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ZnO Varistors made from Powders Produced Utilizing a Urea Process

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ZnO VARISTORS MADE FROM POWDERS PRODUCED UTILIZING A UREA PROCESS*

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ABSTRACT

Small-grained oxide powders of uniform composition, ideally suited for varistor production, have been prepared as follows: ZnO and other components are dissolved in nitric acid. Urea is added and the mixture is heated to remove water and nitrates and to form solid melamine. The melamine is then calcined to burn off the organics and to produce fine oxide powders. Grain sizes, densities, and electrical characteristics have been measured for varistors fabricated from these powders by sintering or hot pressing. The densities and grain sizes increase with processing temperature, the nonlinearity coefficient depends primarily on composition, and the average voltage per barrier for sintered samples is approximately 2.5 eV. The breakdown field for hot-pressed samples is not uniform for different slices of the same varistor and depends on variables other than the grain size.

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1. INTRODUCTION

Metal oxide varistors are polycrystalline zinc oxide ceramics doped with oxides such as Bi_2O_3, Sb_2O_3, and other transition metal or rare earth oxides in a fashion that develops Schottky barriers of approximately 3 volts at grain boundaries.[1] These barriers give rise to highly nonlinear voltage-current characteristics which make these materials suitable for transient voltage suppression in electrical and electronic systems. The usefulness of such devices has been widely recognized and the tendency to miniaturize electronic systems as well as the desire to employ these devices in high voltage transmission systems has generated a need for high voltage capabilities in smaller volumes. The achievement of smaller grain sizes with accompanying higher voltage capabilities requires consideration of varistor production techniques which involve fine grain sized starting powders and/or processing at lower temperatures where grain growth is inhibited. Both approaches have been reported in recent studies. Snow and coworkers[2] have prepared varistors by hot-pressing techniques, which resulted in samples with high field capability (60 kV/cm); Lauf and Bond[3] have described a sol gel processing technique in conjunction with hot pressing. It is the purpose of the present paper to describe powder preparation by a new process involving the addition of urea to a nitrate solution of the varistor constituents and to document some problems associated with hot pressing of varistor materials.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of Fine-Grained Oxide Powders

The additives used for the preparation of the powders are listed in Table 2.1. All components except Sb_2O_3 were easily dissolved in nitric acid. The antimony oxide, which dissolves in nitric acid with difficulty, was first converted to citrate in molten citric acid (monohydrate), then diluted with water and added to the other components. Granular urea was then added to the nitric acid solution, the mass being heated to melt the urea. With the temperature rising to near 250°C, dehydration and denitration occurred slowly and amides (melamine) formed. This product was then calcined at 675°C until the organics decomposed, leaving behind fine-grained metal oxide powders.

2.2 Varistor Production

The fine-grained powders prepared by the urea process were either cold pressed and sintered in air or were hot pressed in vacuum using graphite dies. For the sintering, the heating and cooling cycle was similar to that described by Tahiliani.[4] However, the total cycle time was 10 hours and the samples were held at the maximum temperature, either 1100 or 1200°C, for 45 minutes. For hot pressing, 2-5 g batches of powder were heated in graphite dies to temperatures of 750, 850 or 950°C. Pressure of 7.2×10^7 Pa (10^4 PSI) was normally maintained at the maximum temperature for 45 min. A few of the hot-pressed samples were separated from the graphite die by use of Ni felt; however, this modification had no significant effect on the final product. The pellets resulting from hot pressing were partly reduced by interaction with the surrounding material; therefore, they were subsequently oxidized in air or oxygen at 780°C for 1 to 4 hours. It is

