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Dielectric properties of Lanxide™ Al_2O_3/Al composites

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The dielectric properties of unreinforced Lanxide™ Al_2O_3/Al composites have been investigated over a wide range of temperatures and frequencies. These composites were formed by the directed oxidation of suitably doped aluminium-based alloy melts, with no filler or reinforcing material in the reaction path. As-grown composite materials were good electrical conductors in all directions owing to the presence of an interconnected metallic constituent. As the metallic phases were partially removed (in favour of porosity) by continuing the oxidation reaction to completion, the composites remained electrically conducting parallel to, and became insulating transverse to, the original growth direction of the composite. This anisotropy apparently was caused by different connectivity of the metal phase between the two directions. Thermal treatments at 1600 °C in argon resulted in volatilization of the residual metal in the composite, thus further increasing the porosity. As the metal content was decreased, the composites changed from conducting to insulating along the growth direction. When the metallic phase was removed completely, the porous alumina ceramic maintained anisotropic dielectric properties, due to *c*-axis alignment of the alumina (corundum) phase along the growth direction. The dielectric constants were 8.0 and 6.4, respectively, parallel and perpendicular to the *c*-axis aligned directions of the porous alumina ceramic. A dielectric relaxation phenomenon was observed in some samples of both as-grown and thermally treated material, and was attributed to an unidentified impurity effect.

1. Introduction

Unique physical and electrical properties can be obtained in composite materials because their properties often are determined more by connectivity principles than by the properties of the individual phases. This certainly is the case with the new family of unreinforced Al_2O_3/Al composites formed by Lanxide™ Corporation's ceramic composite matrix process, referred to as the DIMOX™ directed metal oxidation process [1–3]. These composites consist mainly of ceramic (Al_2O_3) and metallic (aluminium) phases, where the amounts and connectivities of the ceramic and metallic constituents are controlled by processing. Dielectric property measurements proved to be an excellent characterization method for these composites. The range of properties that were observed in these materials, produced with varying metallic content, will be described.

The Al_2O_3/Al composites of the present study were prepared by the DIMOX™ process. In this process, aluminium oxide (Al_2O_3) is "grown" in a directed oxidation reaction of suitably doped aluminium alloy melts. The growth proceeds perpendicularly outward from the molten alloy surface, resulting in a three-dimensionally interconnected Al_2O_3 matrix. In the absence of a filler or reinforcing material, the Al_2O_3 phase forms such that there is *c*-axis alignment along the growth direction [2]. If the growth process is stopped before the aluminium alloy ingot is converted completely into Al_2O_3, the matrix also contains a three-dimensionally interconnected metallic phase (typically, 5–30 vol%), primarily aluminium with minor amounts of doping or alloying elements such as silicon. When the growth process proceeds to completion (exhausting the metal supply), the resultant composite is a three-dimensionally interconnected porous Al_2O_3 ceramic, containing less than 5 vol% metal. Hereafter, such materials will be referred to as being in the depleted, or as-grown (depleted) condition. The amount and degree of interconnectivity of the residual metallic phase in these composites varies with the parent alloy composition and dopants, as well as the growth temperature and growth time.

2. Sample preparation and characterization

The parent alloy of the composites studied in this investigation was commercial alloy 5052 (nominally

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97.5% wt% Al and 2.5 wt% Mg). The ingot was doped with a thin layer of SiO_2 on the top surface prior to the growth process. The as-grown composite averaged 3–4 cm in the growth direction by several hundred square centimeters in area. Specimens of 1.0 cm × 1.5 cm × 2.0 cm were cut from the bulk material, with care taken to record the orientation relative to the original growth direction. The orientation of the composite is important to the optical microscopy studies and dielectric measurements to be reported in this paper. The orientation conventions followed are shown schematically in Fig. 1. For the parallel orientation: microstructural observations were made on faces perpendicular to the original growth direction of the composite (i.e. looking down the growth direction), and samples were cut and electrodes applied so that dielectric properties were measured along the growth direction. For the transverse orientation: microstructural observations were made on faces parallel to the original growth direction (i.e. looking along a direction perpendicular to the growth direction, and samples were cut and electrodes applied so that dielectric properties were measured transverse to the growth direction.

