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Electrical conductivity of hot-pressed AlN ceramic: effect of various oxide additives

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The paper describes the effect of the addition of 1 mol% of various oxide additives (MgO, BeO and Y_2O_3) on the electrical conductivity of hot-pressed AlN ceramic in the temperature range 500 to 950 K. It is observed that the electrical conductivity increases quite appreciably at all temperatures, in the above temperature range, when these oxides are added to AlN. The effect of moisture has also been studied for all the samples. The moisture affects the conductivity appreciably only when the porosity is more than 6%. However, in the case of Y_2O_3 additive, no moisture effect is observed even at higher porosity (11.5%). The results have been explained in terms of closed and open porosity in these samples.

1. Introduction

Recently, AlN ceramic prepared at high temperature has drawn great attention due to its inertness to hot and cold mineral acids and alkali solution [1]. The mechanical properties of this material have been studied in detail [2–8] and it is now well established that AlN has a very good thermal shock resistance along with very high oxidation resistance in air. All these properties of AlN make this material suitable for refractory applications and components in heat engines operating at very high temperatures.

Apart from its mechanical properties, the electrical properties of AlN seem to be quite important as it is reported that AlN can be used as a high-temperature dielectric [9–11]. A closer examination of the literature reveals that no systematic study of the electrical conductivity of hot-pressed AlN ceramics has been made in spite of the importance of these measurements to check the insulating ability at high temperatures. We have, therefore, started a project to study the electrical properties of hot-pressed AlN ceramic having different porosity values and various oxide additives in our laboratory.

In our earlier communication [12] we reported the effect of porosity on the electrical conductivity of hot-pressed AlN ceramic. In another communication [13] we have also reported the effect of CaO additive on the electrical conductivity of hot-pressed AlN ceramics having different mole percentages of CaO.

The aim of the present work is to study the effect of adding various other oxide additives (MgO, BeO, Y_2O_3) on the electrical conductivity of hot-pressed AlN ceramic. A low concentration (1 mol%) of these additives has been used for this study. As electrical conductivity depends upon porosity [12], we have chosen samples having porosities close to each other. The porosity varies from 9.0 to 11.5% only.

The electrical conductivity has been studied, in a vacuum of about 10^{-2} torr, as a function of temperature in the temperature range 500 to 950 K after annealing the samples at high temperatures ($\sim$ 800 K) for one hour in the same vacuum.

The effect of moisture on electrical conductivity has also been studied for all samples by keeping the annealed samples in air for a known time period and then studying the electrical conductivity again but without annealing in this case.

2. Experimental details

2.1. Samples

Hot-pressed samples of AlN with and without additives of MgO, BeO and Y_2O_3 were obtained from the Laboratoire de Ceramique Nouvelles, Université de Limoges (France). These samples were in the form of pellets (diameter $\sim$ 1.5 cm, thickness $\sim$ 0.5 cm). These pellets were prepared by applying a pressure of $\sim$ 20 MPa for 30 min at a temperature around 1700° C. The samples were found to have porosity values as indicated in Table I. Commercial grade AlN powder (Koch-Light, UK) (99% pure having grain size < 50 μm) was used for preparing hot-pressed samples of AlN with and without additives. Though the X-ray diffraction of AlN powder contained diffraction peaks of AlN only, a neutron activation analysis of the powder confirmed the presence of 2.7% oxygen [4]. It is believed [5] that the oxygen exists in the powder of AlN as an oxide film of non-crystalline Al_2O_3. When heated to high temperatures of about 1700° C, Al_2O_3 reacts with AlN and forms another phase, AlON, which is evidenced by X-ray diffraction [5, 11]. When oxides (MgO and Y_2O_3) are added to AlN before hot-pressing, X-ray diffraction shows the absence of an AlON phase, and new phases [5] as indicated in Table I appears in hot-pressed samples of AlN. Data from X-ray diffraction for a sample containing BeO is however not available.