TABLE 2.1

Impurity Content of Samples

Sample	(Mole percent)					Trace Impurities (amounts > 10 ppm) (s)
	Bi_2O_3	Sb_2O_3	CoO	MnO	CrO_3	
Amount added to 6 component samples	.50	1.00	.50	.50	1.0	—
QG	.7 (x)	0.9 (s)	.5 (x)	.4 (x)	1.8 (x)	Cu(100) Na(100) Fe(90) Ca(70) Na(50) Ni(30)
QI	.6 (x)	—	.4 (x)	.4 (x)	1.6 (x)	—
QJ	.7 (x)	1.0 (s)	.5 (x)	.4 (x)	1.7 (x)	Ca(100) Si(90) Na(70) Fe(70)
QK	.8 (x)	1.5 (s)	.5 (x)	.5 (x)	1.8 (x)	Na(200) Cl(70) Fe(50) Ca(40) K(30)
QQ	.5 (x)	1.7 (N)	.6 (x)	.4 (x)	1.0 (x)	—
Amount added to 4 component samples	.50	1.00	.50			

(x) X-ray fluorescence analysis
(N) Neutron activation analysis
(s) Spark source mass spectrometry

noteworthy that during this oxidation, bubbles sometimes formed on the pellet surfaces; these bubbles frequently exfoliated and in rare cases caused thin samples to fragment.

2.3 Electrical Characterization

For electrical measurements, electrodes 0.6 cm in diameter were applied using silver paint. The measurements themselves were made with a computer controlled electrometer* and dc voltage supply** which allowed extended delays at each voltage (normally limited to either 10 or 30, min) thus permitting a stable current to be established. Measurements were made by increasing the voltage in steps up to 2000 volts or until the current reached 0.5 or 1 mA. Then, for many of the samples, the measurements were repeated with reversed polarity.

The power supply used had an upper limit of 2000 V; therefore, most of the small grain size samples had to be thinned with SiC paper (240 to 600 grit); until the samples were thin enough (in one case 300 microns) to allow the observation of the nonlinear region of the varistor characteristics. For the sintered samples, where the grain sizes were larger, either the sintered pellets or sliced sections 0.5 to 2 mm thick were used for the electrical measurements.

2.4 Microstructural Characterization

The microstructure of the samples prepared as described above was observed with a scanning electron microscope (SEM)***. In order to allow for detection of structural variation in the varistors, the SEM

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*Model 619, Keithley Instruments, Inc., Cleveland, Ohio.

**Models SN488, APH 2000, Kepco, Inc., Flushing, New York.

***Hitachi X-65.

examinations were made on surfaces obtained by cutting sections from the varistor pellets, parallel to the axis and approximately 1 mm in from the circumference. These pieces were mounted and the cut surfaces were polished using diamond abrasives, with final polishing on 1/4 micron powder. This was followed by etching for varying periods with a 30% solution of $FeCl_3$ in H_2O. Different parts of the surface were then examined with the SEM. The way the surface was cut allowed detection of any structural variation in the original varistor pellet from one flat surface to the other and 1 mm in from the circumference. Photographs were prepared from which grain sizes were determined by the method of maximum diameter.[5] No less than 150 individual contiguous grains were measured from each of three different areas of each sample.

The density of the varistor pellets was determined by two methods. The results reported herein were obtained by the method of Archemedes with water as the buoyant liquid. Pores at the sample surfaces were sealed with parafin to avoid interference caused by capillary infusion of the water. Measurements of the physical dimensions and weights of the varistor pellets also provided values of the density. Results for the two methods agreed within ±2%.

2.5 Chemical Composition

A number of different methods of chemical analysis were necessary to obtain adequate information on the chemical composition of the experimental samples. Semiquantitative spark source mass spectrometry allowed assessments to be made of contaminating impurities in the parts per million range. The same technique, but using samples that had been powdered and "spiked" with an additional known amount of ^{121}Sb yielded quantitative data on the antimony content. Concentrations of the other dopants, Bi, Co, Mn, and Cr were obtained using x-ray fluorescence[6] or neutron activation analyses. These results indicate that the dopants are incorporated in the varistors with little loss and that the initial batch makeup probably yields the most precise measure of varistor composition.

