Effect of Microstructure on Pulse Electrical Strength of MgO

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Pulse electrical strengths of hot-pressed MgO containing 0.3 wt% LiF were measured. Strengths as high as 5.9×10^6 V/in. were obtained on samples 99.8% of theoretical density with 1- to 3-μm grain size. An increase of either porosity or grain size resulted in a monotonic decrease in strength. Single-crystal strengths of 4.0×10^6 V/in. were obtained by polishing samples chemically. A simple recessed-electrode configuration eliminated corona effects.

I. Introduction

ONE of the intriguing aspects of the electrical strength of ceramics is the great disparity between experimentally determined values and values predicted for ideal materials. Current theories of intrinsic breakdown in solid dielectrics are electronic in nature. Cooper[1] described them as either "avalanche" or "collective-electron" types and indicated the difficulty of calculating electrical strengths for any but the simple crystalline alkali halides. For these materials, strengths of 10 MV/in. are predicted,[2] and for single-crystal halides[3] and very thin oxide films,[4] strengths of this order have been achieved. However, electrical strengths of commercial insulating materials such as steatites and porcelains generally fall in the range of 0.2 to 0.4 MV/in.[5]

The parallel of dielectric strength with mechanical strength of ceramics is interesting and perhaps more than coincidental. Just as in the electrical case, mechanical strengths calculated on the basis of an ideal structure are several orders of magnitude greater than those commonly achieved in ceramic materials. Until recently, practically the only exceptions were fibers and single-crystal whiskers, which in the pristine state withstand stresses of $>3 \times 10^5$ psi.

The accepted explanation for the discrepancy between theoretical and practical mechanical strengths is that engineering materials contain defects which raise local stress to the theoretical value with only a relatively small applied stress. It has also been generally accepted, but largely on an intuitive basis, that defects are responsible for the low electrical strengths in ceramics. Defects, in this operational sense, are structural features which raise the local field to the intrinsic breakdown value with a relatively low applied field. The work described in the present paper was an attempt to identify the responsible defects by investigating the effect of various structural parameters on electrical strength of MgO.

II. Experimental Procedure

(1) Sample Preparation

Magnesium oxide was chosen for this study because it can be made relatively easily with very low porosity and small grains and because it has a relatively simple crystal structure; an electronic grade starting material* was used. To achieve the desired high densities in times short enough to retain small grains, 0.3 wt% LiF was added, and the material was hot-pressed in Al_2O_3 dies at 1000°C for 1 h. Porosity was varied from ≈ 0.5 to 15% by adjusting the pressure during hot-pressing. In addition, some samples of essentially theoretical

Table I. Chemical Analysis of MgO

Component	Supplier's analysis (wt%)	Spectrographic analysis (wt% as oxide)	
		Powder	Hot-pressed spec.*
MgO	98.0		
SiO_2	0.01		
Si		0.1–0.01	0.1–0.01
Ca	0.01	1–0.1	1–0.1
Fe	0.03	0.1–0.01	0.1–0.01
Cu	Tr	<0.01	<0.01
B	Tr	<0.01	<0.01
Ti	Tr	0.1–0.01	0.1–0.01
Al	Tr	0.1–0.01	0.1–0.01
Mn	Tr	≈ 0.01	0.1–0.01
Zn	Tr		
Ag	Tr		
Ba	Tr		
V	Tr		

*1000°C, 1000 psi, 1 h.

density were obtained by vacuum hot-pressing. Grain size was adjusted by subsequent heat treatment at 1400°C in air. Grain-growth rates were substantially lower than those reported by Spriggs et al.,[6] particularly for the samples with the higher porosities.

A few disks were obtained† which had been hot-pressed in graphite dies without additive and subsequently heated to obtain grain growth. Bulk densities were determined by displacement in CCl_4, porosities were calculated on the basis of a theoretical density of 3.581 g/cm³, and grain size was determined by the linear intercept method. Values given are the averages of 3 samples of at least 50 grains.

The starting powder and ceramic were analyzed spectrographically (Table I). In addition, the Li content of samples at each stage of treatment was determined by flame photometry. No great change occurred during hot-pressing at 1000°C; the as-fired material generally retained 80 to 90% of the original Li. During heat treatment for grain growth, however, the Li content decreased to 30% of the original value after 10,000 min at 1400°C.