2.2. Conductivity measurements

For electrical conductivity measurements, the pellets were locked between steel electrodes of the same diameter inside a metallic sample holder where a

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TABLE I Characterization of hot-pressed samples of AlN with and without additives

Sample No.	Nature of additive (1 mol %)	Porosity (vol %)	Nature of the secondary phases [5]
1	–	9.0	AlON
2	MgO	11.0	$MgAl_2O_4$
3	BeO	11.0	–
4	Y_2O_3	11.5	$2Y_2O_3 \cdot Al_2O_3$ $3Y_2O_3 \cdot 5Al_2O_3$

TABLE II Electrical parameters for hot-pressed samples of AlN with and without additives

Sample No.	Nature of additive (1 mol %)	ΔE (eV)	Conductivity at 650 K (Ω^{-1} cm^{-1})	σ_0 (Ω^{-1} cm^{-1})
1	–	1.32	1.3×10^{-13}	2.2×10^{-3}
2	MgO	1.02	2.2×10^{-11}	1.8×10^{-3}
3	BeO	1.08	6.5×10^{-12}	1.5×10^{-3}
4	Y_2O_3	1.18	1.7×10^{-12}	2.3×10^{-3}

vacuum of about 10^{-2} torr was maintained in the entire temperature range. Temperature was recorded using a chromel–alumel thermocouple mounted very near to the sample. A heating rate of about 2 K min^{-1} was maintained for the temperature dependence of conductivity measurements.

For resistance measurement, a d.c. voltage of 30 V was applied across the sample and the resulting current was measured by a digital pico-ammeter (Achme, Model SD-100, Kampur).

Uncoated pellets were preferred so to avoid electrode migration into the sample at high temperatures. A small error due to non-uniform contact may not change the conclusions of the present work significantly, as all the samples were studied under the same experimental conditions.

For annealing, the samples were mounted inside the sample holder and the temperature was varied slowly to 800 K in a vacuum of about 10^{-2} torr. After annealing the sample for one hour, they were cooled to room temperature inside the sample holder in the presence of the same vacuum. The temperature was again raised slowly to measure conductivity as a function of temperature.

The effect of moisture was studied by keeping the sample in an open container in air having no significant pollution and a mean relative humidity of 65% for about a month. The conductivity was again measured in the presence of a vacuum of about 10^{-2} torr but without annealing in this case.

3. Results and discussion

3.1. Electrical conductivity in the annealed state

Fig. 1 shows the temperature dependence of electrical conductivity (σ) for hot-pressed samples of AlN with and without additives (1 mol %) of MgO, BeO and Y_2O_3. These measurements were made after annealing the samples in a vacuum.

It is clear from Fig. 1 that the plots of ln σ against $1000/T$ are straight lines showing the presence of an activated process for electrical conduction. The conductivity can, therefore, be written as

