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Investigation of the hydration and dehydration of aluminium oxide–hydroxide using high frequency dielectric measurements between 300 kHz–3 GHz

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Aluminium oxide exists in several forms which on addition of water give a complex range of oxide–hydroxide; boehmite, bayerite and gibbsite. High frequency dielectric measurements {300 kHz–3 GHz} are reported on the hydrated and dehydration of certain of these oxide–hydroxides. The amplitude of the observed dielectric relaxation correlates approximately with the water content, however anomalies can be observed during dehydration due to the retention of water in an immobilized form within the oxide matrix which highlights complexities in their structure and properties. These data indicate the potential of the dielectric method for quantification of the degree of hydration of an oxide in adhesive bonded structures. Two silane coupled alumina samples were studied to simulate the interface generated in the pre-treatment of real adhesive bonded structures.

1. Introduction

Lightweight fabrication of aluminium-to-aluminium structures relies on the integrity and durability of the adhesive bond on exposure to water [1–3]. By distributing the stress over a large area, adhesive bonding improves fatigue resistance, simplifies design and reduces fabrication costs. Most structural adhesives require elevated cure temperatures and careful preparation of the surfaces prior to bonding. In many aerospace applications, the aluminium is subjected to etching and anodization in order to develop a controlled oxide layer which improves the bond characteristics. Many attempts have been made to understand the detrimental effects of exposure of adhesive bonded structures to water [4]. One possible contributing factor is the conversion of the interfacial oxide to a hydroxide. Reaction of aluminium with oxygen gives a 4–8 nm, thick continuous layer of oxide, which on exposure to moisture converts partially to an oxide–hydroxide [5]. Such changes can induce surface stresses which ultimately leads to deterioration of the bonding. Water can change the physical properties of the polymer used as the adhesive, inducing swelling, plasticization and consequent loss in mechanical properties. The adhesive bond strength is a complex interplay of a number of factors; physical adsorption and chemical bonding between the surface and adhesive, physical 'lock and key' interactions as a result of adhesive penetrating the aluminium oxide structure and the tensile, shear and impact properties of the adhesive. Conventional pretreatments [6–11] lead to the generation of 'whisker-like' protrusions of oxide emerging from a layer of oxide with pores of approximately 40 nm diameter and depth ranging from 40 to 400 nm. The adhesive penetrates these structures and generates a 'lock and key' contribution to the bond strength. Hydration of this layer will cause the oxide to change dimensions and lead to a loss in the mechanical properties. Stresses accompanying conversion of oxide to hydroxide will weaken the interface with a consequential reduction of bond strength.

This paper attempts to quantify the relation between changes reported in the dielectric properties of adhesive bonded structures and the process of hydration of aluminium oxide [12]. A dry joint on exposure to moisture develops a new dielectric relaxation process in the frequency range 300 kHz and 100 MHz which has been tentatively attributed to relaxation of the hydroxide functions in the interfacial region [12]. Umeya and Kanno [13] have reported the dielectric spectra of an unspecified aluminium hydroxide and indicated a feature at 10 kHz which is consistent with the changes in the high frequency tail of the relaxation observed previously [12]. Because of the importance of understanding the origins of the process in the content of non-destructive analysis of adhesive

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bonded structures, this model study on various oxides of aluminium in powder form was carried out. Powders allow optimization of the surface area being exposed to moisture and are convenient for investigations of the dielectric properties of materials at high frequencies [12].

Hydrated aluminium oxide can be prepared in atleast three forms [13] and the reaction scheme used in this study is summarized below;

Amorphous hydroxide $\xrightarrow{293\text{ K, pH 7}}$ gelatinous boehmite AlO·OH
$\Downarrow$ 293 K, pH > 9
bayerite $Al(OH)_2$
$\Downarrow$ 293 K, pH > 12
gibbsite $Al(OH)_3$
well crystallized boehmite $\xleftarrow[353\text{ K, pH} > 12]{}$

This study will focus on the various stages of hydration and dehydration presented above. Two silane coupled alumina samples are investigated to simulate the type of pretreatment often used to improve the stability of the adhesive bonded interface.