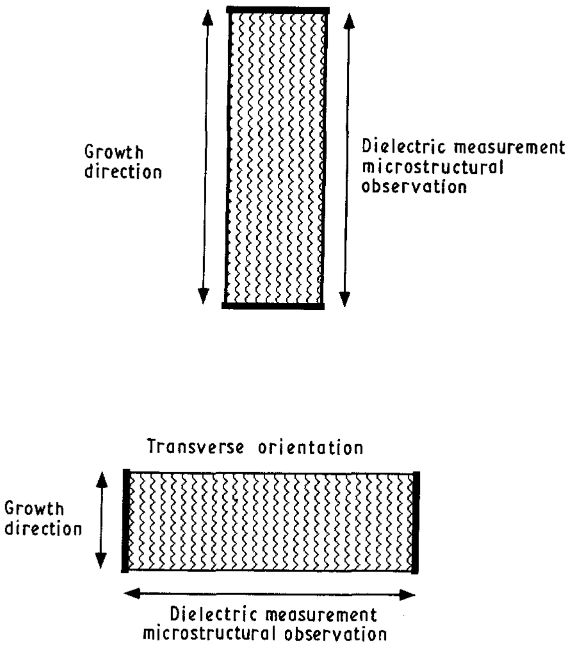


Figure 1 Orientation conventions.

Optical micrographs of as-grown (depleted) composite material, taken with orientations parallel and transverse to the growth direction, are presented in Fig. 2. These micrographs confirm the multi-phase nature of the composites. The areas of grey contrast are alumina, the isolated white areas are metal (predominantly aluminium), and the dark areas are porosity. The alumina phase and the porosity both appear to be highly continuous, whereas the metallic phase seems to be present more in isolated regions. However, the true connectivity of the various phases is difficult to deduce from a two-dimensional micrograph. Optical microscopy of several areas from several samples could not reveal significant differences (in the amount and connectivity of the alumina and metal phases) between samples of different orientation relative to the growth direction of the composite.

Thermal treatments on as-grown (depleted) material were carried out in flowing argon at 1600 °C for times varying from 12–96 h. This bake-out process resulted in the volatilization of the residual metallic constituents, thus increasing the porosity. The weights of all samples were recorded before and after thermal treatment; these weight loss data are presented in Fig. 3. Optical micrographs of baked-out material oriented parallel to the growth direction are shown in Fig. 4. The decreasing amounts of visible metallic phase and increasing amount of porosity with time correlated well with the weight loss data. After 12 h, only a minimal amount of the metallic phase remained. After 48 h at 1600 °C, virtually no metallic phase existed, except in isolated pockets. The removal of the metallic phase with time at 1600 °C also was evident from the gradual colour change of the specimens from dark grey to white. Again, the microstructures of heat-treated samples were similar for both orientations. The density of completely baked-out material (i.e. the 96 h sample) was 2.94 g cm^{-3}, or 74% of the theoretical value for Al_2O_3 (corundum).

