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High-temperature electrical breakdown in single crystal and polycrystalline MgO

HIROSHI MURATA, SEUNG CHUL CHOI, KUNIHITO KOUMOTO, HIROAKI YANAGIDA
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113 Japan

Electrical breakdown strengths of single crystal and polycrystalline MgO were measured at 1000 to 1400° C. Temperature and thickness dependences of the breakdown strength of single crystal MgO firmly indicated that the electrical breakdown was of thermal type. A high correlation between the ionic conductivity and the breakdown strength was found, which together with the observed melted track suggested that the electrolytic decomposition took place. The breakdown strength of single crystal MgO decreased with increase in the dislocation density. The breakdown strength of polycrystalline MgO indicated a significant effect of the microstructural factors, though a quantitative evaluation was impossible in the present study.

1. Introduction

Recently MgO has been expected to be applied to an electrical insulator for MHD power generation. Since this system is operated at high temperatures, one of the most serious problems is the thermal degradation of the properties of an insulating material. The data for the electrical breakdown strength at high temperatures are required in this context.

In contrast to the electrical conductivity, few papers on the electrical breakdown of MgO at high temperatures have been published so far. It was reported that the electrical strength of MgO single crystal was $4.0 \times 10^6\,\mathrm{V\,cm^{-1}}$ at room temperature and an increase in either porosity or grain size resulted in a monotonic decrease in strength [1]. But the electrical breakdown mechanism and the effect of microstructure at high temperatures would differ from those at room temperature. Sonder *et al.* [2] showed that the treatment of MgO single crystal under the field of $1000\,\mathrm{V\,cm^{-1}}$ for 100 h or longer above 1300 K caused breakdown. The effect of various kinds of impurity and their concentrations on the electrical breakdown of MgO single crystal at 1473 K was studied by Tsang [3] using an electrical field of $1500\,\mathrm{V\,cm^{-1}}$. It was found that the presence of copper, cobalt or hydrogen suppressed the breakdown, while the presence of iron, nickel, chromium or vanadium enhanced it.

The electrical breakdown mechanism, however, has not been clarified and the role of microstructure in electrical breakdown is apt to be ignored though it is very important for practical applications. The objective of this study was to clarify the electrical breakdown mechanism for undoped MgO at high temperatures and to examine the effects of microstructure on the electrical breakdown strength.

2. Experimental procedure

2.1. Sample preparation

Commercially available MgO single crystal samples of 99.9% purity (Tateho Chemical, Ako, Hyogo, Japan) were cleaved along (1 0 0) planes and polished with diamond paste. The dimensions of the samples were 1.0 cm by 1.0 cm with a thickness of 0.3 to 1.0 mm. Some samples were quenched from 800 to 1100° C in order to change the dislocation density, which was calculated from the number of etch pits formed by a usual chemical etching technique [4].

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Polycrystalline samples were prepared by sintering 99.99% pure MgO powder compacts at 1500° C for 4 h and polished down to 0.5 mm thick. These samples had relative densities of ~95% and the average grain size was approximately 5 μm.

2.2. Ionic and electronic conductivity measurements

For conductivity measurements, three platinum electrodes were attached to a specimen by sputtering, followed by a thicker coating of platinum paste, which was fired at 1000° C in air. Two of the electrodes were for bulk conductivity measurements and one acted as a guard to eliminate possible surface conduction.

The total conductivity was measured at 1000 to 1400° C by the d.c. three-probe method. The ionic transference number was also measured at 1000 to 1400° C by using an oxygen concentration cell arrangement. Platinum perforated sheets were used as electrodes in this case. The sample with the electrodes were sandwiched tightly by magnesia tubes. A mixture of oxygen and argon was blown on one side of the sample and the oxygen partial pressure (P_{O_2}) was measured by a zirconia sensor, while the P_{O_2} on the other side was kept at 10^5 Pa. The e.m.f. which developed across the specimen was measured by an electrometer and the ionic transference number, t_i, was calculated using the following equation:

$$E = \frac{RT}{4F} \int_{P_{O_2(I)}}^{P_{O_2(II)}} t_i \, d\ln P_{O_2} \qquad (1)$$

where E is the e.m.f., R the gas constant, T the absolute temperature, F the Faraday constant and P_{O_2}(I) and P_{O_2}(II) oxygen partial pressures on the two sides of the specimen, respectively.

