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Effect On The Processing Characteristics Of ZnO Varistors Produced Using Vibratory Milling

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Abstract. Each manufacturing stage in the production of zinc oxide varistors from powder preparation to the final encapsulated device is important not only for the formation of the varistor component with optimum microstructure and thus electrical characteristics but also for avoiding the introduction of flaws and reduced yield. In this paper the authors describe and discuss the effect of multi-elemental oxide additives having been milled for different durations using a vibratory mill with cylindrical zirconia media on the powder characteristics of the subsequent processing stages. A commercial ZnO varistor formulation was used. The subsequent processing stages that are given particular attention include first spray drying and second milling. The characteristics include agglomerate size, powder density and elemental uniformity of the first spray-dried powders, and particle size, specific surface area, zirconium concentration and pore size of the second milled powders. They were evaluated using laser diffraction, scanning electron microscopic, mercury porosimetry, Brunauer, Emmett and Teller (BET) and inductively coupled plasma (ICP) analysis. Some interesting correlations are observed between the powder properties and vibratory milling durations of the mixed metal oxide additives (MMOA).

Keywords: ZnO varistors, Vibratory milling, Powder characteristics, Zirconium concentration.
PACS: 81, 81.20 Ev, 82.80 Dx, 83.50 xa, 83.80 Fg.

INTRODUCTION

Handling of fine, usually sub-micrometer and/or nanometer sized, powders in large quantities require a high degree of process control to achieve the desired microstructural characteristics[1]. The desired microstructural characteristics include small defect size, narrow distribution in grain size, well-dispersed secondary phases and homogeneous composition of all phases present. The processing of ZnO varistors from powders is no different.

ZnO varistors, first discovered by Matsuoka[2] are semiconductor ceramic devices exhibiting high non-linear current-voltage characteristics[3, 4]. Each electrical characteristic is highly reliant on the composition and the atomic, nano-, micro- and macrostructural characteristics, which are in turn highly reliant on each processing stage from powders to final device. Inhomogeneous microstructure can cause a large spread in current-voltage characteristics[4, 5]. Control of the microstructure is required to obtain maximum varistor performance.

Novel powder processing methods investigated to control the microstructure include chemically derived mixed metal oxides[6], incorporation of ZnO seeds[7], prior preparation of secondary phases[8] and mechanical milling[9]. Some of these methods have not been widely implemented on an industrial scale, possibly due to high manufacturing costs and low reproducibility. The endeavour to obtain maximum homogeneity and narrow grain size by using highly mixed powders on atomic and nanometer scales may not be sufficient. Some variables used in the conventional processing of varistor powders, which have their own effect on the microstuctural and electrical properties, may have been over looked. One such variable may be

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the concentration of elements introduced indirectly as a result of media wear during milling. A previous publication by Kelleher et al. (2008) showed that zirconium was present in the metal oxide additive powders in the parts per million (ppm) concentration levels as a result of vibratory milling. Knowledge of the effect of zirconium concentration on the electrical properties of ZnO varistors is scarce. More knowledge is required on the influence of milling on the subsequent processing, microstructural and electrical characteristics of ZnO varistors.

In this study the preparation of high voltage varistor powders ready for compaction and sintering involved a number of processing stages. These stages were conducted on a pilot scale. Mixed metal oxide additives (MMOA) were milled using a vibratory mill with cylindrical ZrO_2 media in the first milling stage for different durations. The effect of different milling durations on the powder properties of the first milling stage was reported[10]. This study focuses on the effect of different milling durations on the powder characteristics of the subsequent processing stages, second spray drying and second milling.

EXPERIMENTAL PROCEDURE

Reagents

The metal oxide additives of a commercial high voltage ZnO arrester formulation were used; Bi_2O_3 0.5 mol.%, Sb_2O_3 1.0 mol.%, MnO_2 0.5 mol.%, Co_3O_4 1.0 mol.%, NiO 0.5 mol.% and SnO_2 0.5 mol.%. These are collectively referred to as mixed metal oxide additives (MMOA). ZnO, 96.0 mol.%, is the main constituent of the varistor formulation.

