JOURNAL OF MATERIALS SCIENCE 25 (1990) 2861–2865

Dielectric behaviour of hot pressed AlN ceramic exposed to inorganic acid vapours

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Dielectric behaviour of hot pressed AlN ceramic is studied before and after exposing the samples to inorganic acid (HCl and HNO_3) vapours with a specific aim to study the effect of these vapours on the dielectric constant (ε') and dissipation factor (tan δ). Four samples having different volume percentage of porosity (0.2 to 15%) are selected for this study. Dielectric dispersion increases after exposing the samples to the above acid vapours. Tan δ also increases quite appreciably; the increase being more at higher porosity. Recovery studies show that the exposure effect is reversible. The exposure time dependence of ε' and tan δ indicates that these parameters show a maxima at a particular exposure time. However, no such maxima is observed in the gravimetric measurements. The increase in dielectric parameters after exposure to acid vapours is explained in terms of the ionic conduction due to the dissociation of these vapours in the presence of moisture. The porosity dependence of this effect is discussed in terms of closed and open porosity reported by other workers.

1. Introduction

AlN is regarded as a useful engineering ceramic material because of its excellent mechanical properties at high temperatures. This material is quite stable [1] and is inert to hot and cold mineral acids and alkali solutions [2]. The mechanical properties of this material have been studied in detail [3–8] 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.

The electrical and dielectric properties of AlN are quite important as it can be used as a high temperature dielectric. A systematic study of these properties of hot pressed AlN ceramic has already been made in our laboratory [9, 10]. The effect of moisture has also been reported by us [11].

The interaction of a ceramic material with its environment is clearly of vital importance as these materials are used as a material of construction outdoors. The corrosion studies of these materials are also important if they are used as substrate or dielectric material for electronic equipment used outdoors. The corrosion studies have been performed in details [12] for various ceramic materials but such studies have not been reported in case of AlN ceramic. We have, therefore, started a systematic study of corrosion in case of AlN hot pressed samples in our laboratory.

The aim of the present paper is to report the effect of hydrochloric acid and nitric acid vapours on the dielectric behaviour of hot pressed AlN ceramic having different volume percentage of porosity (0.2–15 vol %). The two types of measurements are performed on the exposed samples. The frequency dependence of dielectric constant (ε') and dissipation factor (tan δ) is studied at room temperature after exposing the samples for different exposure times. Gravimetric measurements are made after each exposure.

2. Experimental details

Hot-pressed samples of AlN having different volume percentage of porosity were obtained from the Laboratorie de ceramique Nouvelles, Université de Limoges, France. These samples were prepared using commercial powder of AlN (99% pure; grain size, less than 50 μm) obtained from Koch Light, U K. Hot-pressing was done by applying a pressure of about 20 MPa for about 30 min at temperatures between 1773 and 1973 K. The samples were in the form of pellets (diameter $\sim$ 1.5 cm; thickness 0.5 cm) and had a porosity of 0.2–15 vol %. The porosity of each hot-pressed sample was calculated by measuring the density of the pellet with a Doultan mercury densitometer.

The samples were exposed to the vapours of 1 N solutions of analytical grade HCl and HNO_3 inside a desiccator of 3 l capacity, in which 500 ml of solution was kept. The samples were positioned on a porcelain disc with holes in it, in such a way that they were open to the vapour phase. The lid was tightly placed and was opened only for sufficient time to pick up the sample for testing.

Dielectric measurements were made by mounting the samples sandwiched between two steel electrodes (diameter $\sim$ 1.5 cm) inside a metallic sample holder. Three terminal measurements were made to avoid stray capacitances by grounding the sample holder. A GR-1620 AP capacitance measuring assembly was used to measure the capacitance and the dissipation