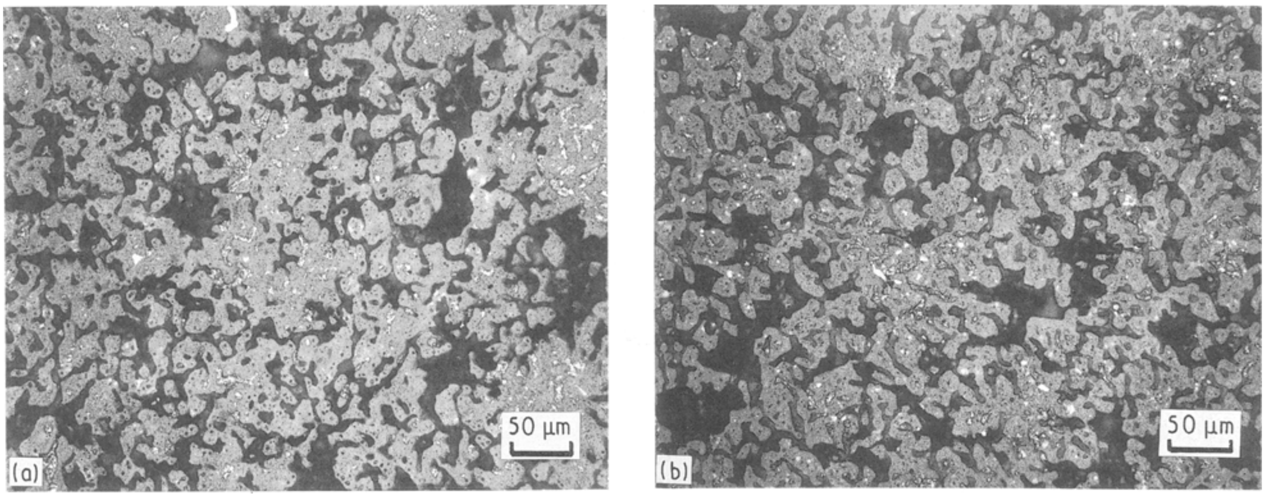


Figure 2 Optical micrographs of as-grown (depleted) composite samples, oriented (a) parallel and (b) transverse to the growth direction.

TABLE I Dielectric measurements on as-grown (depleted) and thermally treated composite samples

Time at 1600 °C (h)	Orientation	Sample number	Dielectric constant, $K(25\,^{\circ}\mathrm{C})$	Strength of relaxation
0	Parallel	1	Conductive	–
		2	Conductive	–
		3	Conductive	–
0	Transverse	1	30.0	Weak
		2	Conductive	–
12	Parallel	1	12.0	Strong
		2	9.7	Strong
		3	Conductive	–
12	Transverse	1	8.3	Absent
		2	8.5	Absent
24	Parallel	1	8.0	Weak
		2	8.1	Absent
		3	8.1	Absent
24	Transverse	1	6.5	Absent
		2	6.5	Strong
96	Parallel	1	8.1	Strong
		2	7.9	Absent
		3	8.0	Absent
96	Transverse	1	6.5	Absent
		2	6.3	Strong