Process Stages and Equipment

The stages used for the preparation of ZnO varistor powders ready for compaction included first milling, first spray drying, calcining, second milling and second spray drying. Six batches of MMOA were prepared using a vibratory mill for durations of 0, 1, 3, 6, 12 and 18 hours in random order. This stage, called first milling, was carried out using a vertical mill (Sweeco Ind., model M-18) and has been described earlier by the authors[10].

Each batch of MMOA was shear mixed with the main constituent ZnO, binder and lubricant for one hour to form six slurries ready for drying. Drying was achieved using a spray dryer (Bowen Engineering Ind., model No.1). This is called the first spray drying stage. Samples were taken from each batch of spray-dried powder and examined for agglomerate size, elemental homogeneity, bulk and tap density. Calcination was carried out using a pilot kiln.

The six batches of calcined ZnO varistor powders were then individually milled using the vibratory mill (M-18) for a standard time of 6 hours in random order. This is called the second milling stage. Each batch used 5 kg of powder with 5 litres of deionized water. Samples of the flowing slurry were taken from the mill at the end of each milling operation and examined for particle size, specific surface area, pore size and zirconium concentration.

Analytical Instruments

The bulk density was determined when the powder was poured without agitation into a 100 ml graduated cylinder. The tap density was determined by tapping a graduated cylinder containing 100 ml of powder 1,000 times with a Quantachrome tapping machine. Scanning Electron Microscopic studies of the elemental homogeneity was determined using a Zeiss FESEM operating at 20 kV. Agglomerate size and distribution was determined with a Malvern MasterSizer Laser Diffractometer with dry state conditions. The distribution in size at 10, 50 and 90 cumulative percent is denoted as D10, D50 and D90, respectively. The specific surface area,

particle size, pore size and Zr concentration were determined by Brunauer, Emmett and Teller (BET), laser diffractometry, mercury porosimetry and inductively coupled plasma (ICP) analysis respectively. These techniques have been described previously by the authors[10].

RESULTS AND DISCUSSION

Characteristics of The First Spray Dried Powders

The influence of vibratory milling duration of the MMOA on the powder density, agglomerate size and elemental homogeneity of the first spray-dried powders was studied. Some characteristics were influenced by the duration of vibratory milling whereas others were not. The density of the first spray-dried powders (Fig. 1) increased slightly, whereas the average and range of agglomerate size (Fig. 2) were unaffected with increasing duration of vibratory milling of the MMOA.

The slight increase in powder density with increasing milling duration of the MMOA appears to correspond with the reduction in size and distribution of the MMOA[10]. The reduction in size and distribution of the MMOA may have resulted in reduced friction between the spray-dried agglomerates causing them to flow easier and move closer together.

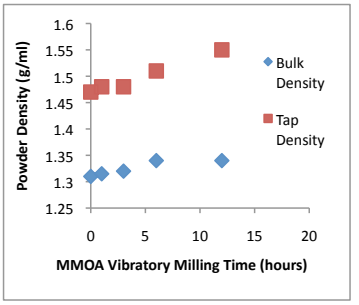


FIGURE 1. Effect of vibratory milling time of the MMOA on the bulk and tap density of the first spray-dried powders.

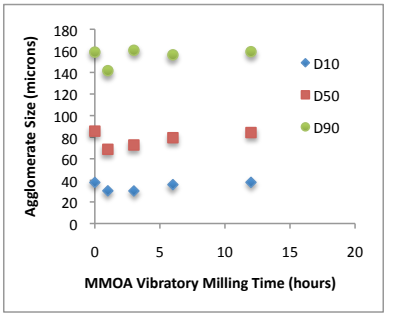
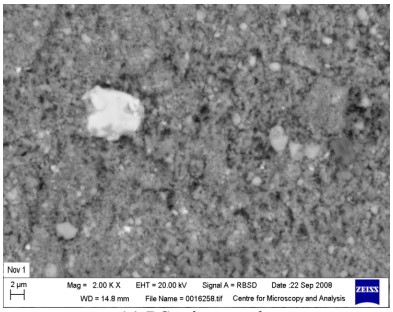
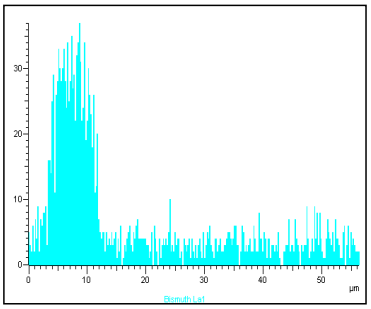


FIGURE 2. Effect of vibratory milling time of the MMOA on the agglomerate size of the first spray-dried powders.