3. RESULTS

The results of microscopic examination of samples prepared as described are typified by micrographs shown in Fig. 3.1, (a), (b), and (c). The microstructure is quite clearly finer grained after hot pressing at 750-950°C than after sintering at or above 1100°C. As may be seen by comparing Fig. 3.1 (b) and (c), the grain size and morphology appears very similar in samples sintered from powder prepared by the urea method or prepared by conventional ball milling. The grain shapes in the sintered samples are typical of recrystalized equilibrium structures. The grains in the hot-pressed samples have not formed as many equilibrium 120° angles at grain triple points as have the sintered samples. It should be noted that the apparent porosity in the micrographs is almost certainly a reflection of crystal "pull out" during polishing, that is, it is an artifact of the sample polishing technique.

Grain sizes determined for samples prepared by hot pressing or sintering are listed in Table 3.1. The data indicate a monotonic increase in average grain size from 1.3 to 3.2 microns for samples hot pressed at increasing temperatures between 750 and 950°C. Samples sintered at or above 1100°C have larger grain sizes as might be expected. Results of density determinations, also included in Table 3.1, indicate that the

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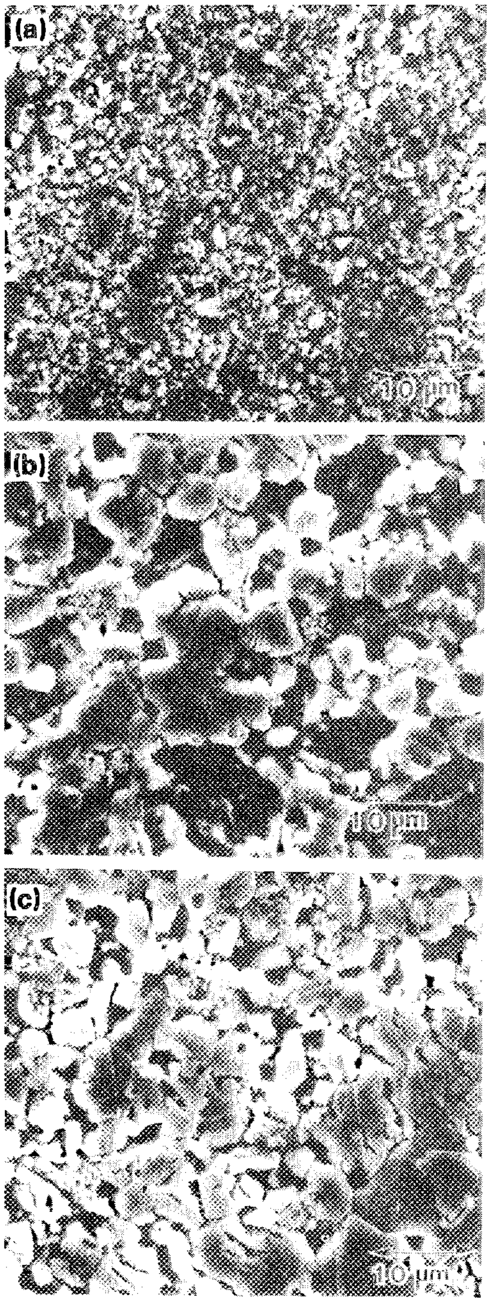

Fig. 3.1. Typical photomicrographs of polished and etched varistor surfaces. a) sample QI2, urea process in urea, hot pressed 750°C; b) Sample QG1, urea process in urea and sintered at 1100°C; c) Sample QQ, prepared by conventional ball milling and sintering at 1100°C.

TABLE 3.1

Average Grain Size and Density of Six Component Varistors Processed at Different Temperatures

Sample Designation	Powder* Preparation	Pellet** Preparation	Treatment Temperature (C)	Average Grain Size (μm)	Density (% of Theoretical)
QI1					
QI2	U	HP	750	1.4	82
3				1.3	89
QJ1	U	HP	850	1.6	90
2				1.9	88
QK1				3.1	93
2	U	HP	950	3.2	92
3				3.5	90
QG1	U	S	1100	5.1	90
QQ2	B	S	1100	5.1	95
QQ1	B	S	1200	9.3	97

*U = Urea process; B = Ball milled

**HP = Hot press and reoxidized; S = sintered density is also a monotonically increasing function of hot pressing or sintering temperature.