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (1)$$

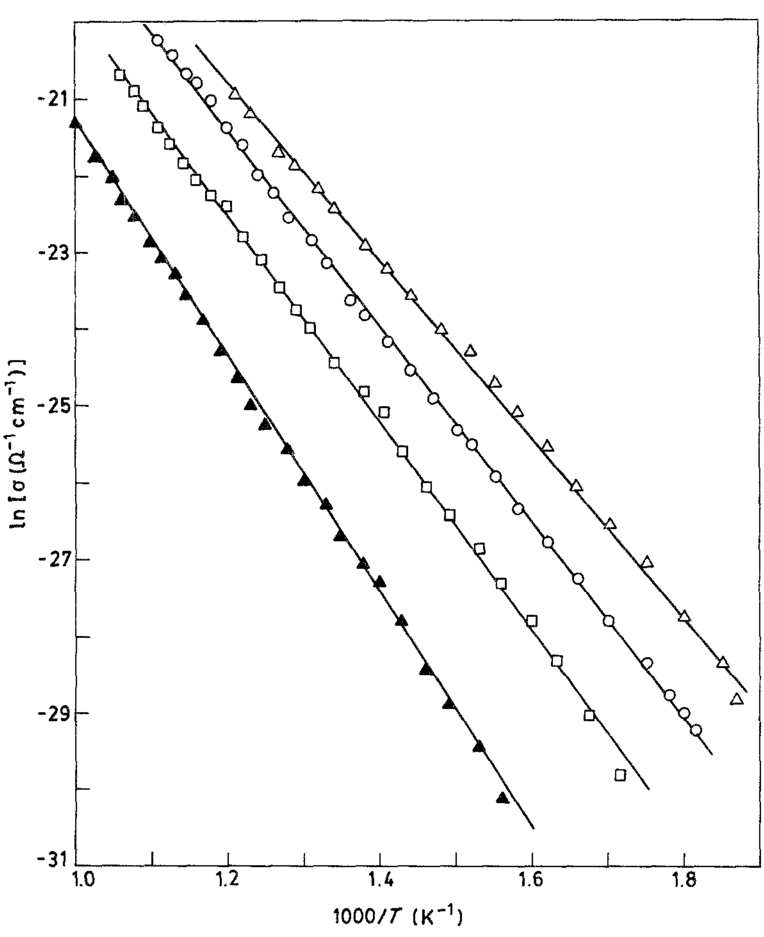

Figure 1 Temperature dependence of conductivity of hot-pressed samples of AlN with and without additives in the annealed state. (▲) Pure AlN, (△) AlN + 1% MgO, (○) AlN + 1% BeO, (□) AlN + 1% Y_2O_3.

where ΔE is the activation energy for electrical conduction and k is Boltzmann's constant.

For all the four samples studied, the values of ΔE and σ at a particular temperature (650 K) are given in Table II. The same table also contains the values of σ_0 calculated from Equation 1.

It is clear from Table II that the conductivity increases and the activation energy decreases as 1 mol % of MgO, BeO or Y_2O_3 is added to AlN. The maximum effect is found in the case of MgO additive, where a change of two orders of magnitude has been observed (see Table II). Though this table contains the conductivity values at 650 K only, Fig. 1 reveals that the conductivity increases with additives in the entire range of temperature (500 to 950 K).

In Section 2.1 we have already mentioned that hot-pressed samples contain secondary phases. Table I shows that in the case of additives, the secondary phases are quite different from those in a pure AlN sample. An increase in conductivity after putting in additives cannot be understood in terms of these phases, as they are more insulating than the AlON which is present in pure AlN.

Porosity is another important parameter on which conductivity may depend. However, Table I shows that the porosity of the samples with additives is more than for a pure AlN sample. An increase in porosity will decrease the conductivity as observed by us in the case of hot-pressed samples of AlN [12]. An increase in conductivity with additives cannot therefore be understood in terms of porosity.

Francis and Worrell [14] studied the high-temperature electrical conductivity in polycrystalline AlN in the temperature range 700 to 1000° C and found that electrical conduction was electronic in nature and the ionic transport number was virtually zero. They also found the conductivity to vary exponentially with temperature with a single activation energy, as observed by us in annealed samples.

The temperature dependence of electronic conductivity in hot-pressed samples of AlN, following Equation 1, is evidence that the conduction in AlN is similar to that in crystalline semiconductors.

An increase in conductivity by one to two orders of magnitude with a corresponding decrease in the activation energy (see Table II) indicates a doping-type behaviour similar to that of crystalline semiconductors. The presence of these additives might increase the concentration of charge carriers and the Fermi level may change. If this is so, then the prefactor (σ_0) in the conductivity expression (Equation 1) should not change after adding these additives. Table II confirms this statement. This table shows that σ_0 does not change significantly after putting in the additives. In our earlier study, a similar type of doping effect was also observed [13] at a low concentration (0.5 mol %) of CaO. We found [13] that the value of σ_0 did not change significantly but the conductivity increased quite appreciably with a corresponding decrease in activation energy when 0.5 mol % CaO was added to AlN before hot-pressing.

The above discussion shows that the behaviour of AlN hot-pressed samples is similar to that of crystalline semiconductors. One may, therefore, call this material a high-temperature semiconductor having a large band gap and a small conductivity at room temperature.

3.2. Effect of moisture

The effect of moisture on the electrical conductivity of hot-pressed samples of AlN with and without additives of MgO, BeO and Y_2O_3 was studied by keeping the samples in air (relative humidity 65%) for a long time (about 1 month) and measuring the variation of conductivity with temperature without annealing them. Figs 2 to 4 show the results of the above study where the conductivity before and after moisture exposure is plotted against the inverse of temperature.

