Mechanical Properties and Microstructure of Zinc Oxide Varistor Ceramics

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Abstract: ZnO varistors are nonlinear resistors used as surge arresters in power transmission and distribution for the protection of electronic devices. Electrical characteristics of these materials have been extensively studied, but their mechanical behavior is not completely understood. It has been suggested that the breakdown of ZnO varistors is related to microstructure heterogeneities and processing defects. These defects are the same that usually control the mechanical strength of ceramic materials. In this work, mechanical properties (flexural strength, fracture toughness, elastic constants, and hardness) of five commercial blocks of ZnO varistors (class I) from different producers were measured and correlated to their microstructure. Pore fraction and size significantly affected the flexural strength.

Introduction

Zinc oxide varistors are strongly nonlinear resistors that have been used to regulate transient voltage surges of unwanted magnitude for high voltage and power-related applications, such as surge arresters in power transmission and distribution for the protection of electronic devices. The ZnO varistor is a multiphase polycrystalline ceramic made by conventional sintering of a mixture of oxides [1]. Current commercial ZnO varistors contain about 10 additives, such as Bi₂O₃, CoO, MnO, Cr₂O₃, and Sb₂O₃ [2]. The amount of ZnO can range from 85 to 98% and the exact composition is largely proprietary. Sintering is conducted in air for 2 to 10 h at temperature ranging from 1100 to 1350°C [1]. The microstructure of a ZnO varistor ceramic generally contains large ZnO grains, spinel (Zn₇Sb₂O₁₂) particles, and continuous intergranular Bi-rich phases (α- and δ-Bi₂O₃, pyrochlore (Zn₂Sb₃Bi₃O₁₄), and amorphous phase) [3]. The electrical properties of ZnO varistors have been extensively studied [1,3], but their mechanical behavior is not completely understood.

Two main types of failure have been observed in ZnO varistors: “puncture” mode and mechanical fracture [4,5]. The puncture mode is believed to occur as a consequence of current localization and associated Joule heating that leads to a hole being melted through the varistor, possibly caused by microstructural inhomogeneities. The short-pulse-induced fracture is caused by the propagation of preexisting processing flaws under the influence of stress waves generated by the rapid Joule heating of the varistor [4].

Ceramics, like ZnO, fracture in brittle mode and the Griffith-Irwin relation defines their strength:

\[ \sigma_f = \frac{K_{IC}}{(Yc^{1/2})} \]  

where \( \sigma_f \) is fracture stress, \( K_{IC} \) is fracture toughness, Y is shape factor, and c is critical flaw. Failure origins in ceramics are generally associated with microstructural defects generated
during processing, like large grains, large pores or cavities, and large inclusions, or with surface cracks produced during surface finishing [6]. Recently, Balzer et al. [2] observed that the bending strength and $K_{IC}$ of a ZnO varistor lowered with increasing sintering temperature and time, caused by microstructural coarsening. The fracture origins were mostly associated to large holes left by hollow, doughnut-shaped or poorly compacted granules.

There are limited mechanical properties data regarding ZnO varistors in the literature. Since fracture is a common type of failure of these materials, their mechanical properties and strength-limiting defects must be characterized to improve their reliability and performance. In the present study, the mechanical properties (flexural strength, fracture toughness, elastic constants, and hardness) of five commercial ZnO varistors from different producers were characterized and the results were associated to their microstructures.

**Experimental**

Five cylindrical blocks of commercial ZnO varistors (4 kV, class 1) from different producers were cut vertically in slices and specimens with $3 \times 4 \times \sim 30$ mm were prepared by cutting and grinding, following the recommendations of ASTM C-1161 standard. One of the 4 mm large surfaces was polished up to $1 \mu m$ diamond suspension in a semi-automatic polisher and the edges were smoothed with SiC grinding paper to avoid fracture originating from edge cracks. The polished surfaces of the specimens were observed in an optical microscope and only specimens without any surface damage were tested in bending.

