from residual porosity formed when solvents and binders are released from a ceramic green body. Without a well-controlled compaction technique, defects between sheets in the stacked body are often present, leading to lamination problems. This paper suggests alternative approaches, using compaction applied before and/or after the process of binder burnout with the intention of reducing the number of stacking-generated defects and the volume of voids formed after binder burn-out. Barium titanate tapes and stacked multilayer electroded discs have been investigated and characterised by microstructural examination and density measurement. The resulting properties are described, and the behaviour of the multi-layers discussed in terms of the microstructure and processing procedures. It is shown that the porosity content of sintered samples compacted at 300 MPa is approximately half that of samples compacted at 30 MPa when both are sintered at 1300°C for 2 h. A further improvement of densification can be achieved by a postcompaction treatment after binder burn out. © 1999 Elsevier Science Limited. All rights reserved

Keywords: $BaTiO_3$, pressing, microstructure-final, porosity, capacitors.

1 Introduction

Tape casting is the most efficient and widely used commercial method for fabricating multi-layer components with screen-printed electrodes on some or all of the ceramic layers.[1] In the last two decades, the applications of tape cast structures have become numerous including multi-layer ceramic capacitors (MLC) and ceramic packaging for integrated circuit boards.[2,3] More recently, multilayer structures have formed the basis of new piezoelectric and electrostrictive actuators. These are of great interest due to their high performance as micro-displacement transducers.[4] Tape casting is commonly employed to fabricate *green* ceramic sheets with a thickness in the range 20 to 100 μm. Thin green ceramic tapes must provide enough strength for the further processing; including handling, cutting, punching, stacking, screen printing, and storage.[5,6] This is usually achieved by addition of a considerable volume fraction of binders and plasticisers. These additives which are used in the early stage of tape formation become one of major sources of defects in the later process. A significant amount of residual pores are formed after drying, after binder burnout and during the sequence sintering process. These defects may cause property degradation and ultimately failure. Typically, 20–30 vol% of porosity is formed during drying and 40–50 vol% porosity during binder burnout. Furthermore, the distribution of pores is heterogeneous in as-dried tapes. The inhomogeneity between the top and bottom surfaces of a green tape is shown in Figs 1 and 2. It is apparent that the bottom surface contains considerably more residual pores and inhomogeneity, formed when the solvent dried out, than does the top.

There have been numerous studies of advanced binder-solvent systems aiming to reduce to the content of binders with better performance.[7,8] The presence of residual pores derived from binders and solvents seems unavoidable in tape cast multilayer ceramic fabrication. To reduce these problems we demonstrate two compaction techniques applied before and/or after binder burnout. Compaction plays an important role in the green sheet

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stacking during multi-layer ceramic fabrication.[9] Without a well-controlled compaction process, defects between sheets in the stacked body are formed during the lamination process. In this study, we demonstrate the effect of compaction pressures on the microstructures of multi-layered structures. In addition, a preliminary experiment was devised to further reduce the level of porosity after binder burn-out by means of a post isostatic pressing technique.

2 Experimental Procedures

As-dried green tapes were supplied by Oxley Developments Company, Ltd., UK. The tapes consisted of submicron BaTiO$_3$ (TAM Ceramics, K4000) with added organic binders and plasticisers. The binder and plasticiser system was a proprietary mixture of tricholoroethene, xylene, MEK resin (methyl ethyl ketone) and butyl benzyl phthalate. The thickness of a single layer of green tape was 65 μm. The tapes were cut into pieces with dimensions of 17·5×10 mm and finally laminated, without internal electrodes, into eight layer stacks. Four samples were made for each test.