It is clear from these figures that the conductivity behaviour is different in the annealed and moisture states for samples of pure AlN and with additives of MgO and BeO. However, in the case of Y_2O_3 additive, no moisture effect was observed (results not shown).

In our earlier study [12] of the effect of moisture exposure on electrical conductivity for various samples of hot-pressed AlN ceramic having different percentages of porosity, we found that the moisture affects the conductivity only when the porosity increases to more than 6%. This was explained in terms of closed and open porosity of the sample. Below 6% porosity, the samples of AlN have mostly closed porosity [4]. At a higher percentage of porosity, AlN samples contain mostly open porosity [4]. This is the reason why moisture affects the conductivity appreciably only above 6% porosity, when the porosity is mostly open porosity and moisture can be absorbed in the pores.

Since our samples in the pesent study contain a porosity of more than 6% (see Table I), the effect of moisture can be understood in terms of open porosity as described above. Water vapour may be absorbed by the open pores and the conductivity therefore increases. As the sample is heated to higher temperatures, the water comes out of the pores and the conductivity therefore decreases after annealing at higher temperatures. As the water comes out of the pores at different temperatures, the conductivity, unlike the case of annealed samples, does not increase exponentially with a single activation energy. If the absorption of water vapour is greater, the conductivity may also show a maximum with temperature. We have observed such a maximum in the case of BeO additive where a maximum effect of moisture is observed.

No irreversible changes were observed after moisture exposure, as after annealing for one hour again the sample returns to its original annealed state. The difference in the conductivity at high temperatures may be due to the slightly higher heating rate.

It is interesting to note that the sample containing Y_2O_3 additive does not show (results not shown) any appreciable effect of moisture exposure, though it has the highest porosity (11.5%) among the samples studied here. This shows that porosity might be of a closed nature in this sample. The reason for this behaviour with Y_2O_3 additive is, however, not clear from these measurements.

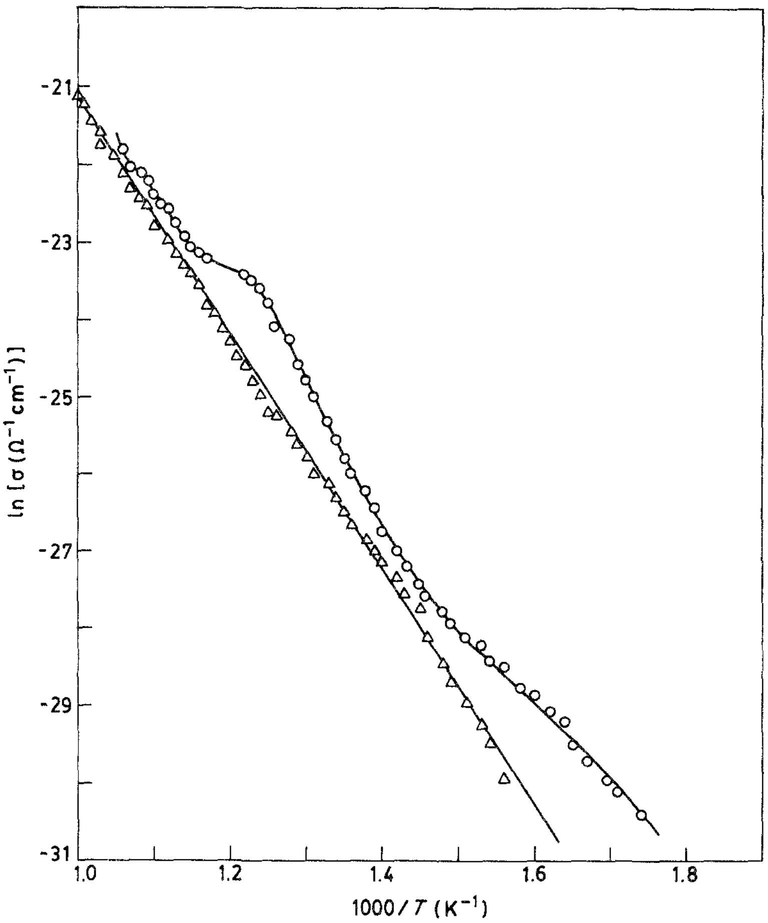

Figure 2 Temperature dependence of conductivity of hot-pressed sample of pure AlN (△) in the annealed state and (○) after exposure to moist air.

