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Effect of solids concentration on particle size distribution of deagglomerated barium titanate in stirred media mills

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ABSTRACT

The effect of solids concentration on particle size distribution of a suspension of barium titanate in toluene/ethanol solvent, deagglomerated in a re-circulating stirred media mill, has been examined by experimentation. The effect on the particle size distribution curves was recorded for solids concentrations ranging from 10% to 85% by weight and for impeller tip velocities of 4 m/s, 6 m/s and 8 m/s. Lower D50 (median) particle sizes were found at both low and high concentrations. Additionally the span of the distribution curves was found to be widest at both the lower and higher concentrations. At low concentrations high specific energies per pass of product through the grinding chamber were measured and this was as a result of high calculated stress numbers indicating high numbers of successful contact between particles and media. At high concentrations, high specific energies per pass were also measured and this was due to the increased density and viscosity of the suspension which had the effect of increasing residence time, reducing the number of passes. Thus an optimum range for solids concentration was determined which gave the narrowest spans of the particle size distribution curve, an important characteristic for deagglomeration of barium titanate for MLCC manufacture.

Keywords: Stirred media mill; Barium titanate; MLCC; Solids concentration; Particle size; Specific energy

1. Introduction

Barium titanate ($BaTiO_3$) is widely used as a dielectric in multi-layer ceramic capacitors (MLCCs), the largest class of capacitor in terms of volume produced (Sato et al., 2011; Buchanan, 2004; Horiba Inc., 2008). MLCCs consist of multiple layers of mainly $BaTiO_3$ dielectric separated by layers of mainly nickel metal electrodes and this type of construction gives a high capacitance density relative to the volume of the component. With advances in technology, the demand for miniaturization and higher capacitance has resulted in designs which increase the number of layers in a device, achieved by thinning of the dielectric and electrode layers. In addition, the demand for MLCCs to operate under harsher conditions (higher ambient temperatures and greater voltages) has increased. Well deagglomerated and dispersed dielectric particles as indicated by reduced and narrower particle size distributions is critical to ensure a homogeneous microstructure and high packing density within the dielectric layers to reduce the occurrence of physical defect sites (Paik et al., 1998; Kim et al., 2003; Ying and Hsieh, 2007).

A commonly used manufacturing technique for the building of MLCCs is the tape casting process. $BaTiO_3$ is dispersed with organic additives in an organic solvent medium to form ceramic suspension (slip). This slip is fed through a precision controlled slot die onto polyester film which passes continuously underneath. The slip forms a continuous layer of precise thickness on the film. Electrode ink is screen printed onto the ceramic sheets to form the electrode pattern and the sheets are stacked to create the multilayer structure.

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Table 1 – Particle size of barium titanate feed.

Particle size distribution	μm
D90	5.33
D50 (median)	0.87
D10	0.47

One of the key elements in the dispersion of $BaTiO_3$ particles is deagglomeration where agglomerates of the particles are broken up into discrete, primary particles (Parfitt, 1981; TTP, 1993). A widely used technique for the deagglomeration of ultrafine materials is high energy media milling in stirred media mills, where the grinding chamber is fixed and the grinding media is stirred by an agitator (Snow et al., 1984; Kwade, 1999). The level of deagglomeration is determined by the number of stress events per unit time and unit volume and the stress intensity at these events. Using grinding media with reduced diameter beads with reduced mass allows operation at high rpm therefore inducing a high number of stress events at reduced stress intensities.

In this paper, the effect of solids concentration of the $BaTiO_3$ suspension on the particle size distribution achieved in a stirred media mill over the same milling time period is examined.

2. Materials and methods

To reflect current MLCC manufacturing techniques, $BaTiO_3$ particles dispersed in a blend of organic solvents (toluene and ethanol) were examined. $BaTiO_3$ powder (BT03, Sakai Chemicals) was used. The $BaTiO_3$ feed particles are approximately spherical and are agglomerated. Particle size distribution of the feed particles (Table 1) was determined by laser light scattering (Horiba LA-950).