Three-point flexural strength was measured in a fixture with 16 mm span and the polished surface of the specimen was stressed in tension. The crosshead speed of tests was 0.5 mm/min. Fracture toughness was determined by SENB (single edge notched beam) method. In the center of the specimen, a straight through notch $\sim 1$ mm depth was introduced using a $\sim 0.15$ mm thick diamond saw. Notched specimen was tested in a three-point flexural fixture with a crosshead speed of 0.5 mm/min. The notch size was measured in an optical microscope and the value of fracture toughness, $K_{IC}$, was calculated using the equation proposed in ASTM C 1421 standard for precracked beam method. Elastic constants (Young’s, E, shear, G, and bulk, K, moduli and Poisson’s ratio, $\nu$) were determined by ultrasonic pulse-echo method, following JIS R 1602 standard, using a 200 MHz ultrasonic pulser-receiver (5900 PR, Panametrics). Vickers hardness was measured with 1 kgf on specimens with polished surfaces. Five specimens were tested for each mechanical property.

Bulk densities of the samples were determined by Archimedean’s method. Microstructural and fractography analyzes were conducted in an optical microscope (Leica, DMRXE) and a scanning electron microscope (SEM, JSM 6300, Jeol), coupled with an energy dispersive spectrooscope (EDS, Noram). An image analyzer (QWin, Leica) was used to quantify the volume fraction of pores and the grain size. The grain size was measured by lineal-intercept method on polished and etched surfaces (5% glacial acetic acid solution).

**Results and Discussion**

All samples presented rounded ZnO grains, characteristic of liquid-phase sintered materials (Fig. 1), and a straight twin boundary was frequently observed inside the etched grains. The average grain sizes showed small variation among the samples ($\sim 6$ to $7 \mu m$), except in sample B which presented a slightly higher value ($8 \mu m$). The differences on chemical composition of additives among the samples could be observed by the type and amount of the second-phases formed in the microstructure. All samples presented spinel particles (light gray areas in Fig. 1) in the intergranular regions and, also, trapped inside the
ZnO grains. The fraction of spinel phase in sample D was significantly higher than in the other samples (Fig. 1b). Moreover, this sample presented the smaller amount of Bi-rich phases (white areas in Fig. 1). The samples A and C presented the highest fractions of Bi-rich phases, part of them forming large pockets of secondary phases in the intergranular regions (Fig. 1a). The samples B and E presented an additional phase (dark gray areas in Fig. 1c), which was not observed in the other samples. This phase was dispersed as discrete particles in the intergranular regions and EDS analysis detected Zn, Si, and O elements. The sizes of these particles were larger in sample B. Silicon is not a common additive for ZnO varistors and apparently its effects in the microstructure and electrical properties have not been published.

In the literature [2,3], the pores observed in Fig. 1 (black areas) are attributed to the grain pull-out during grinding and polishing of the specimen. We repeated careful polishing many times and concluded that they are “real” pores and not an artifact from the specimen preparation. These pores are also clearly visible in the fracture surfaces. All samples presented pores dispersed in the microstructure, but samples A, B, and C presented higher volume fraction of pores (~6%) than samples D and E (~4%). Samples A and B presented larger pores than the other samples (Fig. 2).

Samples D and E, in comparison to the other samples, presented the most homogeneous microstructures with relatively low porosity.

The measured values of mechanical properties of commercial ZnO varistors are shown in Table 1 and the ratio between maximum and minimum values for each mechanical property are shown in Table 2. The minimum and maximum values were statistically different for all mechanical properties evaluated according to Student’t test with 95% confidence interval. The variations of the values of elastic constants were relatively low among the evaluated samples, except for the values of bulk modulus, K (Table 2). The lower values of E, G, and K moduli
of the samples A and B seem to be related to their higher values of volume fraction of pores (Table 1). The higher bulk density of sample C counteracted its high porosity and resulted in intermediate values of elastic moduli. For pure ZnO, the calculated values of $E$, $G$, $K$, and $\nu$ from single-crystal data are 122 GPa, 45 GPa, 143 GPa, and 0.358, respectively [7]. These values are higher than the measured values probably because the commercial ZnO varistors were not fully dense. It has been observed that porosity strongly affects the elastic constants of ceramics [8].