4. Conclusions

The temperature dependence of electrical conductivity has been studied for hot-pressed samples of AlN with and without additives of MgO, BeO and Y_2O_3. The effect of moisture has also been studied on the same samples. The following conclusions are drawn:

1. The electrical conductivity of hot-pressed AlN ceramic is quite small below 650 K. The conductivity

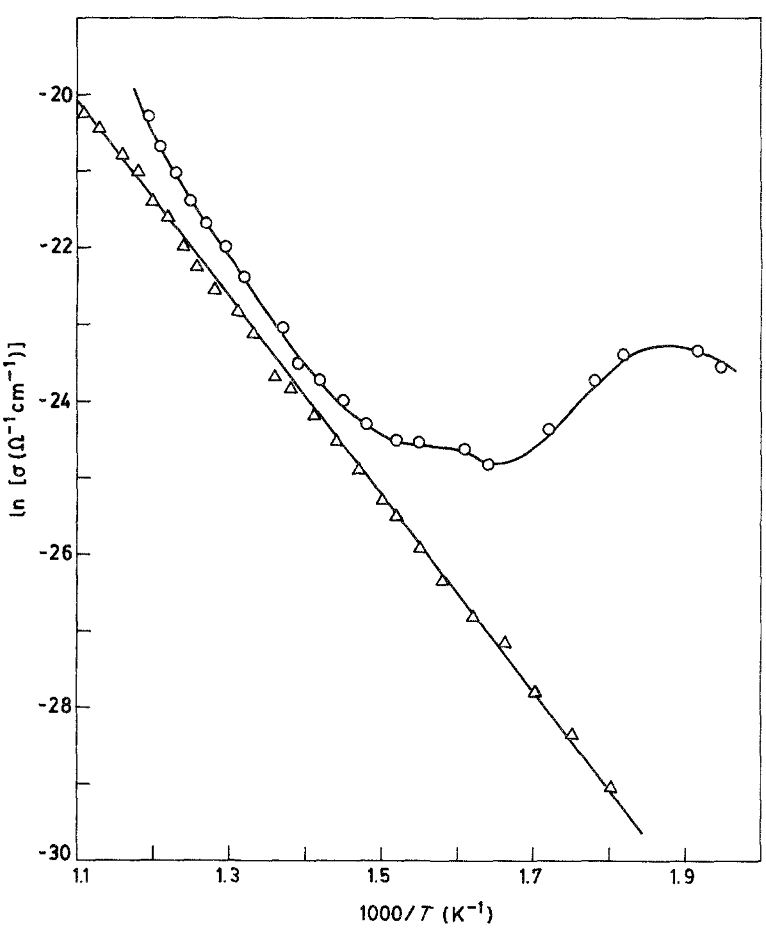

Figure 3 Temperature dependence of conductivity of a hot-pressed sample of AlN with 1 mol % of BeO (△) in the annealed state and (○) after exposure to moist air.