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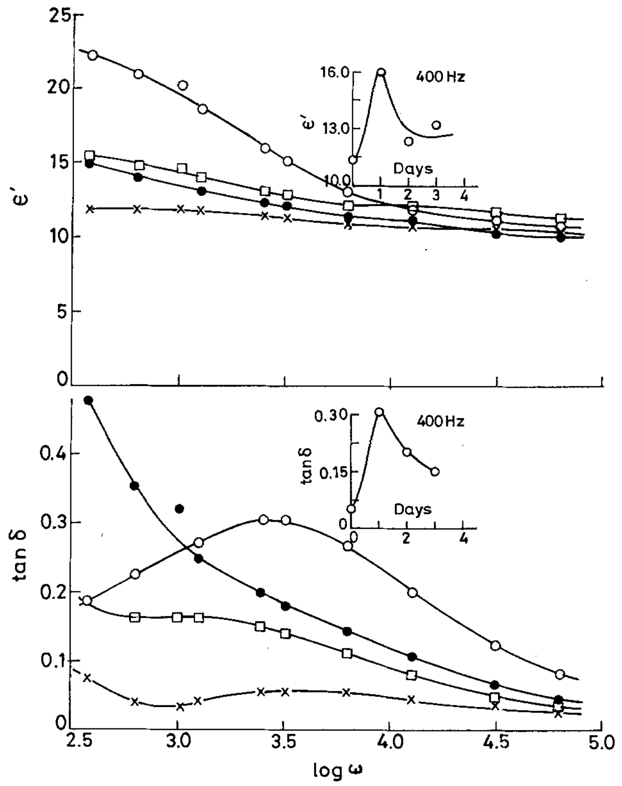

Figure 1 Frequency dependence of ε′ and tan δ at room temperature for initial and HCl vapour exposed AlN sample (porosity 0.2 vol %). Inset shows the exposure time dependence of ε′ and tan δ. (x) Initial state; (○) 1 day; (●) 2 days; (□) 3 days.

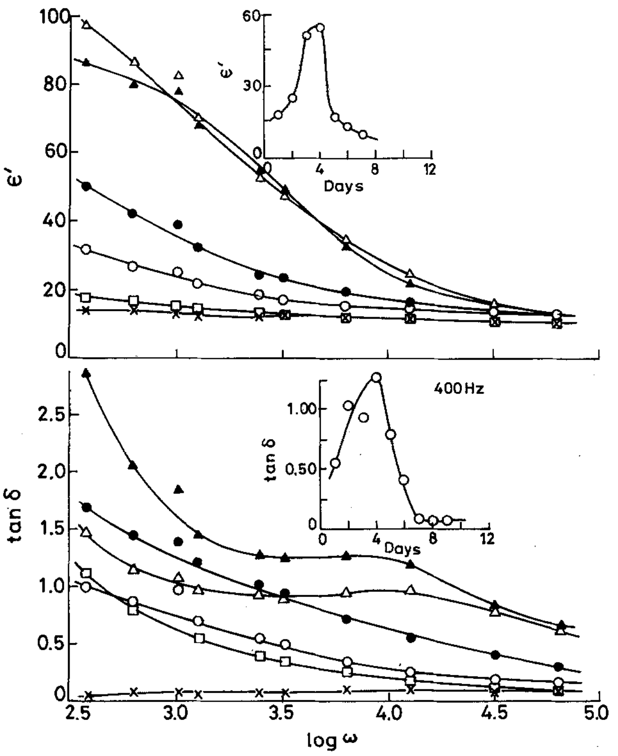

Figure 3 Frequency dependence of ε′ and tan δ at room temperature for initial and HNO_3 vapour exposed AlN sample (porosity 0.2 vol %). Inset shows the exposure time dependence of ε′ and tan δ. (x) Initial state; (○) 1 day; (●) 2 days; (△) 3 days; (▲) 4 days; (△) 5 days.

factor. The instrument was used in the parallel capacitance mode where parallel conductance could be measured directly. The values of tan δ were calculated using the measured conductance at various frequencies.