2.3. Electrical breakdown measurements

Fig. 1 shows a schematic illustration of the apparatus for breakdown measurements at high temperatures. All measurements were made in air and the temperature was measured with a thermocouple (Pt–Pt13Rh) placed near the sample.

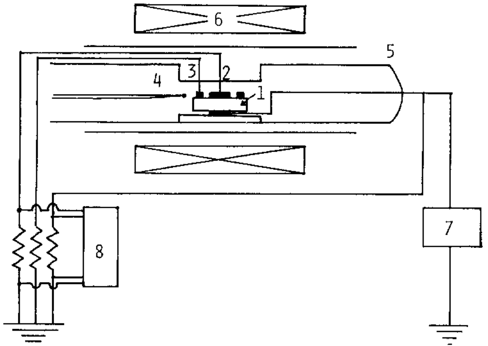

Figure 1 Schematic of the apparatus for the electrical breakdown measurements. 1 – specimen, 2 – electrode, 3 – guard electrode, 4 – thermocouple, 5 – alumina tube, 6 – furnace, 7 – d.c. high voltage supply, 8 – recorder.

To elucidate the electrical breakdown mechanism (of MgO at high temperatures), the (a) temperature and (b) thickness dependences of electrical breakdown were studied for single crystal samples; (a) the sample thickness was fixed at 0.5 mm, then temperature was varied from 1000 to 1400° C (b) the temperature was fixed at 1300° C, then sample thickness was varied from 0.3 to 1.0 mm.

Single crystal samples with different dislocation densities prepared by quenching from 800 to 1100° C to room temperature and polycrystalline samples were also subjected to breakdown measurements to clarify the effect of the microstructure on the breakdown strength.

A stepwise d.c. voltage was applied to a sample using a high voltage supply, while the applied voltage and current were recorded on a strip chart. A typical example of a voltage–current relation is shown in Fig. 2. The breakdown strength was determined from a critical voltage at which the current increased abruptly deviating largely from the Ohmic law (A in Fig. 2).

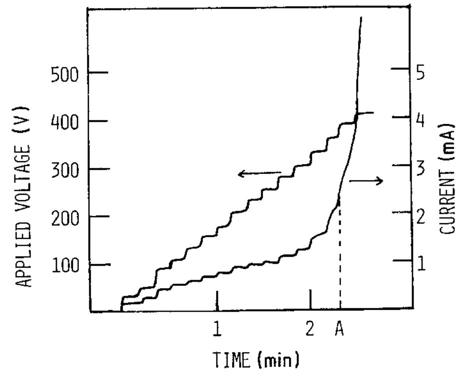

Figure 2 Typical voltage and current curves. A – breakdown point.

3. Results and discussion

3.1. Ionic and electronic conductivities

So far, the electrical breakdown has been discussed only in terms of total conductivity, but for a mixed conductor such as MgO, it is necessary to consider both the ionic and electronic contributions to the electrical breakdown. The total conductivity, σ_t, and ionic transference number, t_i, were measured at 1000 to 1400° C in air. These quantities were used to calculate the ionic conductivity, σ_{ion}, and the electronic conductivity, σ_{elec}, using the equations,

$$\sigma_{ion} = t_i \sigma_t \qquad (2)$$

$$\sigma_{elec} = (1 - t_i)\sigma_t \qquad (3)$$

Mitoff [5] showed that the electronic conduction predominated at high temperatures (> 1300° C) and at high (1 atm) and low ($< 10^{-6}$ atm) oxygen partial pressures. On the other hand, Osburn and Vest [6] indicated that high temperature and high oxygen partial pressure favoured ionic conduction. Fig. 3 shows the total, ionic and electronic conductivities as functions of reciprocal temperature. It is obvious that the electronic conduction predominates at 1000 to 1400° C, which agrees with Mitoff's suggestion.

The ionic conductivity observed probably resulted from magnesium ion transport because the self-diffusion coefficient of magnesium ions ($D = 0.249 \exp[-(79.0/RT)]$) [7] is reported to be much greater than that of oxygen ions ($D = 2.5 \times 10^{-6} \exp[-(62.4/RT)]$) [8]. Sempolinski and Kingery [9] reported that the magnitude of the ionic conductivity was directly proportional to the trivalent solute concentration, while both its magnitude and activation energy were independent of the particular solute used. The calculated activation energy of ionic conductivity for the present sample is 189 kJ mol^{-1} and that of electronic conductivity is 304 kJ mol^{-1}. These data are similar to those reported by Sempolinski *et al.* (185 and 301 kJ mol^{-1} [9, 10], respectively), though both conductivity values are slightly higher in the present sample, the reason of which is not well understood solely from the results of chemical analysis as shown in Table I.

