

A study of powder size combinations for improving piezoelectric properties of PZT thick-film devices

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Summary: This paper details investigations into the effects of different powder size ratios on the d_{33} coefficient of thick-film PZT layers. The two powders used were 5H type PZT supplied by Morgan Electro Ceramics Ltd. These were prepared using ball milling for the large particles, $\sim 2\mu\text{m}$, and attritor milling for the small particles, $\sim 1\mu\text{m}$. These powders were mixed with 10% by weight of Ferro CF7575 lead borosilicate glass and an appropriate quantity of ESL 400 solvent to formulate a screen printable paste. The results show the optimum powder combination obtained and a final formulation for a practical thick-film paste. The highest d_{33} value, 63.5pC/N, was obtained with the 4:1 ball to attritor powder by weight paste formulation.

Keywords: piezoelectric, thick-film, d_{33}

Category: 2 (Materials and Technology)

1 Introduction

Screen printable piezoelectric materials were first reported in 1987 [1] and have since found use in many applications; including motors [2] and micromachined silicon devices [3]. Studies have shown however, that the thick-film PZT samples have lower d_{33} coefficients than their bulk counterparts [4,5] due to differences in processing, composition and the influence of the substrate the film is printed on [6].

Piezoelectric thick-film pastes are produced by mixing milled piezoelectric powders with a suitable binder and organic vehicle. Both cermet pastes utilizing glass binders [7] and polymer pastes with the active material held within a polymer matrix [8] have been demonstrated. The most commonly used piezoelectric material used in the paste preparation is lead zirconium titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ or PZT). Several milling processes can be used to form the powder [9]. The physical nature of the PZT powder, i.e. particle size, distribution and shape are determined by the processing techniques used in its preparation.

Ball milling involves the PZT powder being mixed in a slurry with a suitably abrasive milling media in a horizontally rotating mill. This process results in smooth particles, the extent of this smoothness is determined by the speed of the process and the milling media used. Attritor milling is similar and often uses powder that has already been ball milled. The powder passes through a vertical mill with a rotating central shaft resulting in a more uniform size distribution. It is standard practice to feed the resultant milled powder back into the mill to further

tighten the distribution. The powder is then defined by the number of times it has passed through the mill, i.e. attritor one, attritor three for one and three passes respectively.

Previous work has shown that the large particle size, $\sim 2\mu\text{m}$, of ball milled powder produces the highest d_{33} values, whilst the smaller, more evenly distributed, particles of the attritor milled powders, $\sim 1\mu\text{m}$, produce the most consistent d_{33} values [9]. This paper presents details of the next stage in the paste development; the combination of ball and attritor milled powders and determining their optimum ratios.

2 Theory

The larger particle size associated with the ball milled powder results in increased piezoelectric responses. Therefore, it was important to maintain the ball milled particle as the dominant particle within any powder combination. The smaller attritor milled particles can be used to fill the interstice between the ball milled particles. The increased mechanical density of the film improves both the mechanical coupling and subsequent piezoelectric properties of the film. Hence, it was anticipated that by blending these two powders we would obtain a compromise between the high d_{33} values associated with ball milled powder and the consistency achieved with the attritor3 powders [9].

The attritor particles used in this investigation were milled 3 consecutive times and have been denoted attritor3. The combined ball milled and attritor3 milled powders were mixed with Ferro CF7575 lead borosilicate glass, which forms the binding matrix when fired.

3 Calculations

The initial calculations for the ratio of ball milled to attritor milled powders used a basic 2D model shown in figure 1.

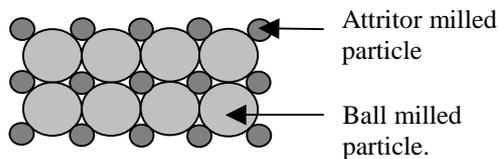


Fig 1: Ideal 2D model for particle distribution.

A ball milled particle is the central particle in the lattice and the interstice between these are filled with smaller attritor milled PZT particles.

The limitations associated with this model are that it is a 2D representation of a 3D problem and it assumes the particles are spherical. The model also assumes the glass binder will melt in the processing and form an ideal bonding matrix surrounding the particles. In addition, it assumes that the optimum solution completely fills the interstice surrounding the central particle with attritor particles and glass binding matrix. The particle sizes used in the model are obtained from the size distributions identified in figure 2.