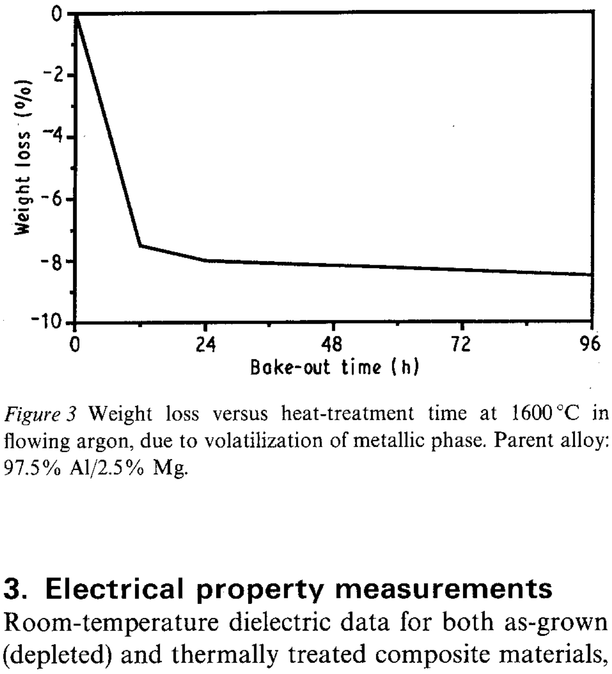


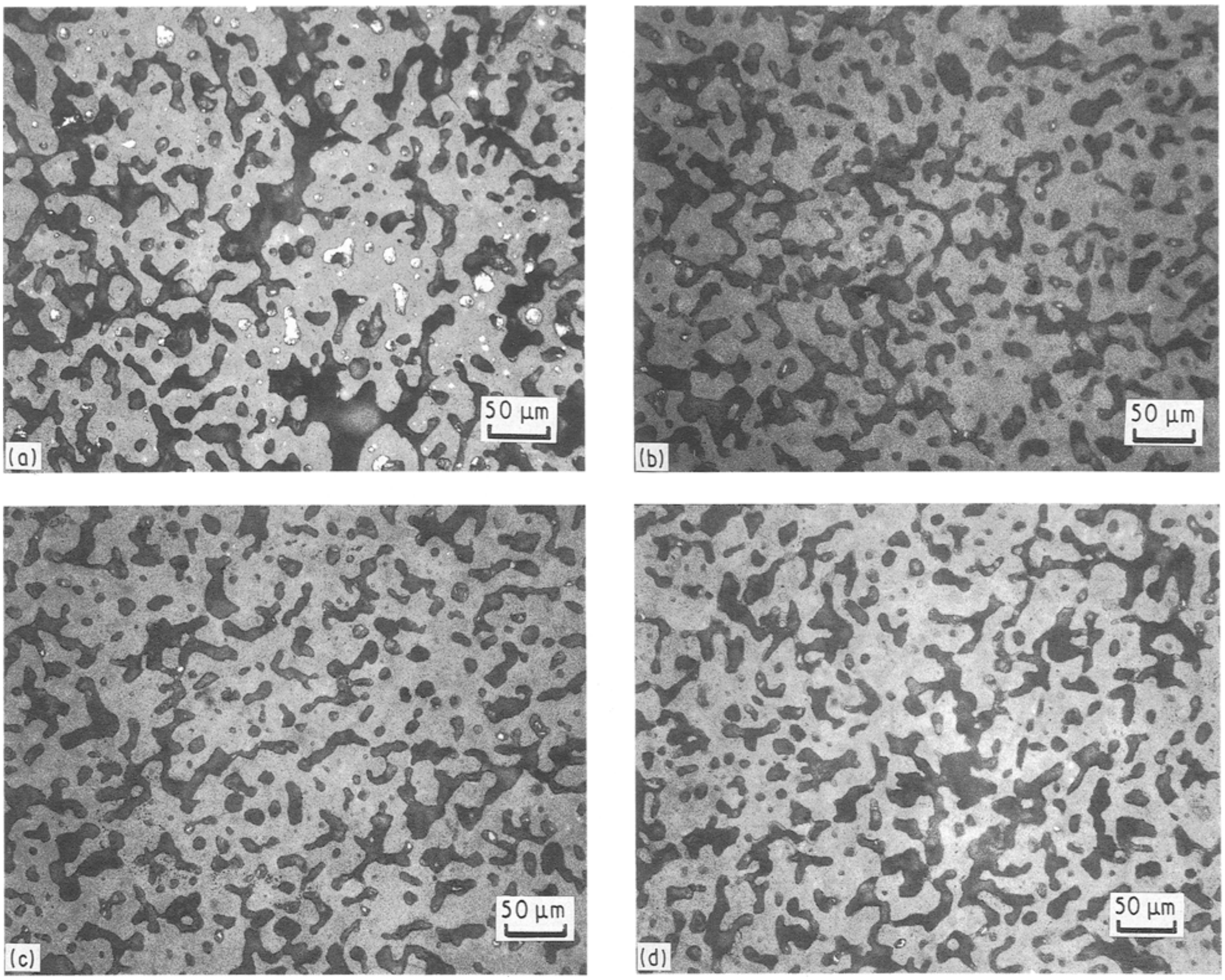
Figure 3 Weight loss versus heat-treatment time at 1600 °C in flowing argon, due to volatilization of metallic phase. Parent alloy: 97.5% Al/2.5% Mg.

3. Electrical property measurements

Room-temperature dielectric data for both as-grown (depleted) and thermally treated composite materials, with orientations both parallel and transverse to the original growth direction, are presented in Table I. It is interesting to note that the as-grown (depleted) material tended to be electrically conductive parallel to the growth direction and insulating transverse to the growth direction. Apparently, the connectivity of the metallic phase in these samples was somewhat greater parallel to the growth direction than transverse to it. This observation contrasts with the optical microscopy results, where no difference in microstructure was observed between the two orientations. Along the transverse direction, one specimen was conductive, and a dielectric constant of 30, with relatively low dielectric loss (tanδ less than 0.02 at 10 kHz), was measured for the second specimen. Electrical properties of the as-grown (depleted) material in the transverse orientation were dependent on sample thickness: samples were conductive with thickness below approximately 1.0 mm, and insulating with larger thickness. This suggests that the metallic phase was continuous over macroscopic distances transverse to the growth direction. Anomalously high dielectric constants (i.e. > 10, the value expected for ceramic alumina) were observed in the insulating samples. This was related to the presence of both insulating and metallic phases in the composite, and thus a Maxwell–Wagner contribution to the dielectric constant [4, 5].

The effect of the 1600 °C heat treatment on the dielectric constant of the composites for the two orientations is shown in Fig. 5. Partial removal of the metallic phase (by thermal treatment) imparted electrically insulating character to the composites, regardless of orientation. Relatively high dielectric constants (> 10) were observed in metal-containing (but nonconductive) samples. The anisotropy present in as-grown (depleted) material was preserved as the aluminium was removed. The dielectric constant always was higher parallel to the growth direction for samples given equivalent thermal treatments. This anisotropy was maintained in completely baked-out (metal-free) material; the dielectric constants parallel and transverse to the growth direction were 8.0 and 6.4, respectively.