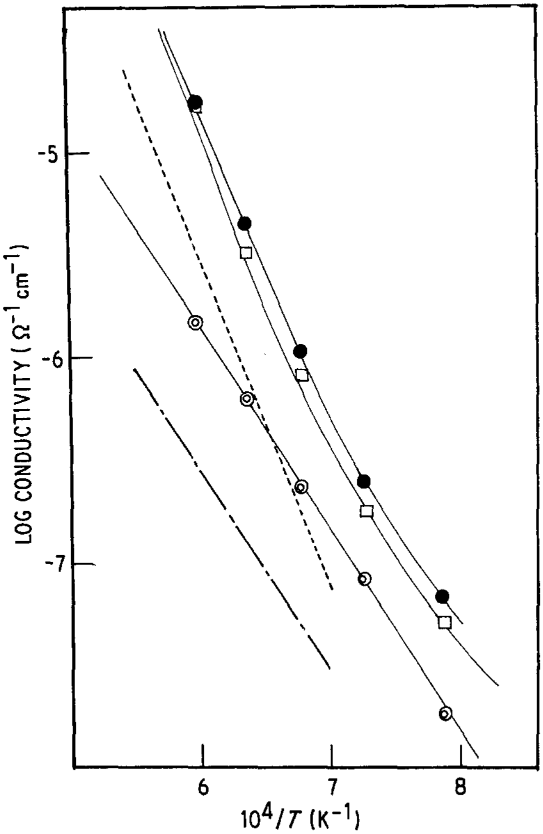

Figure 3 The total, ionic and electronic conductivities of MgO single crystal as functions of reciprocal temperature. ●; σ_t total conductivity, ◎; σ_{ion} ionic conductivity, □; σ_{elec} electronic conductivity, —-—-—; ionic conductivity by Sempolinski and Kingery [9], – – – –; electronic conductivity by Sempolinski *et al.* [10].

3.2. Electrical breakdown mechanism

The electrical breakdown is usually described by three mechanisms: intrinsic, thermal, avalanche types [11–14]. Intrinsic breakdown, which is electronic in nature, occurs in a very short time at low temperatures. The term, "intrinsic", is used because the breakdown strength in this mechanism is independent of the sample or electrode geometry used and of the mode of the applied electric field. Thermal breakdown occurs whenever the Joule heat generated in the sample cannot be extracted fast enough by conduction and convection, so that the sample

TABLE I

Impurity	K	Na	Ca	Al	Fe	Si	S	Cl	F	Cr	V	Mn	Ni	Ti	Zn	B	P	C
ppm	< 5	< 5	< 40	< 15	< 50	< 10	< 5	< 7	< 3	< 10	< 3	< 4	< 3	< 2	< 1	< 5	< 2	< 10

TABLE II

Intrinsic	$\frac{\partial E}{\partial T} > 0$	$\frac{\partial E}{\partial d} = 0$
Thermal	$\frac{\partial E}{\partial T} < 0$	$\frac{\partial E}{\partial d} < 0$
Avalanche	$\frac{\partial E}{\partial T} > 0$	$\frac{\partial E}{\partial d} < 0$

temperature rises until permanent damage occurs. The avalanche breakdown occurs by the avalanche of gradually or sequentially accumulated electrons.

These mechanisms are characterized by the temperature and thickness dependences of the breakdown strength. As shown in Table II, the examination of both $\partial E/\partial T$ and $\partial E/\partial d$ would give us an insight into a predominant breakdown mechanism. Fig. 4 shows the temperature dependence of the breakdown strength for single crystal MgO, indicating that the breakdown strength decreases monotonically with increase in temperature ($\partial E/\partial T < 0$). Fig. 5 shows the thickness dependence of the breakdown strength measured at 1300° C and confirms the relation $\partial E/\partial d < 0$. These two observations would definitely lead us to the conclusion that the electrical breakdown in MgO is of thermal type. There are some other observations which might support our conclusion; (1) after breakdown a circular melted track of 100 μm in diameter, as shown in Fig. 6, is always left between the two electrodes (not an edge effect) and (2) the application of d.c. electric field of 1000 V cm^{-1} at temperatures > 1300 K for a period of 100 h or longer resulted in breakdown of MgO single crystal [2].