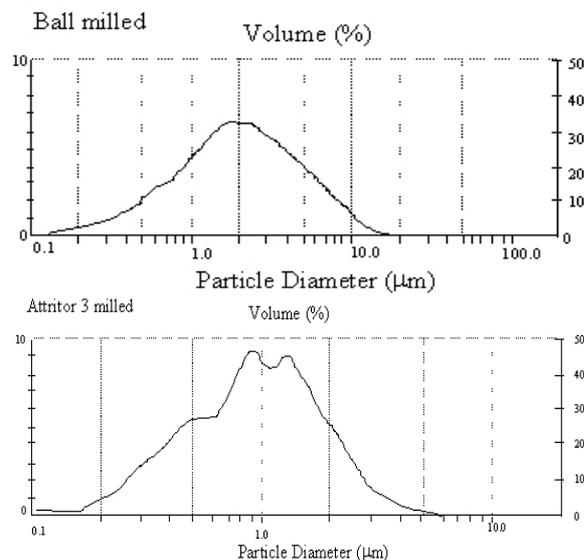


Fig 2: Particle size distributions for ball and attritor3 milled powders respectively.

The average particle size was used in the calculations but clearly in practice there are a range of particle sizes. The particle layout shown in figure 1 was used in the model since the remaining interstice closely matches the average particle size of the attritor3 powder when the ball milled powder is used as the dominant particle in the lattice.

Using the average ball milled particle diameter of 2µm, the largest particle size that will fit the interstice

between the particles is 0.83µm. Using this value, the total area between the ball particles was calculated. This configuration fills 92% of the area, which is the maximum achievable with two particle sizes. A ratio of attritor particles to ball particles required to fill the total area was then calculated based on the assumption the ideal result would be obtained when the remaining interstice was filled. The weight ratio of powders can be calculated using the density of PZT-5H [4], this gives an optimum powder ratio of 8.8:1 ball milled to attritor milled powder by weight.

In practice the attritor3 powder has an average particle size of 1µm, slightly above the ideal. This practical powder size produces a new optimum powder ratio of 7.4:1 ball milled to attritor milled powder by weight. The closest integer number of particles in the lattice of figure 1 to this would give an optimum weight ratio of 4:1. Given this, and allowing for the other assumptions described above and using an integer number of particles in the model, a range of powder ratios from 8:1 to 2:1 by weight were investigated. The calculated percentages of powders for each paste are shown in table 1. The percentage of glass binder remained constant since 10% has previously been identified as the optimum [9].

Table 1. Percentages of Att3 and Ball powders

Paste	Attritor3 percentage weight	Ball percentage weight	CF7575 percentage weight
8:1	10%	80%	10%
4:1	18%	72%	10%
2.6:1	25%	65%	10%
2:1	30%	60%	10%

4 Processing

The four powder combinations in table 1 were mixed with ESL 400 solvent to create thixotropic screen printable pastes. These pastes were then mixed using a triple roll mill, which disperses the powders evenly throughout the paste. The pastes were printed on a 96% alumina substrate using standard thick-film screen-printing process with a DEK 1200 printer. The substrates were dried in a DEK 1209 IR drier at 140°C and then fired on a belt furnace with a firing profile shown in table 2.

Table 2: Furnace firing profiles for Dupont60 and rnt1000.

Stage	1	2	3	4	5	6
Temp (°C)	350	600	885	883	890	870

The screen-printed layers formed a capacitor structure arrangement, with ESL 9936B low migration AgPd

bottom and top electrodes fired with the same firing profile as the PZT layer, figure 3.

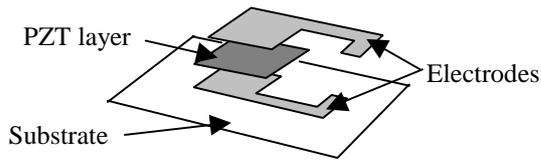


Fig 3: Capacitive structure for the piezoelectric device

This entire process took place within the University of Southampton Microelectronics Centre clean room facility to further reduce any possible sources of contamination in the pastes. Samples from each batch were viewed in a Scanning Electron Microscope (SEM).

Once fired, each sample was poled at 150°C with field strength of 4MVm⁻¹ for 30 minutes and then allowed to cool to room temperature with a continuously applied electric field [4]. The d₃₃ values were measured using a Take Control PM35 piezometer. This measurement method provides consistent and repeatable results but the measured results are limited by the clamping effect of the substrate. This clamping effect increases the influence of the d₃₁ coefficient thereby reducing the effective d₃₃ [6]. The bending moments generated by the substrate must be carefully controlled as the increased stress within the device can amplify the effective d₃₃ and if not accounted for correctly can lead to artificially high results being reported.

5 Results

Five d₃₃ measurements were taken on between 8 and 24 devices with the average value recorded and the standard deviation calculated. Figure 4 and 5 show the average measured d₃₃ values and standard deviations for each of the powder combinations respectively. Included are the previous results for ball and attritor3 milled powder for comparison [9].