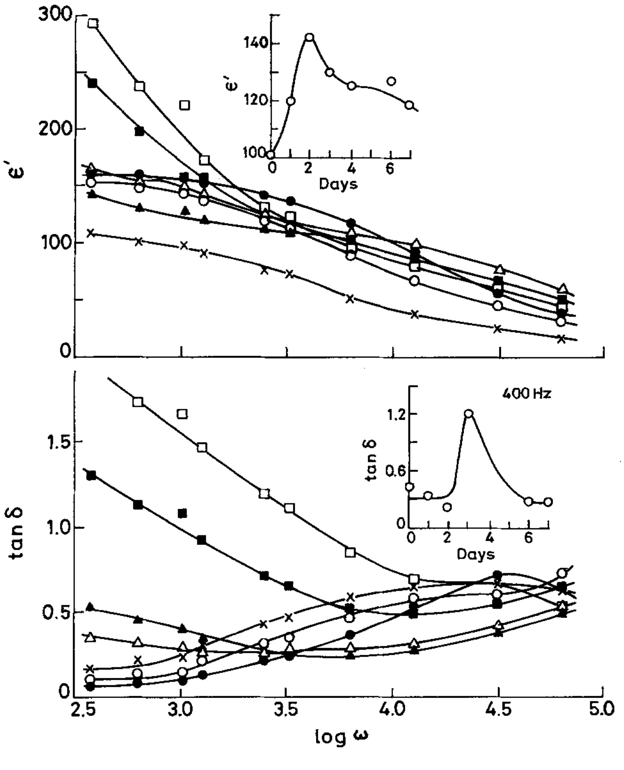

Figure 2 Frequency dependence of ε′ and tan δ at room temperature for initial and HCl vapour exposed AlN sample (porosity 9 vol %). Inset shows the exposure time dependence of ε′ and tan δ. (x) Initial state; (○) 1 day; (●) 2 days; (□) 3 days; (■) 4 days; (△) 6 days; (▲) 7 days.

Lead capacitance (~2.3 pF) was subtracted from the measured capacitance before calculating the dielectric constant.

Uncoated samples were preferred so that the effect of exposure could be observed clearly. As the measurements are done at room temperature where d.c. conductivity is quite small in hot-pressed AlN ceramic, poor electrical contact will not affect the dielectric behaviour [10].

3. Results and discussions

To study the effect of inorganic acid vapours on the dielectric behaviour, ε′ and tan δ were measured as a function of frequency (60 Hz to 10 kHz). First of all, these measurements were made on unexposed sample (exposed to atmospheric humidity only). This we call the initial state. Samples were kept in the respective desiccators for the exposure to acid vapours for a known time period and dielectric measurements were made again. The mass measurements were also made after each exposure. Figures 1 to 4 show the frequency dependence of ε′ and tan δ for two samples (porosity 0.2 and 9 vol %) in case of exposure to HCl and HNO_3 vapours. For comparison purposes, the results of these measurements are plotted in the same figures for initial state (unexposed to acid vapours) also. The measurements were also made on two more samples (porosity 4 and 15 vol %) and the results were found of the same nature as reported in Figs 1 to 4.

It is clear from Figs 1 to 4 that dielectric dispersion increases after exposing the samples of hot pressed AlN ceramic to HCl and HNO_3 vapours. The dissipation factor also increases in the exposed samples. A

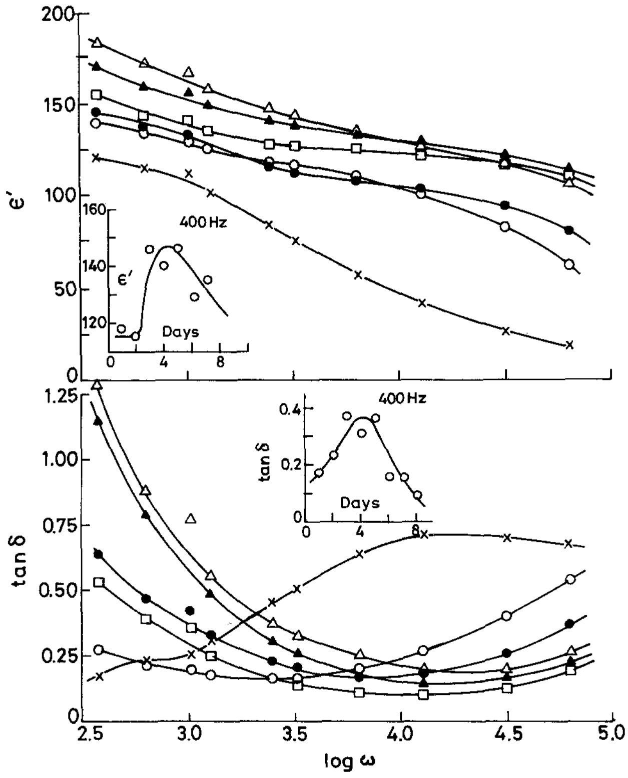

Figure 4 Frequency dependence of ε' and tan δ at room temperature for initial and HNO_3 vapour exposed AlN sample (porosity 9 vol %). Inset shows the exposure time dependence of ε' and tan δ. (×) Initial state; (○) 1 day; (●) 2 days; (△) 3 days; (▲) 4 days; (□) 6 days.