The conditions for thermal breakdown can be

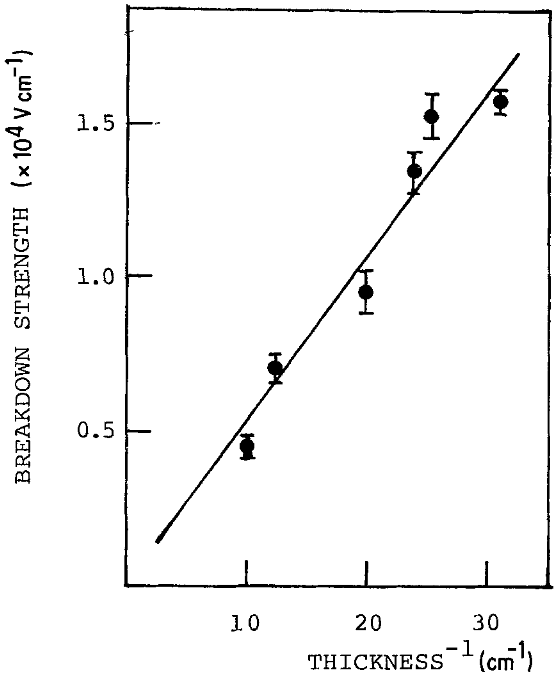

Figure 5 Thickness dependence of electrical breakdown strength of MgO single crystal at 1300° C.

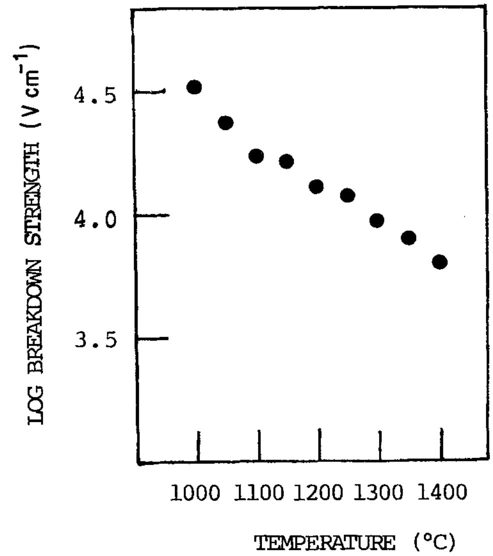

Figure 4 Temperature dependence of electrical breakdown strength of MgO single crystal. Samples used were all 500 μm thick.

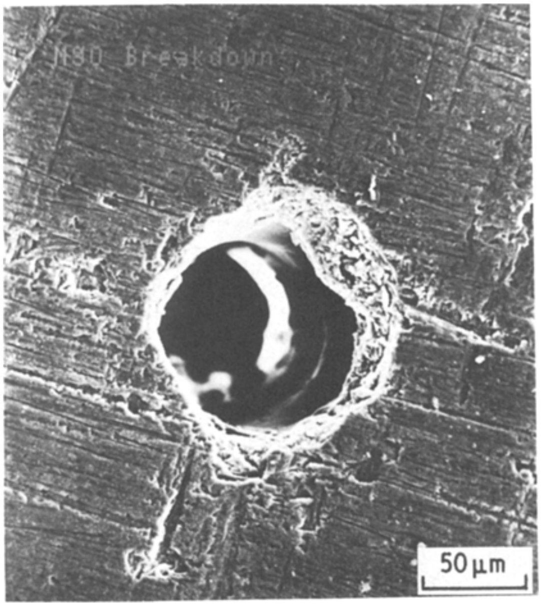

Figure 6 Scanning electron micrograph of a breakdown track.

described by a heat-balance equation [11–14],

$$C_v(\mathrm{d}T/\mathrm{d}t) - \mathrm{div}(\kappa\ \mathrm{grad}T) = \sigma \mathbf{E}^2 \quad (4)$$

where C_v is the specific heat, κ the thermal conductivity, σ the electrical conductivity and $\mathbf{E}$ the electric field. In the case where the lattice processes are almost in a steady state, the time dependent term in Equation 4 vanishes, and then

$$-\mathrm{div}(\kappa\ \mathrm{grad}T) = \sigma \mathbf{E}^2 \quad (5)$$

If there is no charge accumulation, the current is continuous;