In addition to the polycrystalline samples, 1.3-cm cubes were cut from single-crystal MgO‡ prepared by fusing powder of moderate purity.

(2) Dielectric Strength Measurements

The primary requirement in meaningful measurement of dielectric strength is that the field strength at the point of failure be known. In this regard, it is particularly important to eliminate the possibility of corona discharge at the sample surface. Not only does the presence of corona greatly modify the potential distribution by providing fields of unknown mag-
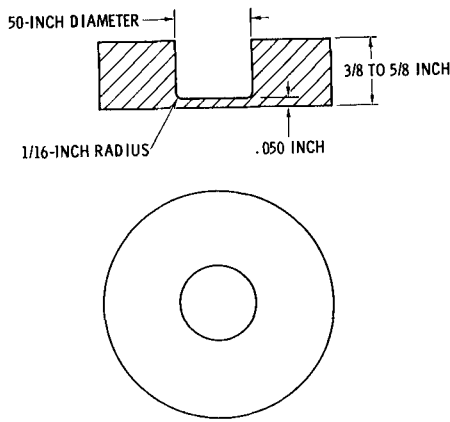
Fig. 1. Specimen for dielectric strength test.

Fig. 2. Dielectric strength of MgO as a function of (*A*) porosity and (*B*) grain size.

nitude at points of incidence on the sample, but bombardment of the sample by the ions and electrons may degrade the sample surface.

For very high fields, a common technique for suppressing corona is to recess one or both electrodes.[7] For the present experiments, a rather simple configuration, a cylindrical cavity with a slight radius at the bottom (Fig. 1), was chosen. Cavities were cut to approximate depth with an ultrasonic impact grinder, using 240-grit SiC. Subsequently, the samples were lapped on the flat side to final dimensions. Most of the samples tested had cavities $\frac{1}{2}$ in. in diameter with 0.050-in. webs and a $^1/_{16}$-in. radius at the bottom of the cup. Samples were from $\frac{1}{4}$ in. to $>\frac{1}{2}$ in. thick. In testing, a 10:1 ratio between sample thickness and web thickness was necessary to prevent edge breakdown in the very strong samples. Air-drying Ag paint* was used to electrode the cavity and the flat surface.

In using this simple geometry, a problem was introduced. Although the field was uniform near the center of the web, it was not uniform at the periphery, and no simple field solution exists for that region. Therefore, tests were regarded as invalid when failure occurred within 0.060 in. of the corner of the cup, and the results were not included. Approximately 80% of the failures occurred within the uniform field region.

The test voltage was applied in the form of a ramp rising at the rate of 50 to 100 kV/μs. The voltage across the samples was monitored and displayed on an oscilloscope screen. Failure, which was indicated by an abrupt drop in the voltage trace, generally occurred ≈ 2 μs after the start of the pulse. Occasionally, in very porous samples, a precursor consisting of small amplitude noise occurred just before the final break. Breakdown fields shown in the data are simply ratios of the impressed voltage at time of failure to the web thickness.