Aside from the anisotropic dielectric properties observed in both as-grown (depleted) and thermally treated composite materials, two separate types of dielectric behaviour were observed during measurements of the temperature dependence of the dielectric properties. A relaxation at about 70 °C and a high-temperature dielectric dispersion were observed in some samples; these two features occurred together. However, no clear trend with respect to the occurrence and magnitude of these loss phenomena with respect to heat-treatment time or sample orientation was encountered. The existence and strength of this relaxation mechanism for the as-grown (depleted) and



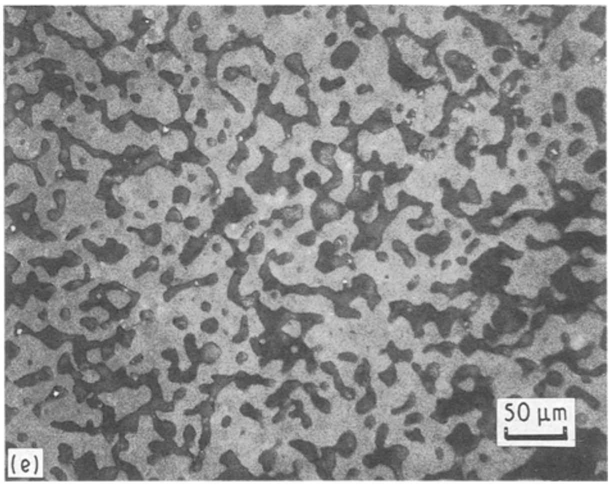


Figure 4 Optical micrographs of composite samples, thermally treated at 1600 °C for (a) 12 h, (b) 24 h, (c) 36 h, (d) 48 h, and (e) 96 h.

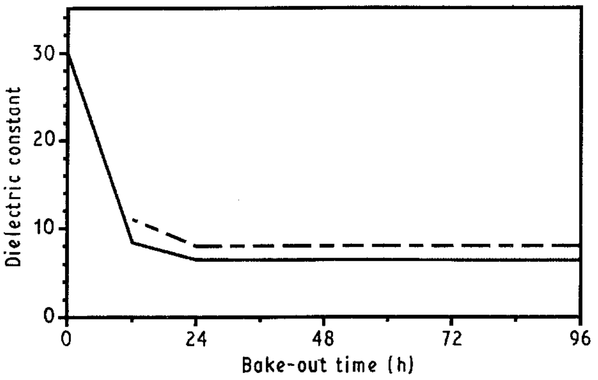


Figure 5 Dielectric constant versus heat-treatment time at 1600 °C for composite samples, oriented both (– – –) parallel and (——) transverse to the original growth direction.

thermally treated composite samples are indicated in Table I.

The relaxation and corresponding high-temperature dispersion were largest parallel to the growth direction in one of the 12 h thermally treated samples. The dielectric constant and loss are plotted versus temperature for this sample in Fig. 6. The dielectric relaxation mechanism becomes more evident, when the same data are re-plotted with additional frequencies over a narrower temperature range in Fig. 7. The shift of loss peak frequency with temperature was in accordance with the Arrhenius equation, as indicated by the straight line Arrhenius plot, presented in Fig. 8. An activation energy of 2.17 eV with a pre-exponential factor of 10^{-36} s was calculated from this plot. The magnitude of the pre-exponential factor strongly suggests a Maxwell–Wagner–Sillars type mechanism, representative of dispersed conducting particles within an insulating matrix [6].

The above-described relaxation mechanism was absent in some of the composite samples with longer thermal treatment times. The dielectric properties of a 96 h thermally treated sample, oriented parallel to the