Table 1 – Microstructural characteristics and mechanical properties of ZnO varistors.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$ (g/cm$^3$)</td>
<td>5.47 ± 0.01</td>
<td>5.43 ± 0.01</td>
<td>5.63 ± 0.02</td>
<td>5.55 ± 0.05</td>
<td>5.55 ± 0.04</td>
<td>5.53 ± 0.08</td>
</tr>
<tr>
<td>$V_p$ (%)</td>
<td>6.4</td>
<td>5.9</td>
<td>6.0</td>
<td>3.6</td>
<td>4.1</td>
<td>5.2 ± 1.3</td>
</tr>
<tr>
<td>GS (µm)</td>
<td>7.1</td>
<td>8.1</td>
<td>6.7</td>
<td>6.7</td>
<td>6.3</td>
<td>7.0 ± 0.7</td>
</tr>
<tr>
<td>$\sigma_f$ (MPa)</td>
<td>80 ± 4</td>
<td>88 ± 3</td>
<td>106 ± 6</td>
<td>117 ± 6</td>
<td>120 ± 4</td>
<td>102 ± 18</td>
</tr>
<tr>
<td>$K_{IC}$ (MPa.m$^{1/2}$)</td>
<td>1.31 ± 0.01</td>
<td>1.30 ± 0.04</td>
<td>1.09 ± 0.04</td>
<td>1.38 ± 0.02</td>
<td>1.29 ± 0.03</td>
<td>1.27 ± 0.10</td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>104.9 ± 1.0</td>
<td>109.2 ± 0.3</td>
<td>114.1 ± 0.8</td>
<td>117.5 ± 0.5</td>
<td>115.4 ± 1.8</td>
<td>112.2 ± 5.1</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>39.5 ± 0.2</td>
<td>40.9 ± 0.1</td>
<td>42.7 ± 0.3</td>
<td>43.9 ± 0.3</td>
<td>43.0 ± 0.7</td>
<td>42.2 ± 1.7</td>
</tr>
<tr>
<td>$K$ (GPa)</td>
<td>101.6 ± 3.6</td>
<td>110.1 ± 0.5</td>
<td>116.2 ± 2.1</td>
<td>121.6 ± 0.9</td>
<td>122.4 ± 1.3</td>
<td>115.7 ± 8.4</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.328 ± 0.005</td>
<td>0.335 ± 0.001</td>
<td>0.336 ± 0.003</td>
<td>0.339 ± 0.002</td>
<td>0.343 ± 0.001</td>
<td>0.336 ± 0.006</td>
</tr>
<tr>
<td>$HV$ (GPa)</td>
<td>1.89 ± 0.09</td>
<td>1.98 ± 0.07</td>
<td>2.06 ± 0.07</td>
<td>2.19 ± 0.06</td>
<td>2.26 ± 0.05</td>
<td>2.08 ± 0.15</td>
</tr>
</tbody>
</table>

Note: $\rho$ is bulk density, $V_p$ is volume fraction of pores, GS is grain size, $\sigma_f$ is three-point flexural strength, $K_{IC}$ is fracture toughness, $E$, $G$, and $K$ are Young’s, shear, and bulk moduli, respectively, $\nu$ is Poisson’s ratio, and $HV$ is Vickers hardness. Results shown as (average ± standard deviation).

Table 2 – Ratio between maximum and minimum values for each mechanical property.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_f$</th>
<th>$K_{IC}$</th>
<th>$E$</th>
<th>$G$</th>
<th>$K$</th>
<th>$\nu$</th>
<th>$HV$</th>
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<tbody>
<tr>
<td>1.50</td>
<td>2.27</td>
<td>1.12</td>
<td>1.11</td>
<td>1.20</td>
<td>1.05</td>
<td>1.20</td>
<td></td>
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</table>

The measured fracture toughness values (Table 1) were close to the values reported by Balzer et al. [2]. The difference between the lowest and highest value was 27% (Table 2). Samples A, B, and E presented ~1.3 MPa.m$^{1/2}$, indicating that porosity and Si containing phase in samples B and E had little effect on $K_{IC}$. The highest value presented by sample D (1.38 MPa.m$^{1/2}$) may be explained by the lower amount of Bi-rich phases in this sample (Fig. 1b). The lowest value presented by sample C (1.09 MPa.m$^{1/2}$) however, could not be explained.