III. Results

(1) Porosity and Grain Size Effects

The dielectric strength is plotted in Fig. 2(*A*) as a function of porosity for three different grain sizes. The ordinates are means of 5 or more values, with bars showing standard deviation. The highest values of strength, from 4 to 5 MV/in., were obtained on 1- to 3-μm 99.5% dense samples. Increase in either grain size or porosity reduced the strength. For samples near theoretical density, including the samples pressed in graphite dies, the data are replotted as a function of grain size in Fig. 2(*B*). A linear relation appears to exist between the breakdown field and the logarithm of the grain size.
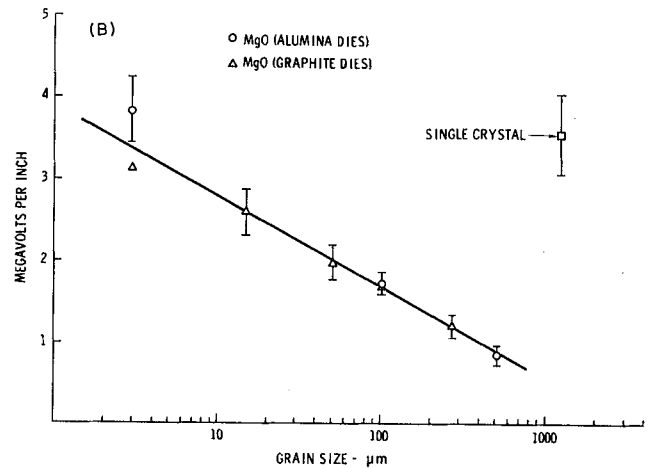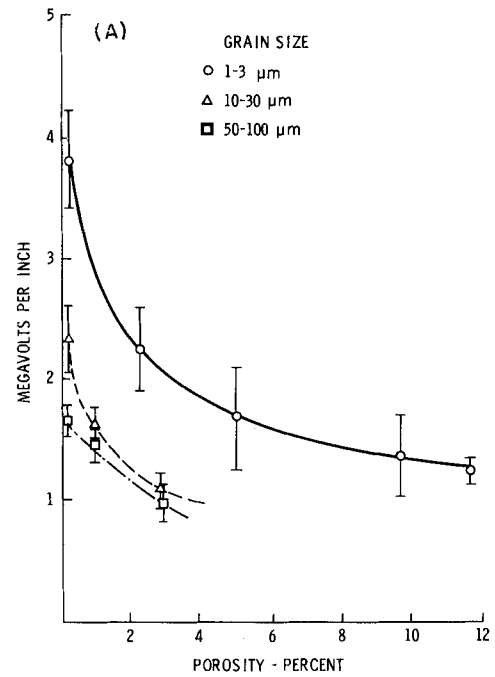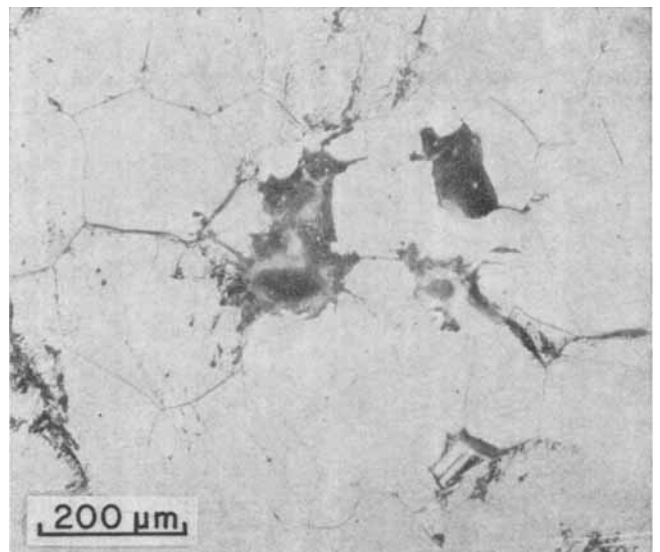
Fig. 3. Breakdown punctures in large-grained polycrystalline MgO.

An indication that the grain boundaries are involved directly in dielectric breakdown was obtained from microscopic examination of large-grained samples after failure. A photomicrograph of one of these samples is shown in Fig. 3. Multiple failures occurred in this sample, with a number of punctures visible. This view is from the plane face of the sample, which was at negative potential during the test. In general, the punctures occurred at grain boundaries and often at three-corner points. This result does not necessarily imply that failure was initiated at the boundaries but merely that it propagated preferentially along the boundaries in the large-grained material.

(2) Dielectric Strength of Single-Crystal MgO

For the initial tests on single-crystal MgO, samples were prepared in the same way as the polycrystalline samples; i.e. by impact grinding and electroding with Ag paint. Breakdown strength values of only 0.98 MV/in. were achieved. Examination of the samples revealed cleavage cracks in the area where breakdown occurred. By chemical polishing in H_3PO_4 to remove 0.010 to 0.015 in. of material inside the cups, a strength value of 4.0 MV/in. was obtained. Breakdown proceeded in straight-line segments in $<110>$ directions in the crystals. These breakdown values are included in Fig. 2(B) to permit comparison with values obtained on polycrystalline samples. The value for the abscissa of the plotted point is the thickness of the web.