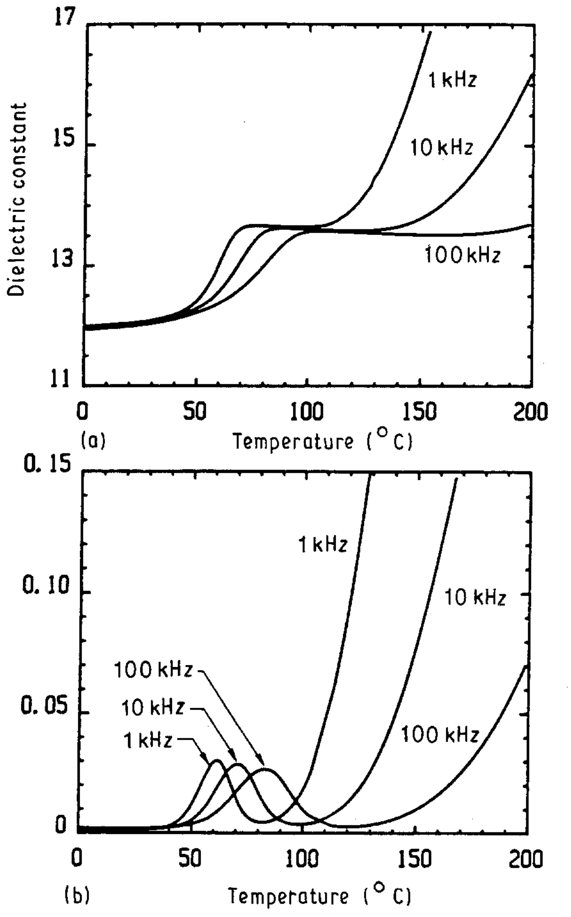


Figure 6 (a) Dielectric constant and (b) tan δ versus temperature for a composite sample, thermally treated at 1600 °C for 12 h, parallel to the growth direction.

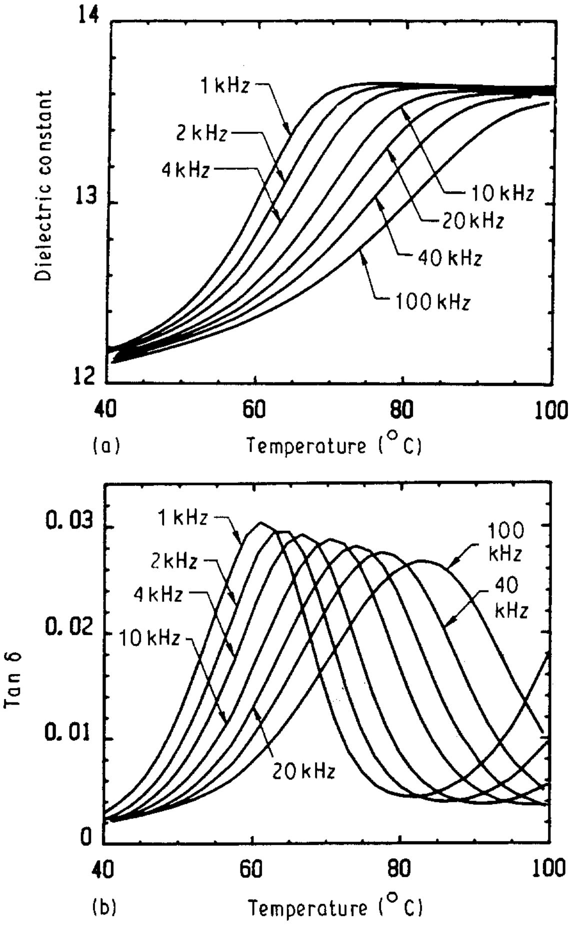


Figure 7 (a) Dielectric constant and (b) tan δ at seven frequencies between 1 and 100 kHz versus temperature (40–100 °C), for a composite sample, thermally treated at 1600 °C for 12 h, parallel to the growth direction.

growth direction, are shown in Fig. 9. In the absence of the 70 °C relaxation and the high-temperature dispersion, the dielectric loss is very low and increases slightly with increasing temperature. The dielectric constant of this relaxation-free sample increased gradually with temperature, with a temperature coefficient (uncorrected for thermal expansion) of 110 p.p.m. $^\circ C^{-1}$, very close to the value expected for Al_2O_3.

4. Discussion

In thermally annealed DIMOX Al_2O_3/Al composites, relatively large dielectric constants (> 10, the value for polycrystalline alumina) were observed when a remanent metallic phase was present. The apparently high dielectric constants observed in these metal-containing composite materials were related to the amount and connectivity of this metallic phase. The apparent dielectric constant increases because electric flux lines in a composite tend to concentrate within the highly conductive phase, i.e. due to the Maxwell–Wagner effect [4, 5]. Based on Maxwell–Wagner theory, the dielectric constant of these composites will remain high, well into the microwave frequency range, where the conductivity of the metallic phase will decrease and a dielectric dispersion will occur. This was confirmed by dielectric measurements performed on a similar Al_2O_3/Al composite material over the frequency range 50 MHz–1 GHz [7]. Only a small dispersion in the dielectric constant and relatively low loss (tan $\delta < 0.02$) was observed over this frequency range, confirming that the large dielectric constant persisted to at least 1 GHz.