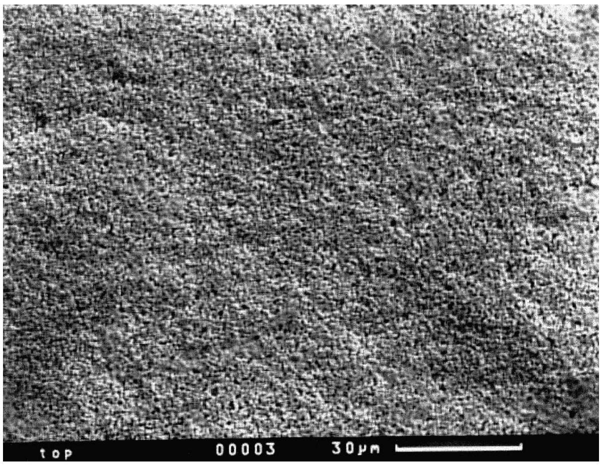

Fig. 1. A top surface of an as-dried tape showing the distribution of pores formed after solvent dry out.

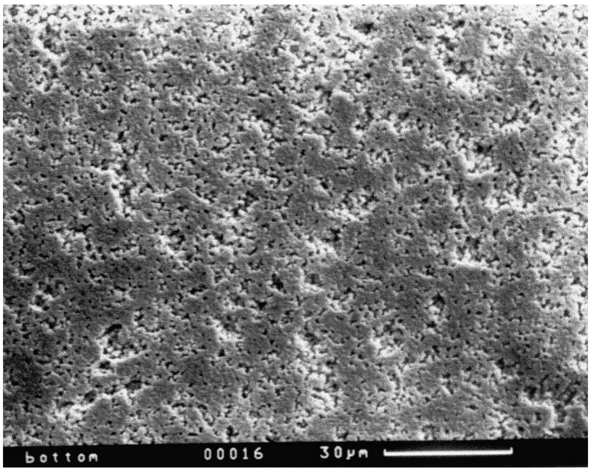

Fig. 2. A bottom surface of an as-dried tape showing the distribution of pores formed after solvent dry out.

The same manufacturer also supplied unfired multilayer discoidal capacitors. These devices comprise stacked discs (of the same composition as above) printed with annular internal electrodes. The hole in the centre of the anulus gives provision for a feed through pin with the outside edge being grounded.

Both stacked tapes and discs were isostatically pressed under various pressures (30, 100 and 300 MPa) at 70°C for 2 min. A multistage binder burnout process followed this for 70 h in total. Heating rates 5°C h^{-1} were used with dwells each of 5 h at 180, 250, 350 and 450°C.

Burnt out samples (green) were then re-compacted using cold isostatic pressing at various pressures (0, 40, 300 MPa). It was necessary to handle these samples with a great care due to the lack of binders in the green body. Sintering conditions were between 1270 and 1300°C for 2 h. Green densities were measured using a gas pycnometer (AccuPyc 1330, Micromeritics Instrument Corp, Norcross, GA, USA). The densities of as-sintered

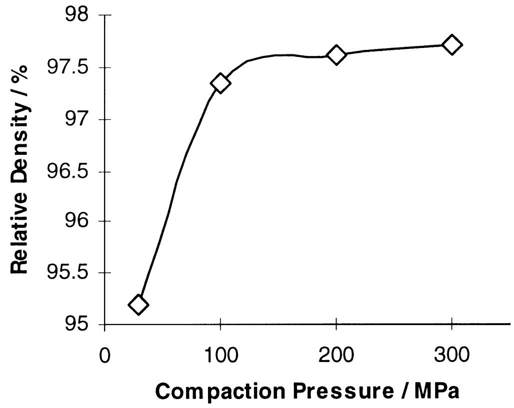

Fig. 3. Density as a function of compaction pressure in compacted tapes sintered 1300°C for 2 h.