comparative study for different samples shows that the effect of exposure is more in case of samples having higher porosity. At a particular porosity and exposure time, the effect is more in case of HNO_3 as compared to HCl.

To assess the effect of exposure time on the dielectric parameters, the values of ε' and tan δ at a particular frequency (400 Hz) are plotted against exposure time in the inset of Figs 1 to 4. For another two samples (porosity 4 and 9 vol %) similar results were obtained. It is interesting to note that ε' and tan δ show maxima at a particular exposure time in case of exposure to HCl and HNO_3 vapours. To understand whether the decrease of these parameters are because of the decreased amount of acid vapours or not, we have measured the mass of the exposed samples after each exposure. The results of these measurements are given in Fig. 5. This figure indicates that the percentage change in mass is more at higher porosity (15 vol %) as compared to lower porosity (0.2 vol %). Moreover, no maxima in the mass variation is seen in all the samples in both cases of exposure (HCl and HNO_3), the amount of acid vapours goes on increasing till a saturation is reached. The decrease of dielectric parameters, therefore, is not because of the decreased amount of absorbed vapours.

To understand the effect of porosity on the corrosion effect of HCl and HNO_3 vapours, we have plotted in Figs 6 and 7 frequency dependence of ε' and tan δ in case of various samples of different porosity for a particular exposure time 24 h. It is clear from these figures that dielectric dispersion is small in low porosity samples (0.2 and 4 vol %) as compared to higher porosity samples (9 and 15 vol %). In our earlier study [11] of the moisture effect also, the behaviour at low porosity ($\leqslant 4$ vol %) was different than higher porosity ($\geqslant 9$ vol %) samples. This was explained in terms of closed and open porosity in AlN hot pressed samples. Boch *et al.* [5] have reported that up to 6 vol % of total porosity, open porosity is negligible in hot-pressed AlN samples. However, as the porosity increases, the open porosity increases and closed porosity decreases. Due to open porosity, higher porosity samples may absorb a greater amount of moisture and/or acid vapours as compared to low porosity samples where open porosity is negligible.

The recovery studies were also performed on the HCl and HNO_3 vapour exposed samples. Evacuating the sample holder to 10^{-2} torr reduces the values of ε' and tan δ but values do not come back to the original state. We had to heat the exposed samples to high

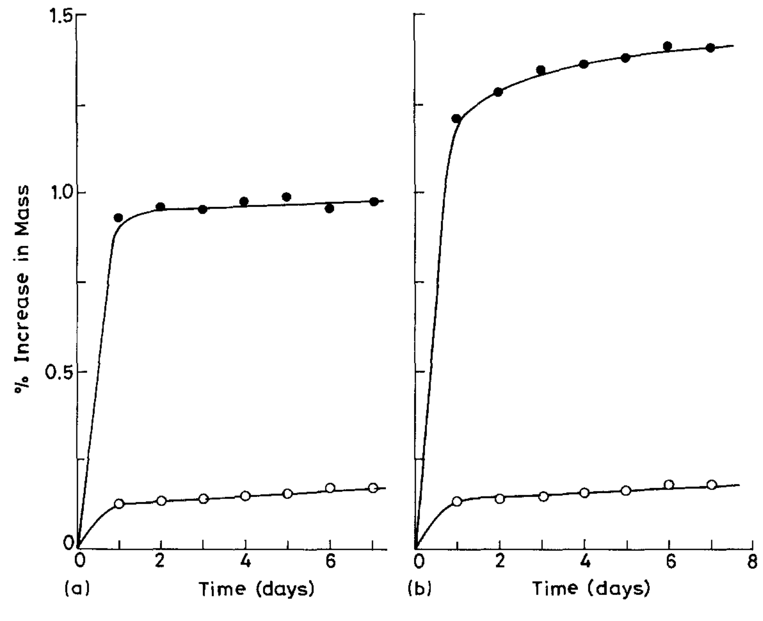

Figure 5 Exposure time dependence of mass variation in (a) HCl and (b) HNO_3 exposed samples of AlN. Porosity (●) 15%, 0.2%.