Electrical data for varistors prepared from urea process powders are depicted in Fig. 3.2 when the electric field is plotted vs current density for samples hot pressed at 750, 850 or 950°C, or sintered at 1100°C. For comparison, the two curves without point symbols are for samples prepared by sintering ball milled powders of the same starting composition at 1100 and 1200°C.

It is clear that high breakdown fields can be achieved by hot pressing varistors from urea prepared powders. The nonlinearity coefficients, α,[7] do not appear to be a function of the processing method, and all samples from the 6 component formulation used here yield alphas in the range 20-30.

We also produced ZnO varistors from a formulation containing only four components, 98 mole% ZnO, 1% Sb_2O_3, 0.5% Bi_2O_3, 0.5%CoO. These samples exhibit lower alphas, with values approximately 10. With this four component formulation we were able to compare samples prepared by sintering powders from the urea process, the sol gel process,[3] and ball milling. Results of electrical measurements are reproduced in Fig. 3.3 and indicate again that the general shapes and nonlinearity coefficients are not a strong function of the processing method. Alpha depends primarily on dopant content.

The data in Figs. 3.2 and 3.3 are typical curves, and it should be pointed out, particularly for the data in Fig. 3.2 obtained with hot pressed samples, that different slices of the same varistor pellet frequently yielded different breakdown fields.[8] Breakdown fields for hot pressed samples regularly varied by a factor of three and for one case