(3) Area and Volume Dependence

To investigate the location of the defects responsible for failure, data were taken in which sample volume and area were varied. All samples were hot-pressed under identical conditions to give 0.2% porosity and 1- to 3-μm grain size. The data are given in an extreme-value plot in Fig. 4 as described by Weber and Endicott,[8] who used extreme-value statistics in analysis of breakdown in transformer oil and derived a relation between variation of modal values and sample size. A similar treatment of polymer materials was given by Milton and Wentz.[9] In this analysis, for two sets of samples with volumes V_1 and V_2, the modal values of the breakdown field differ by

$$E_2 - E_1 = 1.797 S_v \log \frac{V_1}{V_2} \qquad (1)$$

where S_v is the standard deviation of E. For a situation where surface defects, rather than volume defects, are responsible for failure, the relation is

$$E_2 - E_1 = 1.797 S_v \log \frac{A_1}{A_2} \qquad (2)$$

If Weber and Endicott's analysis is applied to Fig. 4, for a volume-distributed defect the modal value for the samples 0.5 in. in diameter and 0.03 in. thick would be expected to be 0.42×10^6 V/in. greater than that of the samples 0.5 in. in diameter and 0.050 in. thick. For a defect distributed on the sample surface, no difference is expected, and essentially no difference was observed. Either a volume distribution or a surface distribution predicts a decrease in modal value of 1.1×10^6 V/in. in going from samples 0.5 in. in diameter and 0.50 in. thick to samples 1 in. in diameter and 0.050 in. thick. The observed change was 0.9×10^6 V/in.

IV. Discussion

From the data obtained by Economos[10] on TiO_2, increase in the electrical strength of MgO with decrease in porosity was anticipated. The dependence on grain size was not expected, however, and very few data that would suggest such behavior exist in the literature. Kainarskii *et al.*[11] observed a decrease in dielectric strength with increase in grain size in Al_2O_3; how-
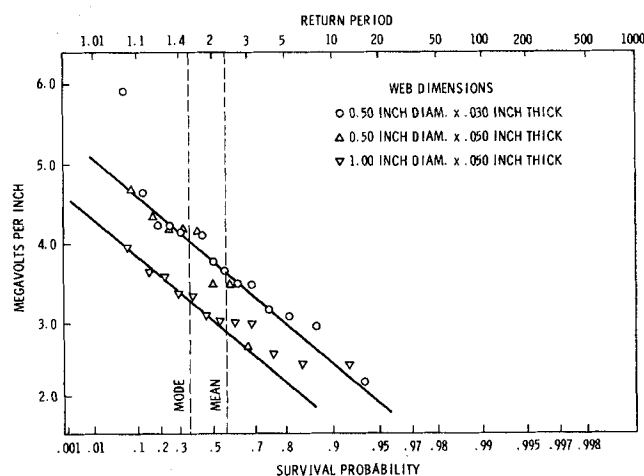

Fig. 4. Extreme-value statistical plot of dielectric strength.

ever, concomitant variations in porosity for samples with different grain sizes might have explained the change.

The data for the polycrystalline samples suggest that the dielectric strength of MgO is determined not by two types of defects associated separately with the presence of pores or grain boundaries but by a single type of defect whose size (in the sense of the local field concentration it produces) is a function of both porosity and grain size. One such defect is the grain-boundary void; its long dimension can be of the order of the grain size, but the probability that it will be that long depends on the porosity of the sample.

One way in which the grain-boundary void might reduce the dielectric strength, particularly if it intersected the sample surface, would be to become contaminated with conductive material. The "field concentration factor" for the resultant "needlepoint conductor" should depend primarily on the radius of curvature at the tip of the void. In this regard, the LiF which was used to promote densification might be regarded as a "contaminant." The decrease in strength with increasing grain size might be explained in terms of an increase in the thickness of the grain-boundary layer as the grain-boundary surface to volume ratio decreased. However, the similarity of the data for the materials with and without LiF argues against such an explanation.

Contamination of a mechanical defect to produce high local fields might also account for the large increase observed in the strength of single-crystal samples when the surface flaws were removed by etching. The field concentration factor at a crack tip might be expected to be even higher than that for a grain-boundary void, since the radius of curvature at the crack tip could be of the order of atomic dimensions. Conceivably, mechanical surface cracks might also be responsible for failure in polycrystalline materials. The role of grain size and porosity might be in determining (1) the ease with which such cracks are produced or (2) the size of the crack, as seems to be the case for mechanical failure.