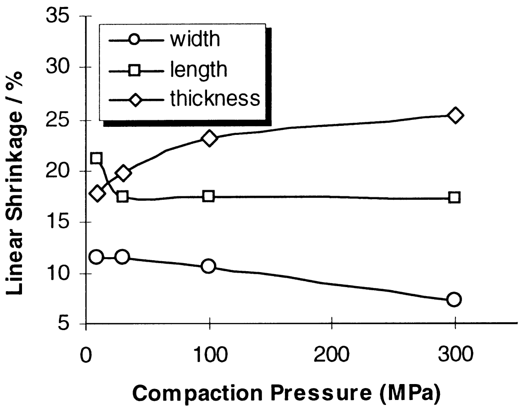

Fig. 4. Linear shrinkages as a function of compaction pressure in compacted tapes sintered 1300°C for 2 h.

samples were measured using a water displacement technique. Both virgin and polished surfaces were examined by scanning electron microscopy (CamScan series 4, Camscan Electron Optics, Cambs, UK) to investigate the resulting microstructure.

3 Results And Discussion

3.1 Effect of compaction pressure on microstructure

As mentioned earlier, a significant amount of residual porosity occurs in as-dried tapes after organic solvents dry out,[1–3] theoretically in the range of 20–30 vol%. These pores are difficult to remove by means of conventional compaction and the sequence sintering process. Based on the experimental results, it is shown that compaction can effectively reduce the amount of porosity with increasing pressure. Figure 3 shows the increase in sintered density with increasing compaction pressure. At low pressure (30 MPa) the relative density is approximately 95% which is increased to 97·5% when the tapes are compacted at a pressure of 100 MPa. Higher compaction pressures were found to only slightly further improve the density.

The shrinkage of sintered tapes also shows a dependence on compaction pressure, as shown in Fig. 4. It is also apparent that the shrinkage after compaction is still anisotropic due to packing anisotropy. As the tape is cast, the solvent most easily disperses and dries uniformly near the top of the tape. This process forms a gradient of pore density after the solvent has dried out. The density in the thickness direction is, therefore, less than in the other directions in green tape with the lowest density at the bottom surface which dried on the carrier film. This is verified by the observation of the greatest shrinkage in the thickness direction (see Fig. 4).

Thickness changes during compaction for electroded multi-layer discoidal samples were also measured for comparison with the tape results. The

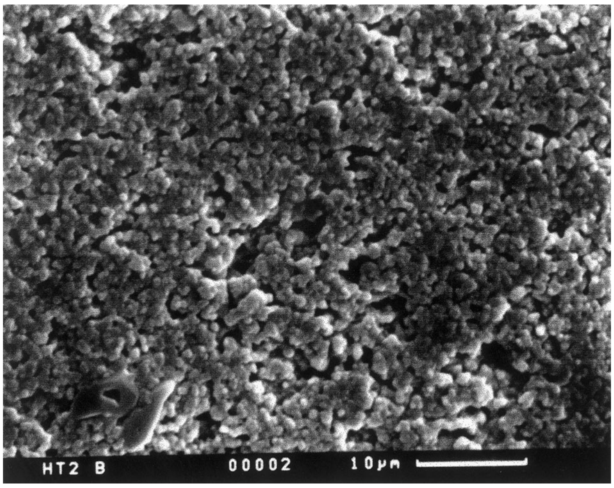

Fig. 5. Bottom surface of an as-sintered tape, isostatically compacted at 30 MPa. Note the large amount of residual porosity formed by solvent and binder burnout.

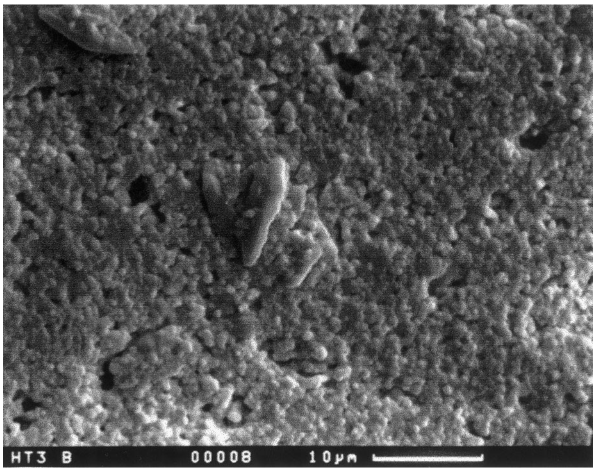

Fig. 6. Bottom surface of as-sintered tape, isostatically compacte at 100 MPa. Note the reduced amount of residual porosity.