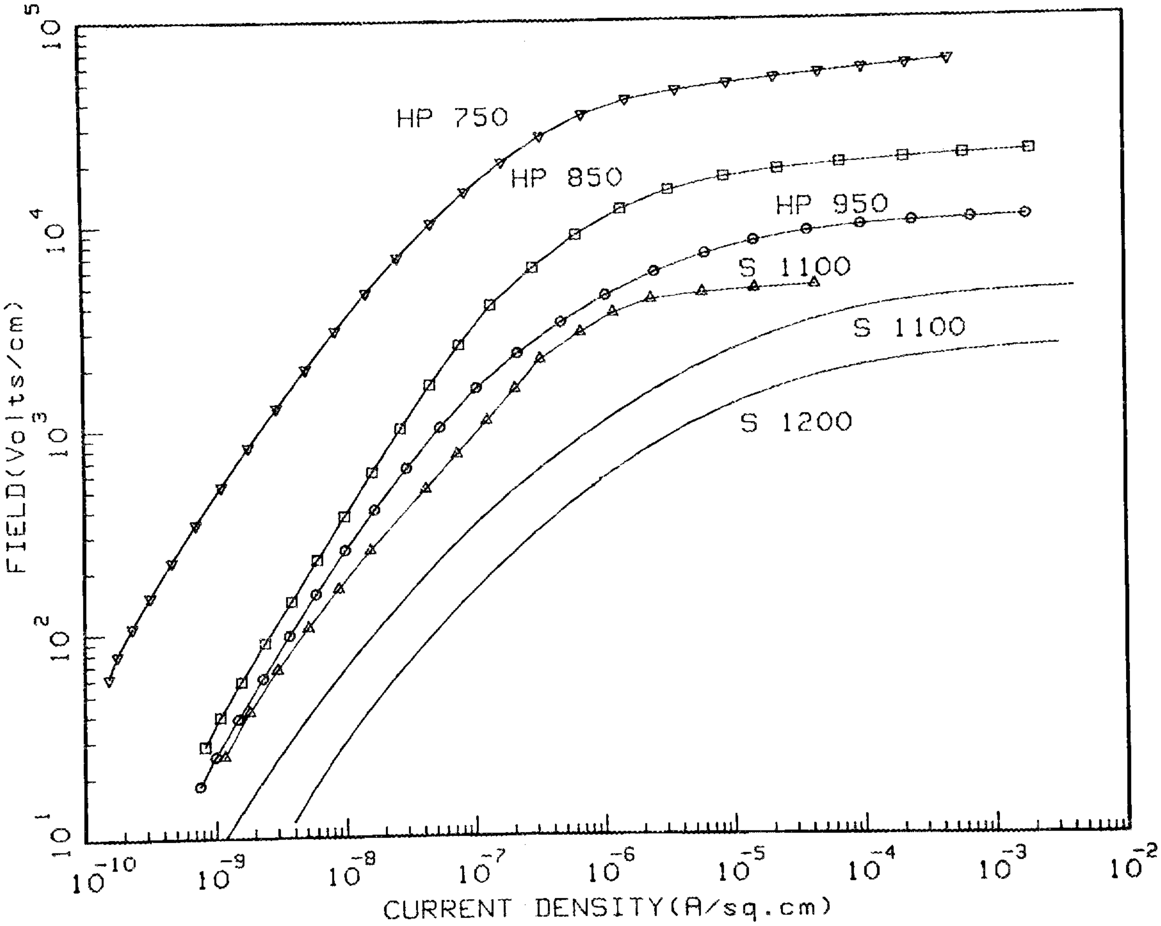

Fig. 3.2. Direct current electrical characteristics of 6 component varistors prepared at different temperatures from urea process powders. The solid lines without data points are for conventionally prepared varistors. The labels indicate preparation by hot pressing (HP) or sintering (S) and the temperature (°C) of treatment.

