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A Study of the Changes Produced by Sintering on the Shape and Densification of Green Compacted Samples

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Abstract. In order to determine the effect of sample shape, compacting pressure and green density gradients on the final shape and density of sintered bodies a study was made on a PZT type powder, pressed within a large range of shapes from long cylinders up to thin discs and at pressures ranging between 40 and 180 MPa. Important shape distorsion were found for both long cylinders and thin discs but surprisingly the final density was not essentially changed even if the green compacted density showed important changes within the samples. Differences in the shrinkage of diameter and thickness brought about by sintering for samples with different shapes were found.

Key words: piezoceramic, PZT powder, grain size, sintering, densification, shrinkage.

1. Introduction

It is well known that any ceramic body is made from a powder compacted to the desired shape by pressing followed by sintering it at high temperatures. Each step of this process is important in obtaining a high quality ceramic. The powder can be obtained by different procedures from the simple conventional way of mixing the raw materials (oxides) followed by calcining, to the chemical methods (coprecipitation, sol-gel and so on) or the most advanced one (a combination of the two)

namely mechanochemical synthesis. If the conventional method produces powders scaled within the micrometric range, the chemical and mechanochemical methods go down to the nanometric range. Such powders are more homogeneous and reactive and the sintering can be accomplished at lower temperatures [1–10]. Anyhow, the choose for one or another procedures depends on the final destination of ceramic. For industrial application the conventional mixing methods is the most adequate being economically cheap and rather easy to use, but for scientific purposes the other methods are generally recommended.

As we have already mentioned, the fabrication of ceramic materials and parts via conventional mixing route is well established and it consists in powder consolidation by uniaxial compaction in a die followed by high temperature heat treatment to achieve the maximum density and the required mechanical strength. During consolidation of the green powder, there appear variations in green density [11] which will produce differences in shrinkage strain from one region to another. These differences are expected to produce densification stresses and warpage during sintering [12]. In addition, the presence of the density gradients in green compacts could lead to defect evolution during the heating process and may induce dimensional changes in the final sintered body [13, 14]. The density gradients appearing during consolidation of particulate systems originates in the die wall friction, in the internal friction between particles, in the particle size distribution, and even in the sample shape and size. The two main mechanism of consolidation, i.e. particle slipage and deformation are influenced by the particle size and size distribution. The contacts between particles are generally point contact and the number of total area of these contacts will be influenced by the particle size, the size distribution and the packing arrangement of the powder. As the compression proceeds, plastic deformation of these contacts will occur, so influencing the consolidation of the powder. The density differences in green compacted bodies as well as the density gradient may affect both the final shape of sintered ceramics and the main properties of material.

For the present experiment we have chosen a PZT type material, since such materials are the most used ones in all fields of activity from the domestic industry as gas lighter (long cylinders) and buzzers (very thin discs) to medical transducers (net of columns), actuators (stacks of thin discs or plates) and space industry (sophisticated transducers of different shapes and sizes). The performances of these transducers depend intrinsically on the quality of the piezoceramic active elements. Particularly dense and structurally uniform ceramics are required when high performance applications are involved [15–17]. To achieve this care must be taken during processing of ceramics and each step of the process must be carefully monitored. Of importance in this process are the sample shape, pressing pressure as well as the sintering temperature [18–23].

In the present study we report on the results of an investigation conducted to reveal the effects of some factors such as compacting conditions, shape of the pressed body, the green compacting pressure, the density gradient of the pressed body as well as the sintering conditions on the properties of ceramic bodies. We aimed at investigating the influence of all these important physical factors on the shape and densification of the final sintered bodies.

2. Experimental

For the purpose of this investigations we chose as material in the experiment a soft PZT type material having the following composition: $Pb_{0.99}Sr_{0.01}Zr_{0.50}\ Ti_{0.47}Nb_{0.03}O_3$. The raw oxides were provided from Merk and had purities ranging from 99.2 up to 99.9% and an average size distribution between 0.5 and 1.5 microns. Mixed oxide and solid state reaction route was the preparation method. The stoichiometric amount of oxides corresponding to the above chemical formula were mixed in a planetary ball mill using hardened steel vials and balls, in a masic ratio ball/oxides of 3/1. Mixing was carried out in methanol for 3 hours and the dried slurry was calcined at 880°C for 4 hours. The calcined product was milled in the same mill for 10 hours, thus producing a fine submicron powder as can be seen in Fig. 1.