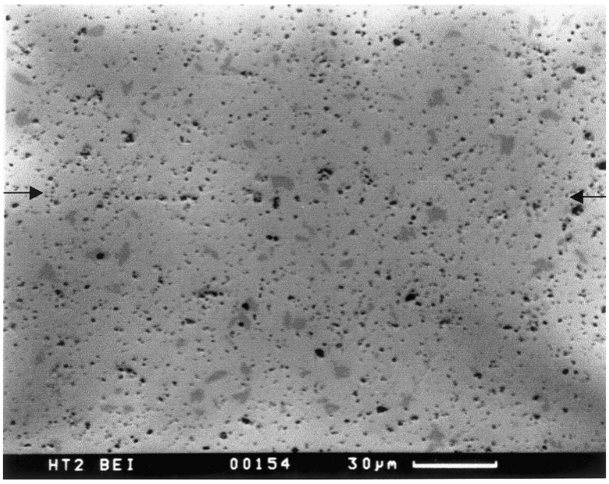

Fig. 7. A polished cross section showing a sintered stack compacted at 30 MPa. Note the line of residual pores between layers (marked by arrows), formed after compaction at low isostatic pressure.

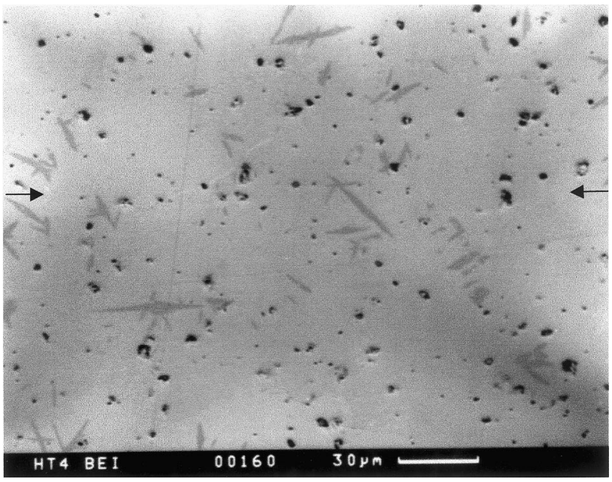

Fig. 8. A polished cross section showing a sintered stack compacted at 300 MPa. Note how defects between layers (marked by arrows) are minimised at high isostatic pressure.

standard production stack of tapes is approximately 2·7 mm thick prior to compaction. After compaction at 30 MPa the stack thickness was approximately 2·3 mm, a thickness change of approximately −14·81%. This is comparable to the results obtained above for unelectroded tapes.

More direct evidence is provided by the SEM micrographs shown in Figs 1 and 2. These plates reveal a large degree residual porosity after organic solvent evaporation. The pore sizes in the top surface and bottom surfaces are approximately 1 and 5 μm, respectively. The distribution of pores is inhomogeneous. These pores are too large to be removed after compaction at 30 MPa (commonly applied in commercial production) and consequently, such defects still exist in sintered samples as shown in Fig. 5. As the compaction pressure was increased, the volume fraction of pores formed in the drying stage is reduced (Fig. 6). In Figs 7 and 8, it can be seen that the stacking defects between layers are significantly reduced at high compaction pressure. The residual pore size is $\sim$3 μm and it is thus considered that these pores were formed after binder-burnout. The compaction process cannot reduce the pores formed after binder burnout, typically in the range of 40 to 50 vol%. A post burn-out compaction processing schedule was therefore devised to attempt to alleviate this problem.