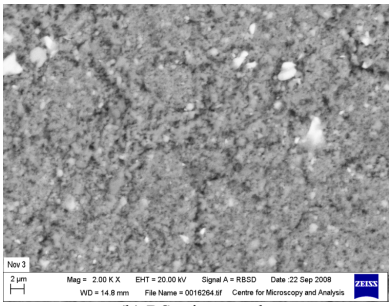
Back scattering electron microscopic and elemental analysis (Fig. 3) illustrates that the level of metal oxide uniformity is strongly influenced by the duration of MMOA milling. The grey, bright grey and white areas correspond with the metal oxide particles of lowest (Mn, Co, Ni and Zn), medium (Sn and Sb), and highest atomic weights (Bi) respectively. The presence of bismuth oxide particles ranging in size from 1 to 10 microns is clearly evident on the surfaces of the agglomerates whose MMOA were milled for zero hours. As the duration of MMOA milling increases the bismuth oxide particles reduce in size and become more scattered. These measurements correspond with the largest particle size dimensions observed by laser diffraction analysis of the milled MMOA[10]. The bismuth oxide particles appear to be the most resistant to being reduced in size during vibratory milling of the MMOA. If the as-received bismuth oxide particles consisted of an alternative morphology, requiring less energy to reduce them to submicron particles, the duration of vibratory milling of the MMOA would be shorter. Less work required by the mill to reduce the size of the MMOA would also result in reduced wear of the ZrO_2 media and thus lower Zr concentrations[10].



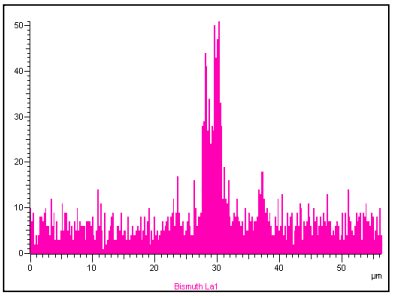
(a) BS micrograph



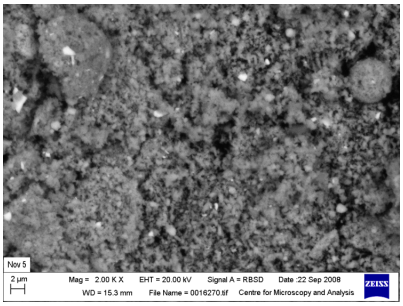
(a) Bismuth line graph



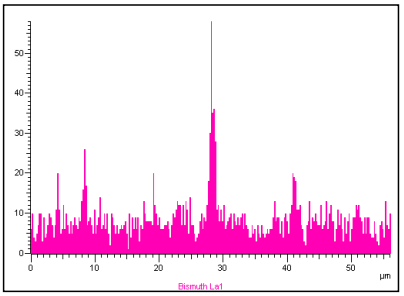
(b) BS micrograph



(b) Bismuth line graph



(c) BS micrograph



(c) Bismuth line graph

FIGURE 3. Back scattering electron micrographs (BS) and bismuth line graphs of first spray-dried agglomerates from batches in which the MMOA were milled for (a) zero hr, (b) 6 hr and (c) 12 hr.

Characteristics of The Second Milled Powders

The duration of vibratory milling of the MMOA during the first milling stage had little influence on the particle size (Fig. 4), specific surface area (Fig. 5) and pore size (Fig. 6) of the second milled powders. The concentration of Zr in the second milled powders was affected by the duration of vibratory milling of the MMOA (Fig. 7).