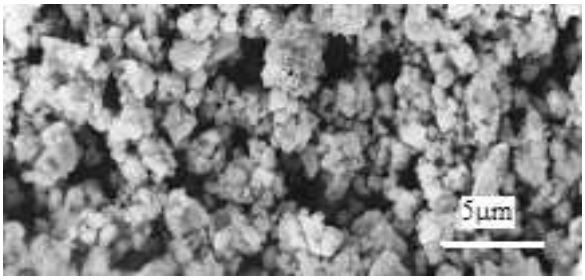

Fig. 1. Photograph showing the grain size and shape of the PZT powder used in the experiment.

The average grain size was estimated to 650 nm. This powder was used further for compacting and sintering experiments.

The shapes of the samples used in the experiments ranged from cylinders to discs. We chose these shapes for two reasons: one since the overwhelming majority of piezoceramic elements used for transducers have cylinder or disc shapes of different sizes and two since the experimental results seem to be more relevant and easy to understand and to interpret theoretically. Therefore, we have limited ourselves to this two shapes because they cover all the sizes from long cylinders up to thin discs. We used as working parameter the diameter to thickness ratio, D/h. The pressing was done in steel dies of different sizes so as to cover all shapes from cylinders to discs. The pressing was uniaxial and the pressures used were between 40 and 180 MPa. The densities of green compacted samples were evaluated only geometrically, while those for the sintered bodies both geometrically and Archimedes procedures were used. The error between the two did not exceed ± 1%.

3. Results and discussions

Figure 2 shows the dependence of the sample density on the sintering temperature measured on standard samples with D/h = 15, pressed during green compaction at 75 MPa, and sintered for 4 hours at different temperatures. This was done in order to see

whether there is an optimum sintering temperature for this material or not and what this temperature would be. One observes from this graph that such a temperature exists around 1 250°C, and the densification recorded for samples sintered at this temperature reached 98%. Consequently, all further sinterings were carried out at this optimum temperature.

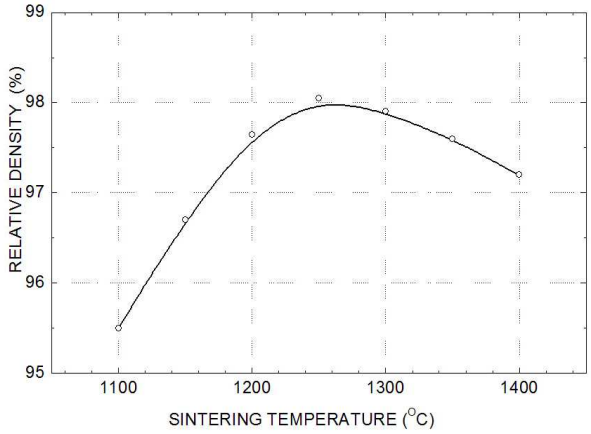

Fig. 2. The dependence of the final density of sintered samples on the sintering temperature.

The first experiment was made to evaluate the effect of sample shapes on densification. For this we used compacted samples with very low D/h ratio (very long cylinders, with D/h = 0.15) up to very high D/h ratio (thin discs, with D/h = 20) and sintered them at the optimum temperature.

The compaction pressure was about 75 MPa. The results are shown in Fig. 3.

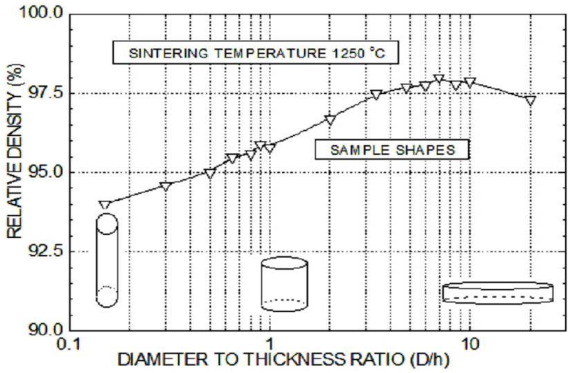

Fig. 3. The dependence of the final density of sintered samples on the D/h ratio. In the inset of the graph there are illustratively shown the shapes of the samples corresponding to some of the representative experimental points.

One can see that the density for long cylinders (low D/h) is lower than for thin discs (high D/h) and it steadily increases from 94% to 98%. At the same time one observes that there is an optimum D/h ratio ranging between 7 and 10 for which the samples reach the maximum density.