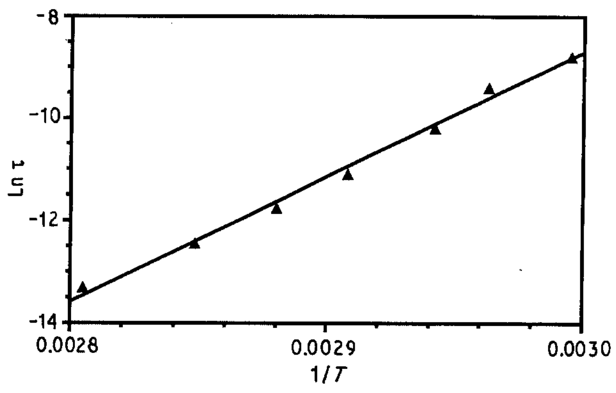


Figure 8 Arrhenius plot, constructed from dielectric data in Fig. 7. $Q = 2.13$ eV, $\tau_0 = 10^{-36}$ s.

Continued depletion of the metallic phase, by thermal treatment, caused the composite material to become insulating in all directions, and further removal of metal decreased the dielectric constant. The anisotropy of composites, remained after thermal treatment, as the dielectric constant became orientation dependent. When the metallic phase was removed completely,

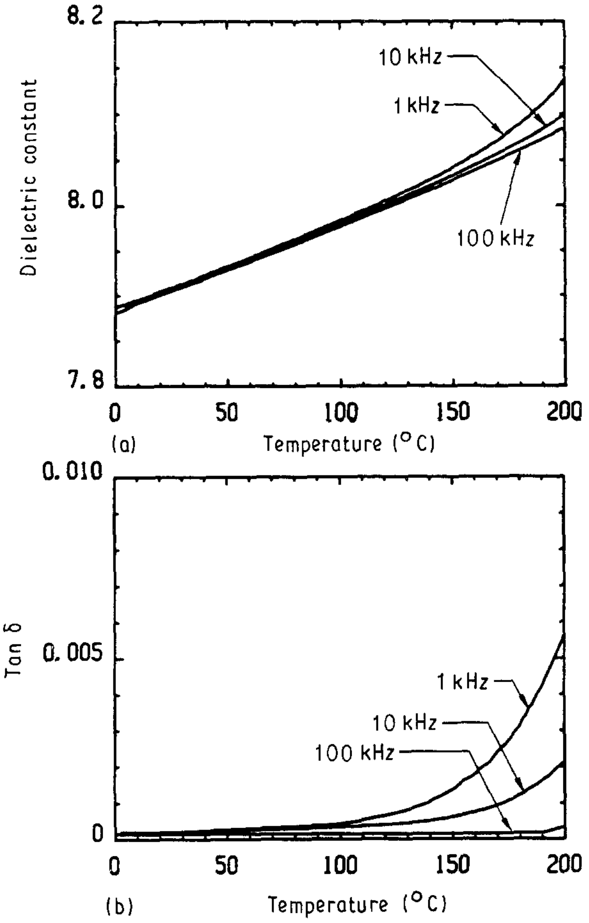


Figure 9 (a) Dielectric constant and (b) dissipation factor at 1, 10, and 100 kHz versus temperature (0–200 °C) for a relaxation-free composite sample, thermally treated at 1600 °C for 96 h, parallel to the growth direction.

the dielectric constant was reduced to values of 8.0 and 6.4, respectively, parallel and transverse to the growth direction. The dielectric loss was very low, with tan δ values less than 0.001 in the 10–100 kHz range. Thus, the dielectric properties of metal-free composites were consistent with those of a porous, oriented alumina ceramic.