A solvent mix of toluene, min 99.5% purity, and ethanol, 97.6–97.9% alcohol content, (Brenntag Group) at a ratio of 1:1 by weight was used as the liquid medium. Blends of these two solvents are used extensively in barium titanate slurry manufacture (Cho et al., 2003). The dispersant used was a commercially available dispersant (NOF Corporation, Japan) composed of a maleic anhydride/styrene copolymer with polyoxy alkylene monalkyl ether side chains which adsorbs onto the surface of the $BaTiO_3$ providing a steric hindrance effect (NCJ, 2010). The dispersant was used at a quantity of 25 mg dispersant per 1 g of powder.

Varying solids concentrations from 10 wt% to 85 wt% (Table 2) were made up by firstly pre-mixing the solvents and dissolving the dispersant and then wetting the powder using a bench-top mixer with a toothed, dispersion-type blade (IKA Eurostar® Model Euro-ST). The 85 wt% solids concentration was determined to be the maximum practical concentration achievable as higher concentrations could not be successfully wetted to form a fluid suspension.

The wetted suspension was then milled for 1 h in a laboratory horizontal stirred media mill (Dispermat® model SL-12C) where the grinding media was contained in 125 ml volume, horizontal chamber and spun by a disc impeller. The grinding chamber was water cooled. The experiments were carried out at three different impeller speeds, 4 m/s, 6 m/s and 8 m/s, measured as the speed of the outer tip of the discs. The suspensions were re-circulated through the grinding chamber by integrated electric pump/stirrer mounted within the product vessel and the pump speed setting was kept constant at 6000 rpm. The grinding media used was 0.3 mm diameter yttrium stabilized zirconia beads and occupied 80% of the volume of the grinding chamber (100 ml of media). The total volume of each suspension was consistent at approximately 240 ml and therefore the ratio of suspension to media was 2.4/1 (Fig. 1).

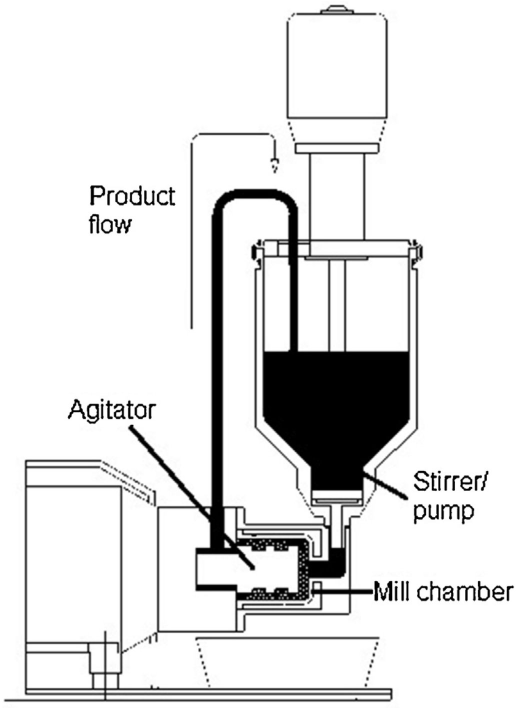

Fig. 1 – Representation of Dispermat® SL-12C laboratory mill (WMA, 2013).

Net mechanical power consumption determines the energy transmitted by the impeller via the media to the product and is the total mill power consumption minus the idling power (power consumption under no product load conditions). The net power consumption relative to the duration of milling is recorded as Wh and was measured by mill instrumentation.

Particle size distribution (PSD) measurements of the milled suspension were determined by laser light scattering (Horiba LA-950). Measurements were made of the D50 (median particle size), D90 (the particle size where 90% of the particles are below that size) and D10 (the particle size where 10% of the particles are below that size). In addition the span of the PSD curve was determined by the formula (D90-D10)/D50. A lower value of PSD span indicates a tighter distribution which implies a more even and consistent milling process (Horiba Inc., 2008; Mizuta et al., 1984).

Viscosity measurements of the suspensions were made with a Brookfield model LV viscometer using a cylindrical spindle (#34) at a shear rate of 56 1/sec (200 rpm). Measurements were taken within a temperature stabilized sample chamber (25 °).

3. Energy considerations in stirred media mills

Energy considerations in stirred media mills are discussed by Kwade et al. (Kwade, 1999; Kwade and Schwedes, 2002)

3.1. *Specific energy*

Specific energy, SE (kJ/kg), is the amount of energy directly transferred into the mill chamber related to the quantity of