The flexural strength values varied strongly among the evaluated ZnO varistors. The highest value presented by the sample E (120 MPa) was 50% higher (Table 2) than the lowest value presented by sample A (80 MPa, Table 1). The lower values of samples A, B, and C seem to be related to the higher volume fractions of pores in these samples (Table 1), and the lowest values of the samples A and B seem to correlate with the large pores of these samples (Fig. 2a). The relatively high strength values of samples D and E seem to correlate to the low porosities and more homogeneous microstructures of these samples. Apparently, the differences related to the second-phases in these samples (Fig. 1b and 1c) did not have any significant influence in the flexural strength.

Fractography analysis of the broken specimens in bending test showed that mostly of the fractures initiated from surface flaws and the fracture origins had semi-elliptical shape. A
typical value observed for the shape factor (Y) of a semi-elliptical surface precrack introduced in the SCF (surface crack in flexure) method for $K_{IC}$ measurement is 1.4. Considering this value and the measured values of $K_{IC}$ and $\sigma_f$ (Table 1), the average depth of critical flaws (c) could be calculated from the Griffith-Irwin relation (Eq. 1) and the estimated values were 137, 111, 54, 71, and 59 for samples A, B, C, D, and E, respectively. Balzer et al. [2] estimated the critical flaw size ranging from ~50 to 150 $\mu$m, assuming the value of the shape factor as 1.13, for a penny-shaped volume flaw. They showed that large circular holes left by hollow, doughnut-shaped or poorly compacted granules were the strength-limiting defects for ZnO varistor ceramics. Large elongated pores resembling the original granule poorly compacted were, in fact, observed in sample A (Fig. 3a), but not in the other samples. At this point, it is not clear if the defects originated during pressing were the fracture origins for all samples. Fractography analysis also indicated that crack extension by subcritical growth could have increased the original flaw sizes. The slow crack growth (SCG) susceptibility of ZnO varistor ceramics must be investigated in order to clarify the results of fractography.

Fig. 3 – SEM images of polished surface of sample A, SEI, (a) and of fractured surface of sample E: (b) SEI and (c) BEI.

A typical fracture surface of ZnO varistor is shown in Fig. 3b. Large ZnO grains tended to present transgranular fracture mode, but the crack path was predominantly intergranular. The higher amount of Bi-rich second-phases observed in the fracture surfaces (Fig. 3c), in comparison to the polished surfaces (Fig. 1c), is indicative that intergranular fracture mode was dominant.

ZnO varistors are soft ceramics. The higher Vickers hardness value measured was 2.26 GPa for sample E (Table 1), less than 50% of the hardness of soda-lime glass. The hardness value increased in the order of samples A, B, C, D, and E, that is, with decreasing volume fraction of pores, with decreasing pore size, and with increasing microstructure homogeneity. The bulk modulus, $K$, followed the same tendency (Table 1).

No correlation was observed between flexural strength and fracture toughness (Table 1), but a direct dependence of flexural strength on Young’s modulus was observed, although with some scattering in the range of high values (Fig. 4).
Conclusion

There are differences on microstructural level among the commercial ZnO varistors from different producers, mainly related to the type and content of the secondary phases and fraction and size of pores. Pore fraction, however, probably had more influence on the variation of elastic constants and hardness. Fracture toughness showed no clear dependence on any microstructural characteristics, although the higher value was observed in the sample with low Bi-rich second-phases. The variations of the values of these properties among the ZnO varistor ceramics were, however, relatively low. The average values of fracture toughness, Young’s modulus, Poisson’s ratio, and hardness were 1.3 MPa.m$^{1/2}$, 112 GPa, 0.34, and 2.1 GPa, respectively. Flexural strength, however, varied 50% among the samples, defined mainly by pore fraction and size. The weak sample presented large elongated pores left by the poorly compacted granules. Flexural strength showed dependence on Young’s modulus, but not on fracture toughness.

Acknowledgments

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References