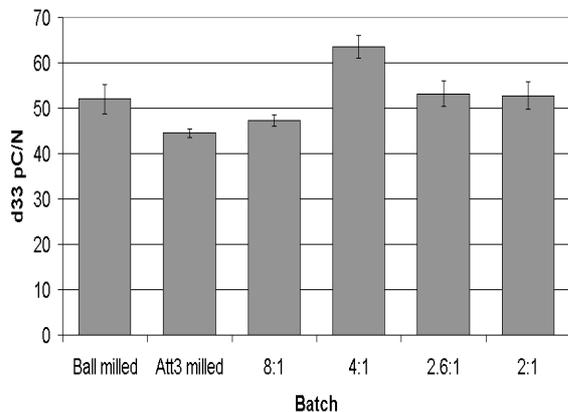


Fig 4: Average measured d₃₃ value for each powder combination.

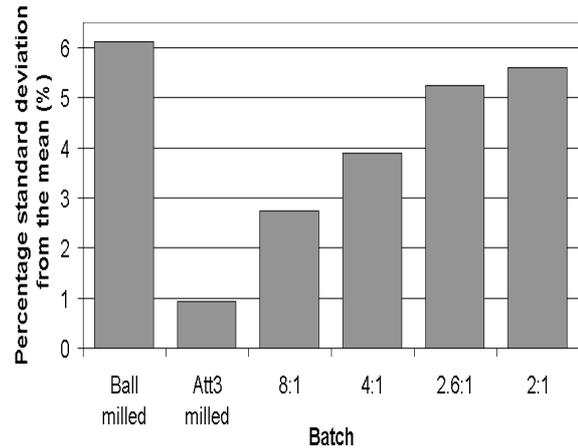


Fig 5: Percentage standard deviation for the measured d₃₃ value of each powder combination.

Figure 6 shows a SEM micrograph of the 4:1 ball to attritor PZT layer. It appears that the level of sintering between the PZT particles is low but that the glass bonding matrix and the combination of powders has produced a relatively dense film with reduced interstices.

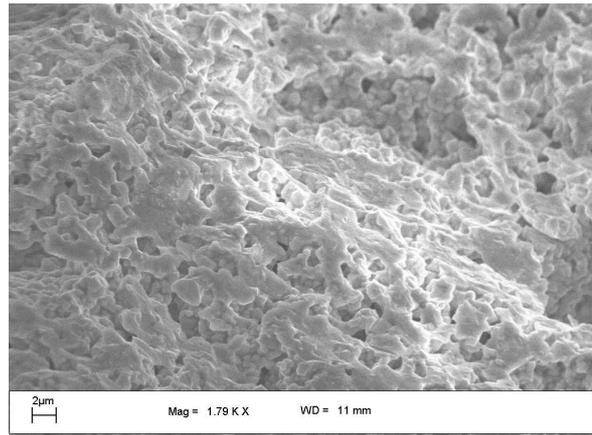


Fig 6: SEM micrograph cross-section of 4:1 ball to attritor PZT layer.

The results show that there is a clear improvement in the d₃₃ value obtained by combining powder types together. In addition, there is an optimum ratio of powders which occurs at a ratio of 4:1 by weight. This gives a d₃₃ value of 63.5pC/n and also shows an improved standard deviation when compared to the original ball milled paste.

6 Discussion of results

The combination of 4:1 by weight of ball milled to attritor milled powder (18% attritor3, 72% ball and 10% CF7575 powders) produces the highest d₃₃ coefficient with an average measured value of 63.5pC/N. Figure 4 shows that the number of smaller particles added to the paste indicates a saturating effect past ratios of 2.6:1 as the interstice gaps within

the matrix have been already filled. This result agrees reasonably closely with the basic 2D model.

The previous optimum paste, obtained from purely ball milled powder, had a d_{33} coefficient of 52pC/N. The new 4:1 paste has resulted in an increase in piezoelectric activity of over 20%. The results also show that the percentage of deviation has decreased from 6.2% to 3.9% from the previous ball milled paste. This indicates the optimum paste not only produces a more active film, but also results in a more repeatable material.

7 Conclusions

This paper has demonstrated that the blending of $\sim 2\mu\text{m}$ and $\sim 1\mu\text{m}$ diameter ball and attritor3 milled PZT powders with a respective weight ratio of 4:1 results in improved piezoelectric thick-film behaviour. Increasing from a previous high of 52pC/N to 63.5pC/N, a 20% improvement, with an almost 50% increase in consistency.

Further work will develop a 3D model to seek further optimisation and confirmation of the experimental work. Once confirmed, a further investigation into improving the process parameters for the film will be conducted, specifically, the firing temperature and poling parameters. In addition, the use of multilayer structures in combination with this new paste formulation will be investigated to further increase the effective d_{33} coefficient.

8 Acknowledgements

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9 References

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