It may not be necessary to contaminate the grain-boundary void or the crack with conductive material to produce large field concentrations. The void can be made effectively conductive by initiating a discharge in the contained gas. Calculation of the requisite breakdown field presents a very difficult problem. Apparently no data exist on discharge inception voltages in gas-filled voids in ceramics, even for simple void geometries. There are, however, data for breakdown fields in gases between metal electrodes.[12] Furthermore, measurements on a variety of materials containing cylindrical voids[13] indicate that the initiation of a discharge in the void depends, essentially, only on the nature of the gas, its pressure, and the

BREAKDOWN BETWEEN PARALLEL
PLATES IN AIR

—— 1 ATM PRESSURE
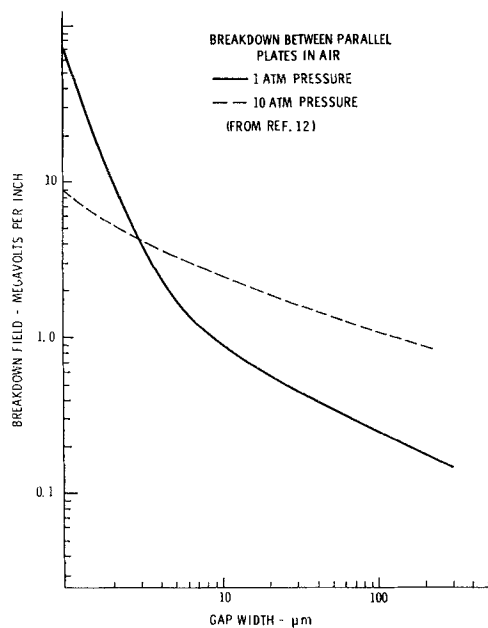
— — 10 ATM PRESSURE

(FROM REF. 12)

Fig. 5. Breakdown field in air as a function of electrode spacing.

geometry of the cavity. The work function and other properties of the enclosing surface are of minor importance. A rough idea of the field necessary to produce a discharge in a void in the ceramic can be obtained by considering the idealized situation of a cylindrical void of length d containing air at standard pressure, p (76 cm Hg). The axis of the cylinder is oriented in the direction of the field, and the radius is large compared with d. Using the curves for the breakdown voltage of air at low pressure in Ref. 12 and assuming that Paschen's law ($V=$ constant for $pd=$ constant) holds for d of the order of 1 μm, the breakdown fields for such a defect were calculated and plotted (Fig. 5) as a function of d; a curve for 10 atm pressure is also included.

It is apparent from the curves that it is not necessary for defects to be very large to result in internal corona at fields much less than the estimated intrinsic strength of the ceramic. At 3 μm a field of 4×10^6 V/in. would be expected to result in failure. Moreover, the possibility of an enhancement of the field inside the void because of the much higher dielectric constant of the ceramic was neglected. With certain geometries, the enhancement could amount to a factor $\varepsilon_{cer}/\varepsilon_{void}$, i.e. almost 10 times the field in the MgO crystallites.

Development of a discharge in a void does not necessarily mean failure of the ceramic. As soon as enough charge is displaced that the field drops below the extinction value, the discharge stops. The noise preceding breakdown in the more porous samples tested may be explained in terms of discharges which were extinguished before the ceramic failed. Consider-

ing the results in plastics,[14] it is not likely that surface damage resulting from the discharge is sufficient to cause failure of the ceramic. It seems much more probable that the redistribution of charge changes the field distribution to the point where the intrinsic strength of the MgO is exceeded locally.

V. Conclusions

(1) Electrical strength of MgO decreases with increase of the porosity and/or grain size. These parameters mutually determine the "size" of the responsible defect. Strengths as high as 5.9×10^6 V/in. were achieved by reducing porosity to 0.5% and grain size to 1 to 3 μm.

(2) Defects are distributed on the sample surface rather than through the volume.

(3) Punctures in polycrystalline MgO propagate primarily along grain boundaries (at least in large-grained samples).

(4) Mechanical surface cracks reduce the electrical strength of single-crystal MgO. Punctures develop primarily in <110> directions.

Acknowledgments

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