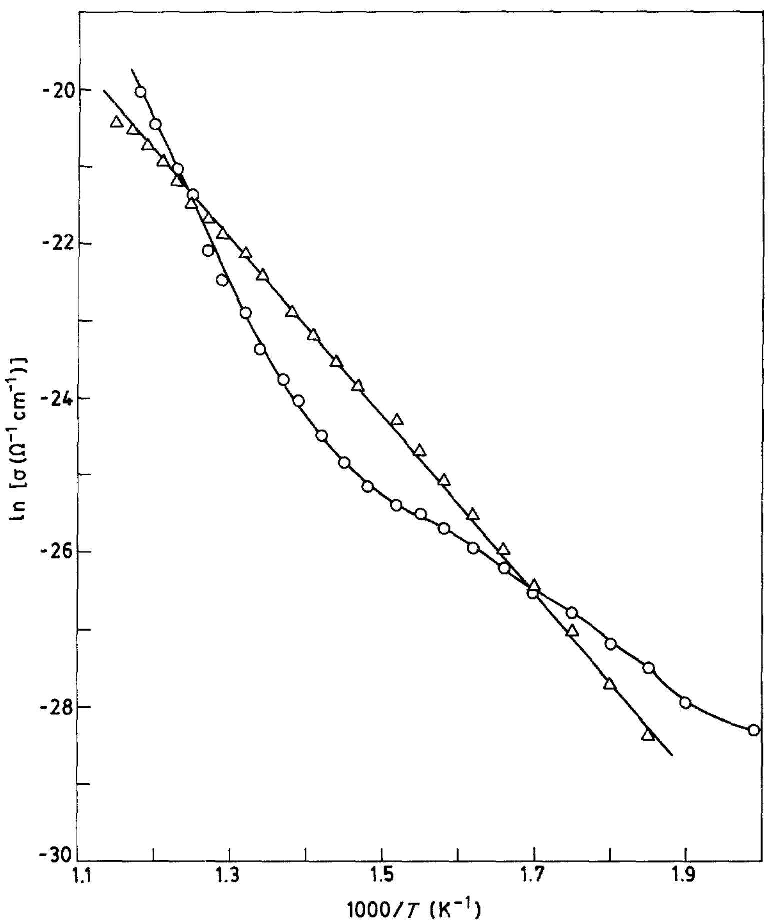

Figure 4 Temperature dependence of conductivity of a hot-pressed sample of AlN with 1 mol % MgO (△) in the annealed state and (○) after exposure to moist air.

increases exponentially with a single activation energy and at higher temperatures (around 950 K), an appreciable conductivity is observed.

2. The electrical conductivity increases quite appreciably when a small percentage (1 mol %) of MgO, BeO and Y_2O_3 are added to AlN before hot-pressing. The maximum effect was observed in the case of MgO additive where an increase of two orders of magnitude is observed.

3. The increase in conductivity with a corresponding decrease in activation energy for d.c. conduction, without having an appreciable effect on σ_0, suggests that the effect adding these additives is similar to the doping effects in semiconductors.

4. The samples of AlN with and without additives of MgO and BeO show an appreciable effect of moisture absorption. However, the sample containing Y_2O_3 does not show an appreciable effect of moisture absorption though it had the largest porosity (11.5%). This behaviour suggests a different kind of porous structure in the case of Y_2O_3 additives.

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References

1. J. A. KOHN, P. G. COTTER and R. A. POTTER, *Amer. Miner.* **41** (1956) 355.
2. K. M. TAYLOR and C. LENIE, *J. Electrochem. Soc.* **107** (1960) 308.
3. C. DEVIN, J. JARRIGE and J. MEXMAN, *Rev. Int. Hautes Temp. Refrac.* **19** (1982) 325.
4. P. BOCH, J. C. GLANDUS, J. JARRIGE, J. P. LECOMPTE and J. MEXMAN, *Ceram. Int.* **8** (1982) 34.
5. M. BILLY, J. JARRIGE, J. P. LECOMPTE, J. MEXMAN and S. YEFSAH, *Rev. Chimie Miner.* **19** (1982) 673.
6. O. YAMADA, M. SHIMADA and M. KOIZUMI, *J. Soc. Mater. Sci.* (*Jpn*) **32** (1983) 1269.
7. Yu G. TKACHENKO, V. K. YULGUGIN and T. V. DUBOVIK, *Sov. Powder Metall. Met. Ceram.* (*USA*) **22** (1983) 405.
8. V. F. LITVINENKO, T. V. DUBOVIK and N. S. ZYTKEVICK, *ibid.* **22** (1983) 490.
9. K. H. TAYLOR and L. CAMILLE, *J. Electrochem. Soc.* **4** (1960) 308.
10. T. U. ANBREEVA and T. V. DUBOVICK, *Dielectriki Poluprouodniki* **6** (1974) 31.
11. A. KUMAR, J. P. LECOMPTE and A. MOLITON, *Rev. Phys. Appl.* **17** (1982) 285.
12. M. ZULFEQUAR and A. KUMAR, *ibid.* **21** (1986) 525.
13. *Idem, J. Mater. Sci. Lett.* **5** (1986) 1230.
14. R. W. FRANCIS and W. L. WORRELL, *J. Electrochem. Soc.* **121** (1974) 103C.

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