2. Experimental

2.1. Materials

2.1.1. Preparation of the oxides investigated

Initial water uptake studies were carried out using a non-porous form of γ-Al_2O_3 [Degussa]. 'Boehmite', 'Bayerite' and 'Gibbsite' were prepared by dissolving $Al(NO_3)_3$ in distilled water. Dilute ammonium solution was added until the pH was at the required value and is a very important factor in determining the final structure of the oxide prepared. The resulting slurry was filtered and then rinsed thoroughly with distilled water to remove any remaining ammonium solution. To remove 'excess' water, the filtered material was dried at 423 K overnight, since this water may mask the dielectric response of the oxide itself.

The preparations were intended to reproduce various types of oxide hydroxide, which are termed 'BOE', 'BAY' and 'GIB' according to the preparation conditions. No attempt was made to produce well characterized Boehmite, which requires critical attention to synthesis and is beyond the scope of this investigation. These preparations do however cover the type of structures which may be expected to be observed in surface oxide.

2.1.2. Preparation of silane coupled alumina powders

Two silane coupled forms of γ-alumina were prepared by firstly drying the alumina powder at 423 K prior to reaction. Solutions of 3-aminopropyltriethyloxysilane ($H_2N(CH_2)Si(OC_2H_5)_3$) and methyltrimethoxysilane ($CH_3Si(OCH_3)_3$) were prepared by addition of 1 g of silane coupling agent to 0.1 g of water and the volume made up to 10 g by addition of 1-butanol (bpt 390 K). A mixture of 1 g of solution to 10 g of dried γ-alumina was refluxed for 1 h to produce a slurry. After thorough mixing the slurry was heated in a vacuum oven at 333 K for 30 min and then dried at 423 K for a further hour to remove both excess water and 1-butanol. This method is believed to give a complete surface coating of siloxane.

2.1.3. Method of hydration

Water uptake studies on the coupled and non-coupled alumina's were performed in a desiccator containing a saturated solution of hydrated calcium nitrate ($(Ca(NO_3)_2).4H_2O$) which maintained a relative humidity [RH] of 50% or water which produces a 100% RH. All measurements of water uptake were carried out at room temperature, (293 K).

2.2. Dielectric measurements in the frequency range 300 kHz to 3 GHz

The equipment used for these studies has been previously described [12]. The powdered sample was packed into a General radio GR900 50 Ω coaxial line which was used in an open circuit mode. Prior to performing dielectric measurements the oxide was crushed to a powder and packed uniformly into the line. The packing density was calculated from the total weight of the filled line and the true density of oxide {3.5 g cm^{-3}}. The ratio of reflected to incident waves for such a line is given by ρ[14], where:

$$\rho = \frac{1 - \varepsilon^{\frac{1}{2}}\tanh(\gamma l)}{1 + \varepsilon^{\frac{1}{2}}\tanh(\gamma l)} \qquad (1)$$

and $\varepsilon = \varepsilon_1 - j\varepsilon_2$, with ε_1 and ε_2 respectively the dielectric permittivity and loss, $\gamma = j\omega\varepsilon^{\frac{1}{2}}/c, j^2 = -1$, $\omega = 2\pi \times$ frequency, c is the velocity of light in free space and l is the physical length of the coaxial line. Measurements were performed using a Hewlett Packard 8753A vector network analyser connected to a HP 85044A transmission set and calibrated with a HP 85032B standard termination set. Using this configuration it is possible to measure the reflection coefficient of the line over the frequency range 300 kHz to 3 GHz. Iterative fitting of the data to Equation 1 was achieved using the National Arithmetic Group (NAG) routine CO5NAF and allowed calculation of the dielectric constant and loss. The main contribution to the errors arises from the precision in phase measurement giving rise to largest errors at low frequency.

3. Results and discussion

This study aims to explore changes in the dielectric properties of various forms of aluminium oxide on exposure to moisture.

3.1. Water sorption on dried γ-alumina

After 1 h exposure to water vapour at 100% RH, only a small increase in ε'' was observed at the low frequency end of the spectrum, with no corresponding increase in ε'. This type of behaviour is indicative of surface water which is forming a conducting layer but is not bound to the surface. After 15 h, water has reacted with the oxide to give a marked increase in both ε' and ε'', Fig. 1. The conversion of oxide to hydroxide will lead to a dipole relaxation located at 100 kHz and appearance of a dielectric dispersion in the megahertz region. After 24 h exposure there is development of a feature in the dielectric permittivity and loss at 7×10^5 Hz. After three days further exposure a shift in the dielectric permittivity and loss occurs leading to a definite feature at *ca.* 3×10^6 Hz, Fig. 1, and increase in the tail at lower frequencies. Further exposure for seven days increases only slightly the lower frequency tail. The expected correspondence between ε' and ε'' for a single dipole relaxation process is observed.