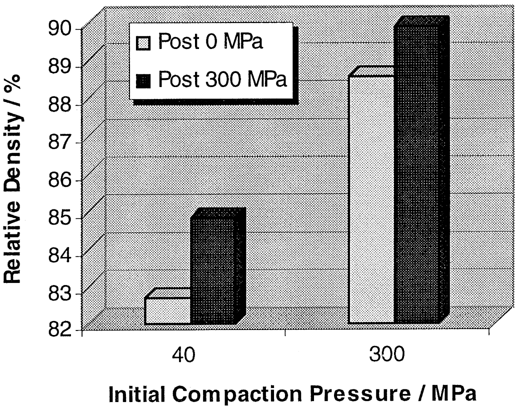

Fig. 9. The dependence of sintered density on post-compaction pressure for *tapes* sintered at 1270°C for 2 h.

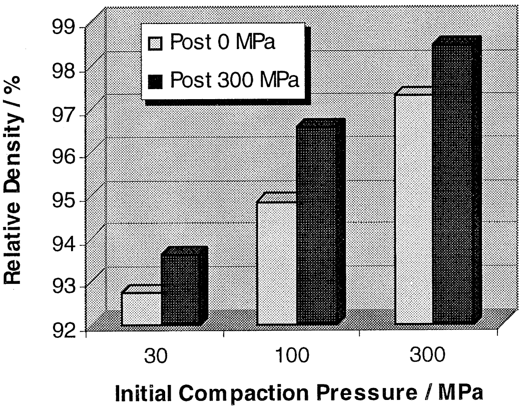

Fig. 10. The dependence of sintered density on post-compaction pressure for *multi – layerdiscs* sintered at 1280°C for 2 h.

3.2 Effect of post-compaction pressure on microstructure

Samples were isostatically re-compacted after binder burn-out as described above. The samples treated at a higher post-compaction pressure were indeed of a higher density indicating closure of the porosity described above. Figure 9 shows the improvements to the sintered densities of tapes. Densities were improved by approximately 2% by the post-compaction treatment. Similar trends were also observed in sintered multilayered discs, as is shown in Fig. 10.

4 Conclusions

Residual pores in multi-layer ceramics formed during solvent evaporation of tape casting can be reduced by means of careful control of the cold isostatic pressing conditions. The results revealed that multi-layered barium titanate devices compacted at 300 MPa can achieve a density of 97·5% sintered at 1300°C for 2 h. It is clearly shown that the relative density of sintered multi-layer ceramics was increased with increasing compaction pressure. Many device failures occur due to stacking defects between layers. In some cases these cause catastrophic delamination during sintering but more often are responsible for in-service degradation of insulation resistance. Such defects are formed due to the highly porous nature of the bottom surface of the tape and are observed in samples compacted at 30 MPa. Isostatic compaction at 100 MPa was, however, sufficient to remove any observable (by SEM) traces of the layer interfaces.

Isostatic pressing is obviously more costly than uniaixal lamination. For many electronic components (such as EMI/RFI filters, high voltage parts and multi-layer sensors) isostatic pressing is used as standard in commercial production. The improved microstructure and reduced lamination of the resultant high value added parts easily warrants the additional production costs. Obviously this technique would not be cost effective for high volume multi-layer chip capacitors and the like.

A post binder-burnout compaction technique has been shown to yield further improvements in sintered density. Again, the volume fraction of residual pores formed after binder burnout can be reduced with increasing post compaction pressure. Multi-layered discs have been fabricated with relative densities of $\sim$98·5% under 300 MPa post-compaction and sintered at 1280°C for 2 h. Post burnout compaction is a difficult and potentially expansive process to consider in a commercial environment. It is however a practical solution for niche type multi-layer components where porosity reduction is paramount such as for use in high voltage applications.

Acknowledgements

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