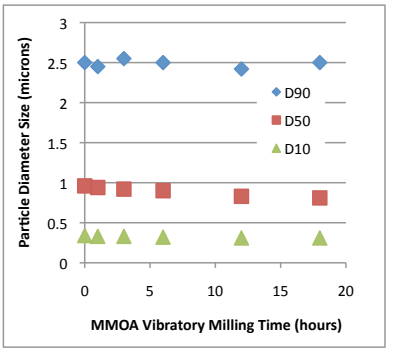


FIGURE 5. Effect of MMOA vibratory milling time on the particle size distribution of the second milled powders.

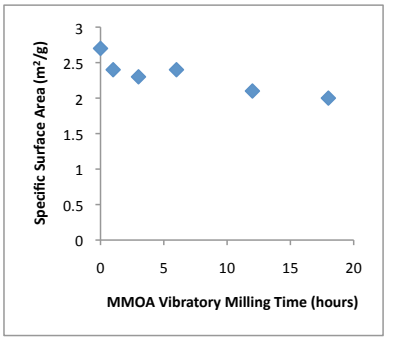


FIGURE 6. Effect of MMOA vibratory milling time on the specific surface area of the second milled powders.

ICP analysis shows that Zr is present in the second milled powders in the ppm range, 12 to 200. A linear relationship between the duration of MMOA milling and the concentration of Zr exists. Figure 8 also compares the concentration of Zr before (calculated from the concentration of Zr in the MMOA[10] combined with 96 mol. % ZnO) and after the second milling stage. The ZnO powder contained zero ppm Zr.

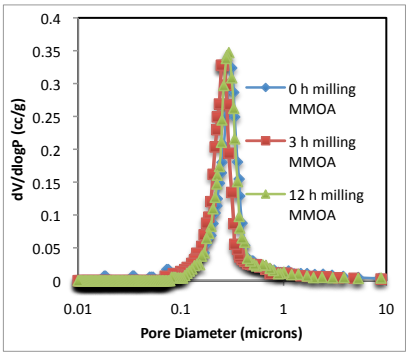


FIGURE 6. Effect of MMOA vibratory milling time on the pore size distribution of the second milled powders.

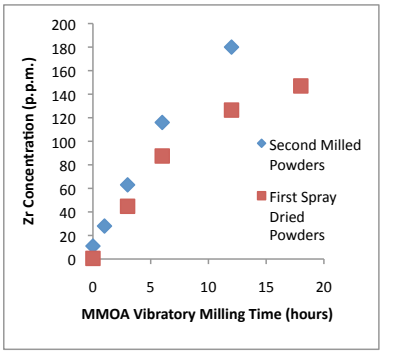


FIGURE 7. Effect of MMOA vibratory milling time on the zirconium concentration of the second milled powders.

The gain in Zr concentration indicates that wear of the ZrO_2 media occurred during the second milling stage. However, it is much lower than that observed after the first milling stage of the MMOA (5 to 1300 ppm)[10]. Most of the Zr picked up from the media by the varistor powders occurs during the first milling stage. If the concentration of Zr in the ppm range is important towards varistor behaviour, then control of the media wear during the first milling stage is critical.

Even though all of the calcined varistor powders were milled for 6 hours the gain in Zr concentration was not equal for all powders and appears to be influenced by the duration of MMOA milling. It increased as the duration of MMOA vibratory milling was increased. The calcined powders made from the MMOA with the smallest particle size and highest Zr concentration may be more abrasive than those made from MMOA with largest particle size and lowest Zr concentration.

CONCLUSIONS

Some of the powder characteristics of the first spray drying and second milling stages were influenced by the duration of milling of the MMOA. Most noticeable were the elemental homogeneity within the first spray-dried agglomerates and the concentration of Zr in the second milled powders. The level of homogeneity of the MMOA, in particular bismuth, within the first spray-dried agglomerates increased with the duration of MMOA vibratory milling. The concentration of Zr increased further during the second milling stage. The increase in Zr concentration was less than that observed during the first milling stage and increased with the duration of milling of the MMOA. It is anticipated that the improved homogeneity of the MMOA around the ZnO particles with increasing vibratory milling duration will result in improved ZnO grain growth control during sintering and thus better electrical characteristics. The level of Zr may need to be controlled.

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