$$\mathrm{div}\,\mathbf{E} = 0 \quad (6)$$

The electrical conductivity is described as;

$$\sigma(T) = \sigma_0 \exp(-\phi/kT) \quad (7)$$

where σ_0 and ϕ are the constants and the thermal conductivity as

$$\kappa(T) = \kappa_0 \quad (8)$$

since κ of MgO can be approximated to be constant from 1000 to 1400° C [15]. Combining Equations 5 to 8, the following equation is obtained

$$\mathbf{E}_c \approx \frac{1}{d}\left(\frac{8\kappa_0 k T^2}{\sigma_0 \phi}\right)^{1/2} \exp(\phi/2kT) = C\frac{1}{d}\left(\frac{T^2}{\sigma(T)}\right)^{1/2} \quad (9)$$

where $\mathbf{E}_c$ is the critical electric field (the electrical breakdown strength), d the sample thickness and C a constant. Equation 9 indicates that the electrical breakdown strength is reciprocally proportional to the thickness, and decreases with increase in temperature since the change in $\sigma(T)$ with temperature is usually much greater than that in T^2 in the range of 1000 to 1400° C. The results shown in Figs. 4 and 5 are well explained by Equation 9.

If the sample thickness is kept constant, Equation 9 can be transformed into the

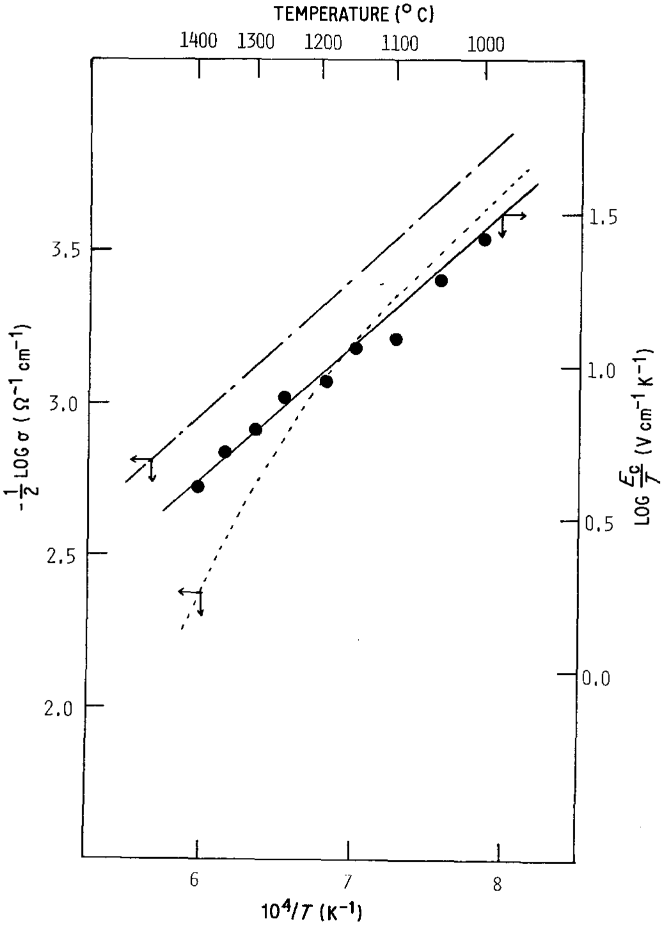

Figure 7 Relation between ionic or electronic conductivity and electrical breakdown strength. See the text for discussion. ●——; electrical breakdown strength, — · — · —; ionic conductivity, - - - - -; electronic conductivity.

following logarithmic equation;

$$-\tfrac{1}{2}\log\sigma = \log\frac{E_c}{T} + C' \qquad (10)$$

where C' is a constant. Equation 10 shows the relationship between the electrical conductivity and the electrical breakdown strength. To examine which conductivity, ionic or electronic, is more effective to the electrical breakdown, σ in Equation 10 was divided into σ_{ion} and σ_{elec}. Fig. 7 shows the plots of $-\frac{1}{2}\log\sigma_{\text{ion}}$, $-\frac{1}{2}\log\sigma_{\text{elec}}$ and $\log E_c/T$ against $1/T$, respectively, according to Equation 10. The slope of the electrical breakdown strength ($\log E_c/T$) is seen to be similar to that of ionic conductivity ($-\frac{1}{2}\log\sigma_{\text{ion}}$). This suggests that the electrical breakdown of MgO (thermal-type) is closely related to ionic conduction rather than electronic conduction. At present it is not obvious why the thermal breakdown is related to the ionic conductivity which is lower than the electronic conductivity. One possible reason may be associated with the assumption that the chemical reaction like "electrolytic decomposition" occurred after Joule heat generation, as could be judged from the fact that a melted track is always observed after breakdown.

