Effect of Exposure to Acid Vapours on the Dielectric Behaviour of Hot Pressed Aluminium Nitride Ceramic With and Without Oxide Additives

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Dielectric behaviour of hot pressed aluminium nitride (AIN) ceramic with and without additives is studied before and after exposing the samples to some inorganic and organic acid vapours. It is observed that the dielectric dispersion increases after exposing the samples to acid vapours over and above the atmospheric humidity. In all the cases the presence of oxide additives (BeO, MgO, and Y$_2$O$_3$) is found to increase the exposure effects.

Introduction

Aluminum nitride (AIN) ceramic has received considerable attention as an useful engineering material because of its excellent mechanical and electrical properties at high temperatures. The kinetics of densification and mechanical properties of this material have been studied in detail by various workers and it is now well established that AIN is highly thermal shock resistant and has high oxidation resistance in air. The electrical conductivity and dielectric behaviour of AIN ceramic having different volume percentages of porosity have earlier already been reported from authors laboratory.$^{1,2}$

The interaction of a ceramic material with its environment is of great importance as these are used as construction materials which are subjected not only to atmospheric humidity and pollutants but also to vapours (including phenol, formaldehyde, formic acid, acetic acid, higher fatty acid, and alkaline vapours such as ammonia) given out by the organic materials comprising packaging, e.g. wood, insulating tape, synthetic adhesives resins, paints and varnishes.

In view of the above facts the authors started a systematic study of the effect of exposure to various inorganic and organic acid vapours. The effect of such exposure on the dielectric behaviour of pure AIN ceramic has already been reported$^{14,15}$ and it is found that exposure to these acid vapours increases the dielectric loss over and above the humidity effect.

As various oxide additives (MgO, BeO, SrO, Y$_2$O$_3$) are used with AIN for getting highly dense ceramic samples during hot pressing the effect of such oxide additives on various properties of AIN is of great importance. Earlier results from our laboratory indicate that oxide additives do affect the electrical and dielectric parameters.

Thus, we have studied the effect of inorganic (HCl, HNO$_3$) and organic (HCOOH and CH$_3$COOH) acid vapours on AIN with and without oxide additives (MgO, BeO, SrO, Y$_2$O$_3$). It is found that barring SrO, other oxide additives increase the exposure effects.

Materials and Methods

Sample Preparation

Hot pressed samples of AIN were obtained from the universite de Limoges (France). Hot pressing of the samples was done between 1500 to 1700°C by applying a pressure ~ 20 MPa for 30 min. The samples thus formed had a diameter ~1.5 cm and thickness ~0.5 cm. The porosity of each hot pressed sample was calculated by measuring the density of the pellet with a Doultaan mercury densitometer. The porosity varied from 0.2 to 15 volume per cent.

For studying the acid exposure effect the samples were kept in a dessicator of 3L of capacity in
which 500 mL of 1 N solution was kept. The samples were positioned on a porcelain disc, with holes in it, in such a manner that they were open to the vapour phase. The lid of the desiccator was tightly placed and was opened only for just sufficient time so as to pick up the sample for testing.

Experimental Procedure

For the dielectric measurements the samples were sandwiched between the two steel electrodes (diam - 1.5 cm) inside a metallic sample holder. Three terminal measurements were made to avoid the stray capacitances. A GR-1620 A P capacitance measuring assembly was used to measure the capacitance and the dissipation factor. The instrument was used in the parallel capacitance mode, where capacitance and conductance could be directly measured.

Results and Discussion

To study the effect of exposure to acid vapours, dielectric constant $\varepsilon'$ and dissipation factor $\tan \delta$ were measured as a function of frequency for unexposed and exposed samples of hot pressed AlN ceramic with and without oxide additives. It was observed that dielectric dispersion increased on exposure to acid vapours over and above the atmospheric humidity (initial state). The dissipation factor also increased on account of such exposure. The effects were found to be exposure time dependent. To demonstrate this, the results for AlN + 1 per cent MgO have been shown in Figure 1 for an exposure of HCl vapours. Similar results were obtained in the case of other acid vapours.

It is evident from Figure 1 that both $\varepsilon'$ and $\tan \delta$ increase after exposing the sample to acid vapours. The inset of this figure shows the exposure time dependence of $\varepsilon'$ and $\tan \delta$ at a particular frequency (400 Hz). A maxima is observed at a particular exposure time. However, no such maxima has been observed as gravimetric analysis on these samples after such exposures. This indicates that the decrease in $\varepsilon'$ and $\tan \delta$ after a certain exposure time is not due to decreased amount of absorbed vapours. The exact reasons for these maxima are however not clear from the present measurements.

To understand the effect of oxide additives on such exposure effects, results of $\varepsilon'$ and $\tan \delta$ as a function of frequency, after an exposure of 2 d, are plotted in Figure 2 in the case of HCl vapours. It is clear from this figure that $\varepsilon'$ and $\tan \delta$ both increase after addition of oxide additives (BeO, MgO and Y$_2$O$_3$) as compared to pure AlN. Only in the case of SrO additive, the value of $\varepsilon'$ and $\tan \delta$ are found to be less as compared to pure ones, which may be due to small porosity in this samples as compared to pure AlN (Table 1). It has already been reported that porosity plays an important role in such exposures.

From the above results it is evident that under the same conditions of exposure the effect is more in samples containing oxide additives as compared to pure AlN ceramics. Similar results were found in the case of other acid vapours (HNO$_3$, CH$_3$COOH and HCOOH).

The increase in the values of $\varepsilon'$ and $\tan \delta$ after exposure to acid vapours may be understood in terms of the absorption of such vapours in hot pressed AlN with and without oxide additives. In the presence of moisture the dissociation of acid vapours into ions may appreciably increase the conductivity. A heterogeneous system may thus be formed which might result in Maxwell-Wagner type losses.
If the above argument is accepted, the dissociation constant and the mobility of the ions should play an important role in the increase of ionic conductivity and, in turn, dielectric constant and dissipation factor. Accordingly HCl which has lower dissociation constant than \( \text{HNO}_3 \), should have a lesser effect on dielectric parameters. This is found true in the present case. Similarly HCOOH, which has higher mobility and higher dissociation constant than \( \text{CH}_3\text{COOH} \), produces greater effect on the dielectric constant and dissipation factor as compared to \( \text{CH}_3\text{COOH} \).

### Conclusions

From the present measurements the following conclusions can be drawn:

(i) Upon exposure to acid vapours the dissipation factor increases in the case of pure as well as with oxide additives.

(ii) In general, organic acid vapours are found to have more effect on dielectric parameters.

(iii) The dissociation constant and the mobility of ions play important role in the increase of dissipation factor on account of acid exposure.

(iv) The oxide additives increase the exposure effect in hot pressed AlN ceramic.

### References