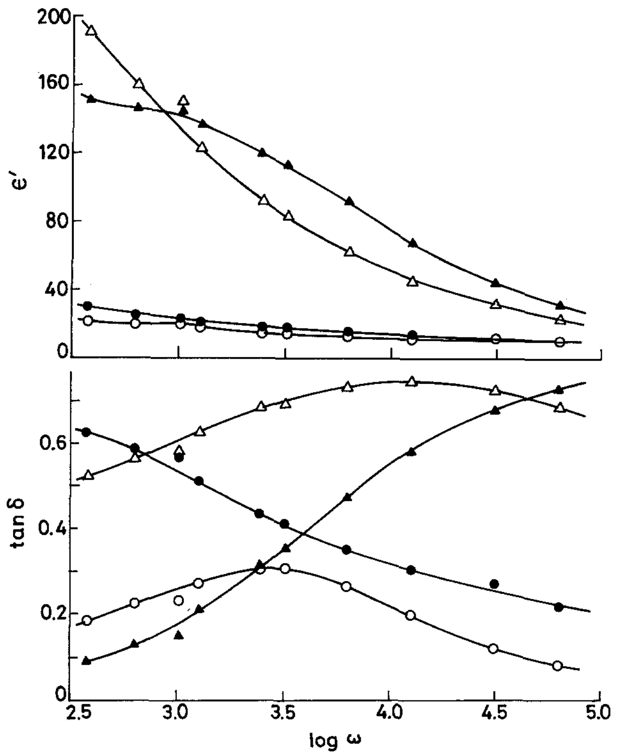

Figure 6 Frequency dependence of ε' and tan δ for hot pressed AlN ceramic having different volume per cent porosity after exposing to HCl vapours for 24 h. (○) 0.2%; (●) 4.0%; (△) 9.0%; (▲) 15.0%.

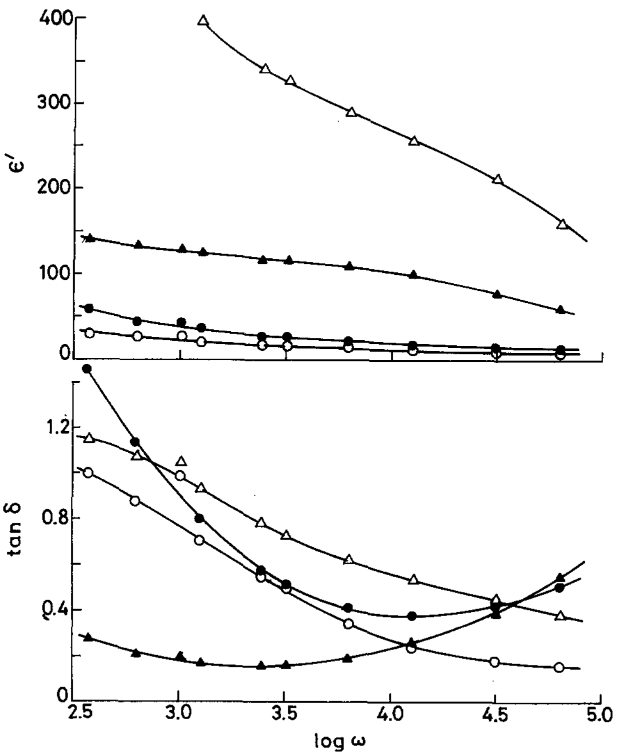

Figure 7 Frequency dependence of ε' and tan δ for hot pressed AlN ceramic having different volume per cent porosity after exposing to HNO_3 vapours for 24 h. (○) 0.2%; (●) 4.0%; (△) 15.0%; (▲) 9.0%.

temperatures (more than 600° C) to remove the exposure effect. It was found that the corrosion effect due to absorbed acid vapours was completely reversible (results not shown here). A further exposure to HCl and HNO_3 vapours reproduces the results shown in Figs 1 to 4 within an experimental error of $\pm 2\%$. A maxima in the ε' and tan δ against exposure time curves (insets of Figs 1 to 4) is also found reproducible if the annealed samples are re-exposed to acid vapours.