The differences in density for the extreme shapes of samples are less than 5%. A supplementary experiment was made with samples of D/h = 10, being compacted from very low pressure of 40 MPa up to very high pressure of 180 MPa respectively and then sintered at the same temperature of 1 250°C. The differences in the density for these samples was less than 1% but with a slight tendency to increase with increasing the pressing pressure (Fig. 4). This means that compacting pressure is not an important factor for the final density of the sintered ceramics.

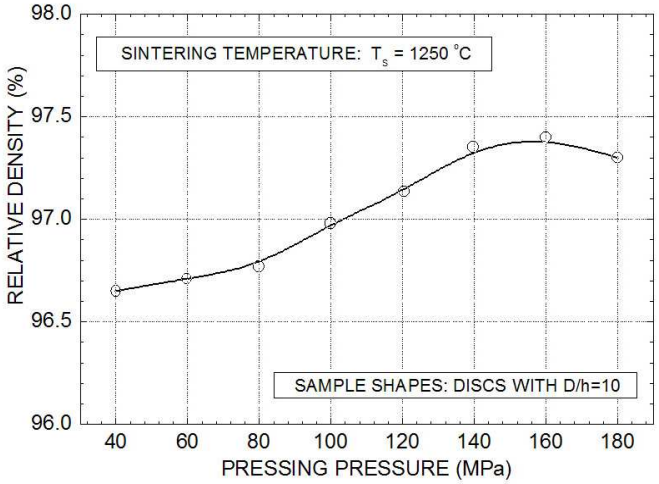

Fig. 4. The relative density of disc shapes with D/h = 10 sintered at 1 250°C and initially pressed at different pressures.

The most important changes brought about by sintering on compacted samples are visible for the extreme shaped samples, i.e. for long cylinders and thin discs as can be seen illustratively in Fig. 5a for a cylinder with D/h = 0.125 and in Fig. 5b for a disc with D/h = 25.

One can see that the cylinder deformates by shrinking more pronounced in the middle (Fig. 5a) while the disc become concave (Fig. 5b). This means that in order to be used in application they must be processed by grinding, meaning supplementary increase of the production cost and time spending.

Another experiment was aimed at checking the effect of the density gradient in compacted samples on the final density of sintered body. For this purpose we took a compacted cylinder and carefully sliced it along the long axis into 10 pieces and recorded the density of each slice. A similar operation was made on the sintered cylinder and the density of each sintered slice was measured. The results are shown in Fig. 6.

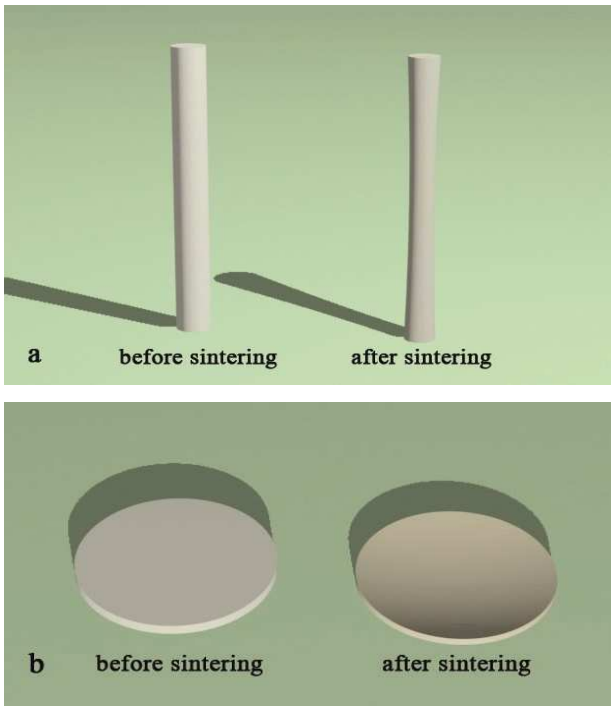

Fig. 5. The shape distortions produced by sintering on long cylinders (a) and thin discs (b) respectively. The cylinders shrinks at the middle, while the discs become concave.