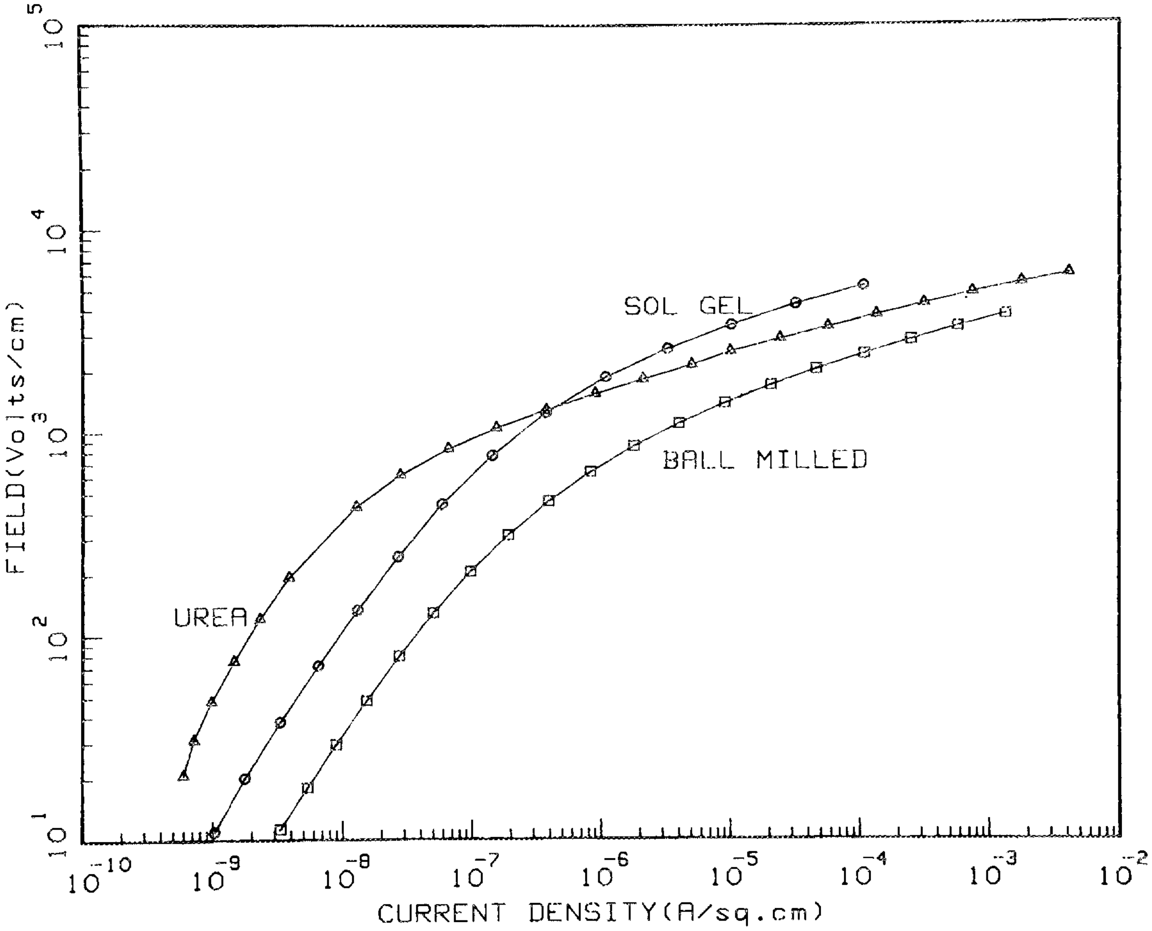

Fig. 3.3. Comparison of dc electrical characteristics of 4-component varistors prepared by different powder processing methods: Δ, urea process; 0, sol gel; □, ball milled. All pellets sintered at 1100°C.

the field for two slices from the same pellet differed by an order of magnitude. This extreme variability was not observed in sintered samples. Also it should be pointed out that the variability was evident only in electrical results; it was not reflected in either the density or the grain sizes. These latter parameters appeared quite uniform throughout a varistor pellet.

4. SUMMARY AND DISCUSSION

The grain size depends upon processing variables in these samples in a fashion which was anticipated. The hot pressed samples have the finest grain sizes achieved and as the hot pressing temperature increases, so does the grain size. Sintering at more elevated temperatures produces larger grain sizes. The same behavior is observed also for samples sintered from ball milled powder. The microstructure in any particular sample does not appear to vary greatly from location to location, and the temperature dependence of average grain size observed is undoubtedly due to the usual well known coarsening with increasing temperature. Also, the increasing density with treatment temperature is expected.

The breakdown voltage of samples sintered at 1100 and 1200°C were not greatly affected by differing powder preparation techniques. The breakdown field decreases with increasing sintering temperature as expected and the nonlinearity parameter α depends primarily on the dopant composition. The average breakdown voltage measured on a number of different portions of hot-pressed samples treated identically decrease with increasing hot-pressing temperature. A plot of breakdown voltage as a function of reciprocal grain size is shown in Fig. 4.1. The error bars