The increase in ε' and tan δ after exposure to acid vapours may be understood in terms of a heterogeneous system which might result in Maxwell–Wagner type losses. An increase in the dielectric loss or tan δ after exposing the samples to acid vapours may be due to an increase of ionic conductivity which arises due to the dissociation of acid vapours in moisture. The dissociation constant and the mobility of ions may be the important parameters on which the ionic conductivity may depend [13]. According to this point of view, HCl which has lower dissociation constant than HNO_3 should have a lesser effect on dielectric parameters. This is found true in the present case (see Figs 1 to 4).

The effect of HCl and HNO_3 vapours on the dielectric behaviour of some polymeric laminates has recently been studied by Singh *et al.* [14]. In their samples also, an increase in dielectric loss was observed over and above the atmospheric humidity after exposure to HCl and HNO_3 vapours. As in the present case, the corrosion effects were found to be reversible in their samples also.

4. Conclusions

The effect of exposure to HCl and HNO_3 vapours is studied on the dielectric behaviour of hot pressed AlN ceramic having different volume percentage of porosity. The results indicate that the porosity plays an important role in the change of dielectric parameters (ε' and tan δ) on account of exposure to acid vapours. Dielectric constant and tan δ both increase after exposure to acid vapours over and above the atmospheric humidity. A maxima in dielectric parameters against exposure time curve is observed in both the cases of exposure in all the four samples studied. The reasons for such a maxima are not yet clear as no such maxima could be observed in gravimetric measurements as a function of exposure time. The dissociation of acid vapours in the presence of moisture may increase the conductivity due to ion formation which may cause higher values of ε' and tan δ.

The corrosion effects are found completely reversible as, after annealing, the exposed samples give the similar results as found in unexposed samples. Re-exposure reproduces the results within the experimental error.

A different behaviour at low and higher porosities is explained in terms of closed and open porosities as reported [5] in literature in case of hot pressed samples of AlN ceramic.

Acknowledgement

Work supported by the Council of Scientific and Industrial Research, New Delhi, India.

References

1. G. LONG and L. M. FOSTER, *J. Amer. Ceram. Soc.* **42** (1959) 53.
2. J. A. KOHN, P. G. COTTER and R. A. POTTER, *Am. Mineral* **41** (1956) 355.

3. K. M. TAYLOR and C. LENIE, *J. Electrochem. Soc. (USA)* **107** (1960) 308
4. C. DEVIN, J. JARRIGE and J. MEXMAIN, *Rev. Int. Houtes. Temp. Refrac.* **19** (1982) 325.
5. P. BOCH *et al.*, *Ceram. Int.* **8** (1982) 34.
6. M. BILLY *et al.*, *Rev. Chime Miner.* **19** (1982) 673.
7. G. DEWITH and N. HATTU, *J. Mater. Sci.* **18** (1983) 503.
8. O. YAMADA, M. SHIMADA and M. KOIZUMI, *J. Soc. Mater. Sci. (Jpn)* **32** (1983) 1269.
9. M. ZULFEQUAR and A. KUMAR, *Revue Phys. Appl.* **21** (1986) 525.
10. *Idem, Adv. Ceram. Mater.* **3** (1988) 332.
11. M. ZULFEQUAR, D. B. SINGH and A. KUMAR, *Mater Sci. Eng. A.* **102** (1988) 131.
12. Catalogue Good Fellow Metals (USA).
13. B. BARKATAKOVA and B. HARANICKOVA, *Technical Digest* **10** (1968) 730.
14. D. B. SINGH, A. KUMAR, V. P. TAYAL and B. SANYAL, *J. Mater. Sci.* **23** (1988) 528.

Received 20 January
and accepted 24 August 1989