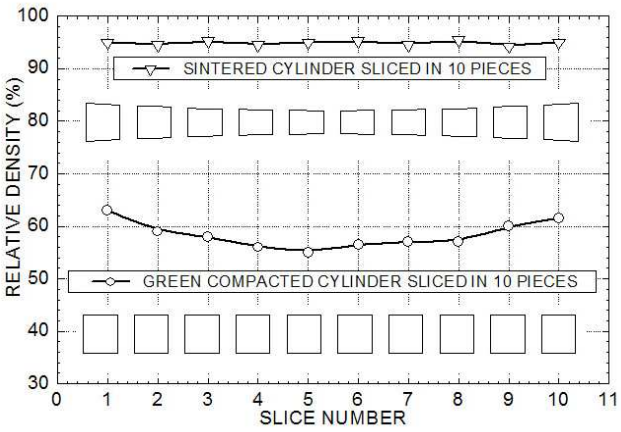

Fig. 6. The distribution of the density in a cylinder along the long axis both before and after sintering.

One can see that there is a density gradient into the green compacted cylinder, of about 13% between the middle and the ends of it while for the sintered one practically

there is no density gradient along the cylinder. The gradient disappeared during sintering being "swallowed" by the shape deformation.

The effect of green compacted pressure on the density of both green and sintered samples is shown in Fig. 7 for samples with a D/h = 5.

The density for the green compacted samples increases with increasing pressing pressure. The increase is very slow about 0.05 g/cm^3/MPa for pressures between 40 and 120 MPa and become a little higher for higher pressure (about 0.17 g/cm^3/MPa) between 120 and 180 MPa. For the sintered body practically no difference in density was recorded regardless the compacting pressure.

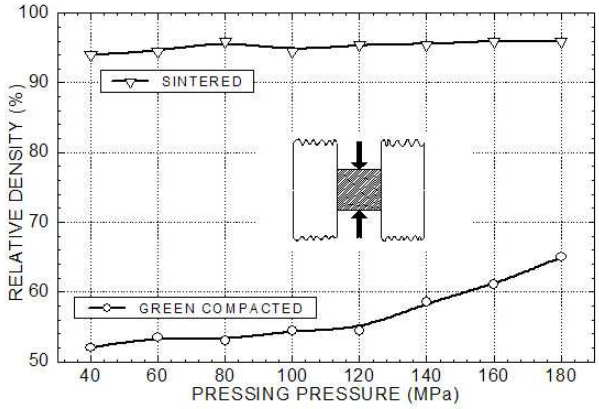

Fig. 7. The density of green and sintered samples as a function of the compacted pressure of a disc shaped sample.

Finally, the last experiment concerned the effect of compacting pressure on the sample shrinkage during sintering both in diameter and thickness. This effect is illustrated in Fig. 8.

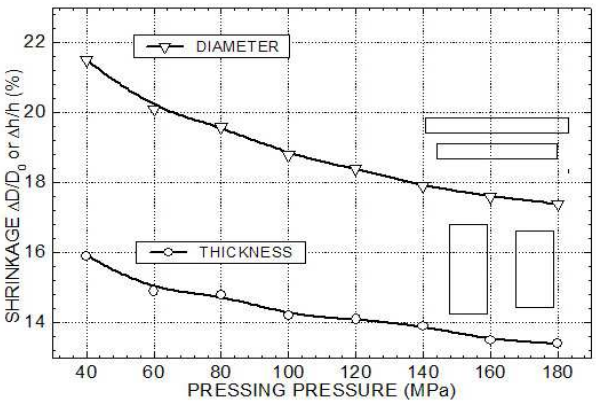

Fig. 8. Shrinkage in diameter and thickness produced by sintering as a function of the compacted pressure.

The figure clearly shows that both diameter and thickness shrinkages behave similarly, the only difference being that the diameter shrinkage for thinner samples is more intense than thickness shrinkage for thicker samples. For example the diameter shrinks between 21.5% for lower compacting pressures and 17.5% for high compacting pressures, while for thickness the shrink varies between 16% and 13.5% for the same compaction pressures interval.

Such a behavior could possibly be due to a slight pressing anisotropy between axial and radial pressing. For thinner discs the movement distances are lower in the axial direction and higher in the radial one thus giving rise to density gradients in green sample with consequent deformation during sintering.

4. Conclusions

Cylindrical shaped samples of a soft piezoelectric PZT type powder were compacted at pressures ranging between 40 and 180 MPa and then fired at 1 250°C for 4 hours. The densities of the sintered samples are practically independent on the initial forming pressure.

Shrinkage decreased nearly linearly with increasing packing pressure, more important being the shrinkage in diameter than in the thickness one. The density of the sintered samples slightly depends on the samples dimensions, the optimum value being reached for samples with a diameter to thickness ratio of about 10.

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