The tendency toward anisotropic conductivity of as-grown (depleted) material suggests that the metallic phase was connected over longer distances parallel rather than transverse to the growth direction. After removal of the metal, the remaining porosity might also have anisotropic connectivity, and could account for the anisotropy in the dielectric constant. However, anisotropic connectivity of the metal phase and/or porosity were not confirmed by microstructural studies. It is more likely that *c*-axis orientation of the Al_2O_3 (corundum) along the growth direction was responsible for the observed dielectric anisotropy in metal-free material. The dielectric properties of single-crystal alumina are anisotropic; the dielectric constant along the *a* and *c* directions are 8.6 and 10.55, respectively [8]. The use of a dielectric mixing argument to explain the observed dielectric mixing was supported by the calculations below.

Two dielectric mixing formulae can be considered to model the dielectric constant of composites (in this case, porous alumina ceramics), the parallel model and Licktenecker and Rother's logarithmic mixing rule [9].

parallel model:

$$K_T = (1 - V_2) K_1 + V_2 K_2 \qquad (1)$$

logarithmic rule:

$$\ln K_T = (1 - V_2) \ln K_1 + V_2 \ln K_2 \qquad (2)$$

where K_T is the observed dielectric constant (8.0 and 6.4 along the parallel and transverse directions, respectively), K_1 is the dielectric constant of alumina (8.6 and 10.55, along the *a*- and *c*-axes, respectively), K_2 is the dielectric constant of porosity ($K_2 = 1$), and V_2 is the effective volume fraction of porosity. The effective volume fraction of porosity was calculated using both equations, for both the parallel and transverse directions of the metal-free composite samples. Using the logarithmic rule, the amount of porosity along the parallel and transverse orientations are 12 and 13 vol%, respectively. Using the parallel mixing rule, the corresponding porosity values are 27 and 28 vol%, respectively. The density of the 96 h sample is 2.94 g cm^{-3}, which corresponds to approximately 26% porosity. This, it seems that the parallel mixing model is more appropriate to describe the dielectric mixing in this porous alumina material. The close correlation between the calculated and observed porosities, tends to confirm that the observed anisotropy of the dielectric properties in metal-free material was related to crystallographic anisotropy of the Al_2O_3 (corundum) phase, and not to anisotropic connectivity of the porosity.

Anomalous dielectric loss behaviour (a relaxation phenomenon at 70 °C and high-temperature dispersion) was observed in certain insulating specimens of these composites. Although a definitive explanation cannot be provided, the presence of semi-conducting impurities (e.g. silicon), which were present during the growth of this composite, may have been responsible. Generally, the presence of a dispersed conductive phase in an insulating matrix results in Maxwell–Wagner–Sillars effects [4–6], typified by dispersion in the dielectric constant and increased losses, usually occurring at high temperatures (> 100 °C). The simultaneous occurrence of the relaxation at 70 °C and the high-temperature dispersion suggest that the two phenomena are related to the same compositional or microstructural aspects of the composites. The fact that these dielectric loss features occurred in as-grown (depleted), partially baked-out, and completely baked-out material rules out metallic aluminium as a cause and suggests that another phase in the composite was responsible. Perhaps the silicon was not removed from the composite during thermal treatment, and the distribution of the silicon was not uniform within the composite. This would explain the occurrence of the dielectric loss anomalies on a random basis in thermally annealed samples.

5. Conclusions

The dielectric properties of Al_2O_3/Al composites formed by the Lanxide ceramic matrix composite process have been investigated.

1. Microstructures of as-grown (depleted) Al_2O_3/Al composite materials consisted of interconnected alumina and porosity, with isolated regions of metal. Thermal treatments at 1600 °C in argon removed the metallic phases by volatilization and increased the porosity. Optical microscopy failed to reveal any microstructural differences between directions parallel and transverse to the original growth direction.

2. As-grown (depleted) composite tended to be electrically conductive along the original growth direction and insulating transverse to the growth direction. This electrical anisotropy was apparently due to anisotropic connectivity of the metal phase.

3. Anomalously high dielectric constants (larger than expected for ceramic alumina) were observed in non-conductive, metal-containing composites, because of a Maxwell–Wagner contribution to the dielectric constant.

4. In metal-free material (without a filler phase), dielectric constants of 8.0 and 6.5 were observed parallel and transverse to the original growth direction, respectively. This anisotropy was due to *c*-axis alignment of the alumina (corundum). The parallel mixing rule adequately described the dielectric mixing between the alumina and porosity phases.

5. A Maxwell–Wagner–Sillars type relaxation at 70 °C and a corresponding high-temperature dispersion occurred randomly in both as-grown (depleted) and thermally treated composites, apparently due to an impurity effect.

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