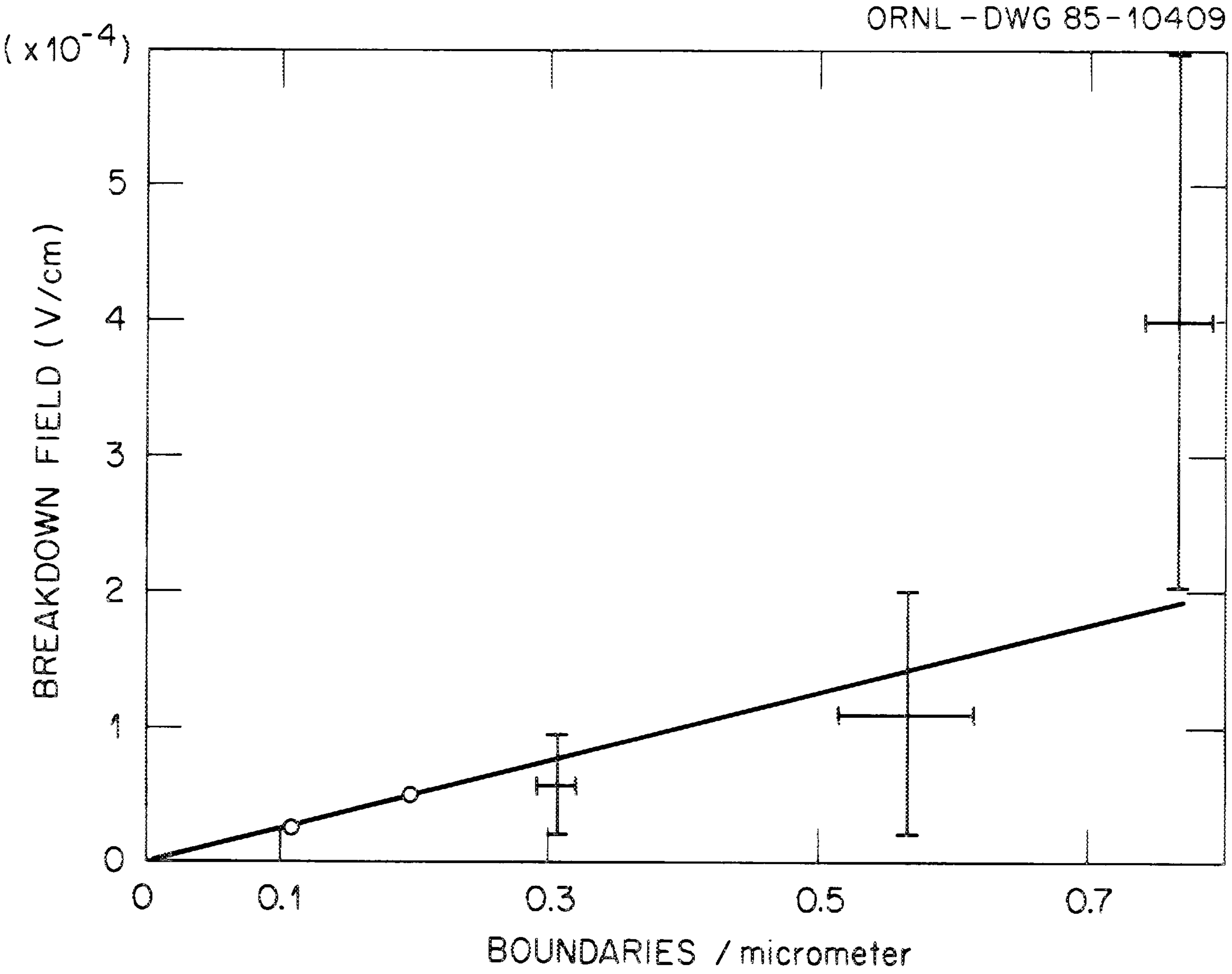

Fig. 4.1. Breakdown field vs inverse grain size for sintered and hot-pressed 6-component varistors. The points indicated are results for sintered pellets. The error bars indicate the maximum range of values obtained for hot-pressed pellets. The line drawn through the experimental points corresponds to 2.5 eV per boundary.

extend over the range of breakdown field observed as well as over the range of grain sizes observed. It is to be noted that the variability for hot-pressed samples is much greater than noted in the sintered samples discussed above. Although the observation of such variability has not been mentioned explicitly in print, Snow and coworkers do mention that variables other than grain size affect the breakdown field. Lauf[9] also found large variations in the breakdown field of hot-pressed varistors which were not correlated with average grain size. If a line is drawn through the points in Fig. 4.1 for sintered samples its slope corresponds to 2.5 volts per boundary. This is within the range 2→3 eV previously published[10] for varistor ceramics.

5. CONCLUSIONS

The urea process is a convenient technique for producing small grained uniform powders for varistor production. We found that hot pressed varistors made from the usual Bi, Sb, transition metal formulations, in which liquid phase sintering occurs above 750°C, yield high but widely variable breakdown fields. Samples sintered at 1100 and 1200°C behaved in a consistent fashion; breakdown fields and linearity coefficients were not dependent on the mode of powder preparation; sintered, ball milled, sol gel derived, or urea process powders of identical composition all exhibited comparable breakdown fields and nonlinearity coefficients.

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7. The nonlinearity coefficient is generally defined by the equation $I \propto CV^{\alpha}$, where I and V are corresponding current flow and applied voltage across a varistor. See for example, Ref. 1 or L. M. Levinson and H. P. Philipp, Appl. Phys. Lett. 24, 75-77 (1974).
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