3.3. Effects of microstructure on electrical breakdown

To clarify the effect of the microstructure on the breakdown strength, single crystal samples with different dislocation densities and polycrystalline samples were also subjected to breakdown measurements.

The effect of dislocation has not been studied so far. The samples quenched from 800 to 1100° C were etched in HNO_3 for 15 min. The etch pit density was assumed to be equal to the dislocation density. The dislocation density of the as-received single crystal was $\sim 1 \times 10^6\,\text{cm}^{-2}$, that of the sample quenched from 800° C was $\sim 3 \times 10^6\,\text{cm}^{-2}$ and that of the sample quenched from 1100° C was $\sim 7 \times 10^6\,\text{cm}^{-2}$. The electrical breakdown measurements of these samples were made at 1300° C (the sample thickness was fixed at 0.5 mm). As seen in Table III, the electrical breakdown strength decreases with increasing dislocation density. Since the breakdown mechanism is assumed to be unchanged and the ionic conduction is more effective to the breakdown strength in MgO as discussed in the previous section, the decrease in breakdown strength is considered to be due to the acceleration of ionic conduction along dislocations.

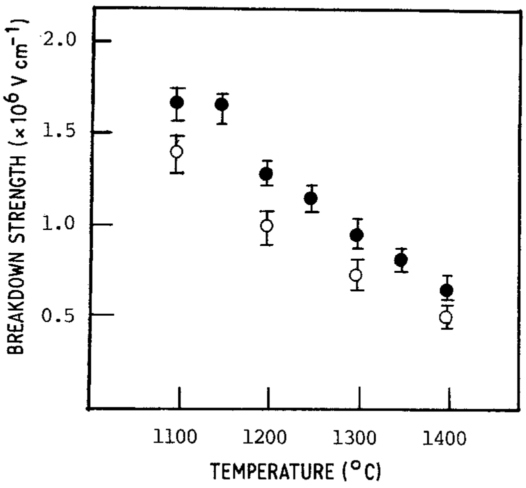

Figure 8 Comparison of the electrical breakdown strengths of polycrystalline samples with those of single crystal samples (at 1300° C). ●; single crystal, ○; polycrystalline.

The electrical breakdown strengths of polycrystalline samples were also measured at 1300° C (the sample thickness was fixed at 0.5 mm). Fig. 8 shows the comparison of the electrical breakdown strengths of polycrystalline samples with those of single crystal samples, indicating that the breakdown strengths of polycrystalline samples are lower. The structural factors to determine the breakdown strength of a polycrystal are considered to be grain-boundary, dislocation and pore. It was already suggested above that the presence of dislocations leads to an increase in ionic conductivity and hence a

TABLE III

	As-received	Quenched from 800° C	Quenched from 1100° C
Dislocation density (cm^{-2})	$\sim 1 \times 10^6$	$\sim 3 \times 10^6$	$\sim 7 \times 10^6$
Electrical breakdown strength (V cm^{-1})	9.6×10^3	8.5×10^3	5.6×10^3

decrease in breakdown strength. Osburn and Vest [6] reported that the ionic conductivity of MgO was greater at the grain-boundary than in the bulk. If this is also the case in our samples, the grain-boundary would be one of the factors to decrease the breakdown strength. Also the role of pores cannot be neglected as all the samples had ~5% porosity. Generally, it is expected that the electrical breakdown strength decreases with increase in porosity.

Unfortunately, the size of the melted track (0.1 mm in diameter) was too large to determine the breakdown path, so that it is still ambiguous which structural factor predominantly affects the electrical breakdown of polycrystalline MgO. Systematic changes in microstructure will be necessary to further elucidate the microstructural effect on the breakdown.

4. Conclusions

The following conclusions can be drawn from the present study;

1. Electrical breakdown mechanism for MgO at high temperatures is of thermal type closely related to the ionic conduction.
2. Dislocations accelerate the ionic conduction and hence decrease the electrical breakdown strength of MgO.
3. The electrical breakdown strength of polycrystalline MgO is lower that that of a single crystal. The microstructural effect should be subject to further investigation.

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