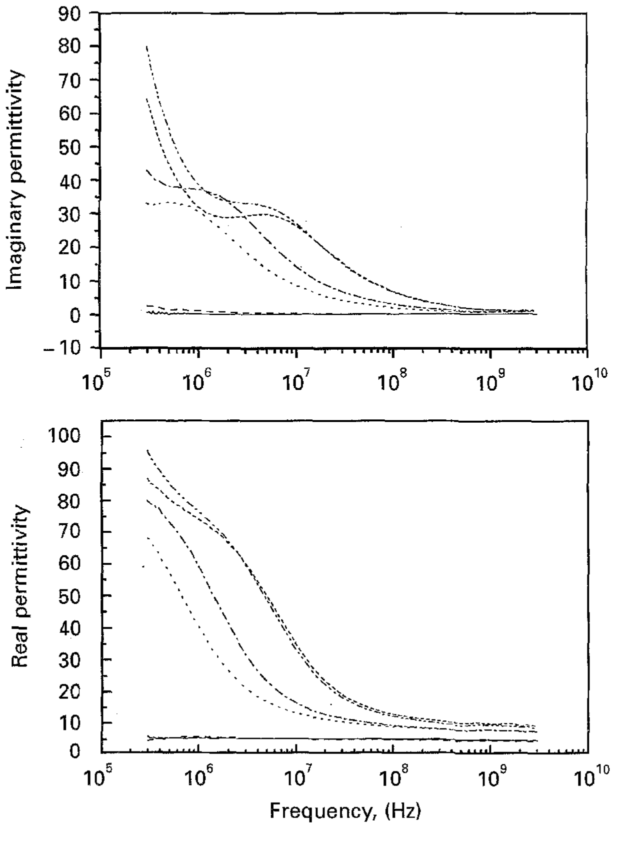

Figure 1 Dielectric properties of γ alumina as a function of time of exposure to 100% relative humidity. Key: 0. h, 1 h, 15 h, 24 h, 3 days, 7 days.

Gravimetric changes in the γ-alumina with exposure to water vapour, Fig. 2, can be divided into three regions. A very rapid sorption of water occurs during the first hour, then uptake increases more slowly reaching *ca.* 0.5 mole H_2O per Al_2O_3 in one day, after which the sorption increases very slowly. A plot of sorption versus the square root of time, indicates that the process was non-Fickian.

The non-porous γ-alumina has an area of *ca.* $100\ m^2\,g^{-1}$ and the initial sorption process corresponds to the very fast uptake of a monolayer of water, 0.16 mole $H_2O:Al_2O_3$. Dry alumina absorbs a 0.5 monolayer of H_2O to give a monolayer of surface hydroxyl groups and the new surface will have a high affinity for water and can react to give surface oxide–hydroxide. The dielectric constant and loss are not affected significantly at this stage in the mega hertz region, because the dielectric process associated with hydroxyl rotation occurs at frequencies in the kilo hertz region [13].

Further sorption requires build-up of water on the surface and/or conversion of subsurface oxide to oxide–hydroxide and involves absorption of water well beyond monolayer coverage. During this process a loss peak at 1.5×10^6 Hz develops associated with loosely bound water to the surface oxide–hydroxide layer and physically may have a gel like form.

Subsequent sorption only increases the water content by 0.08 mole H_2O per Al_2O_3, but the dielectric loss showed major changes, with a shift in the peak maximum to higher frequency and an increase in intensity at low frequency. The formation of sub surface oxide–hydroxide requires diffusion of water through the surface oxide and expansion of the outer layer. This process will be slow, giving a build-up of hydrated surface structure. The latter will contain loosely bound water so shifting the dielectric loss to higher frequencies. Unbound water in capillaries and voids will exhibit a relaxation at *ca.* 18 GHz and is above the range of this study [17]. Dielectric data for γ-alumina exposed to 50% RH are similar to those for γ-alumina hydrated at 100% RH, except at the highest levels of exposure, Fig. 3.

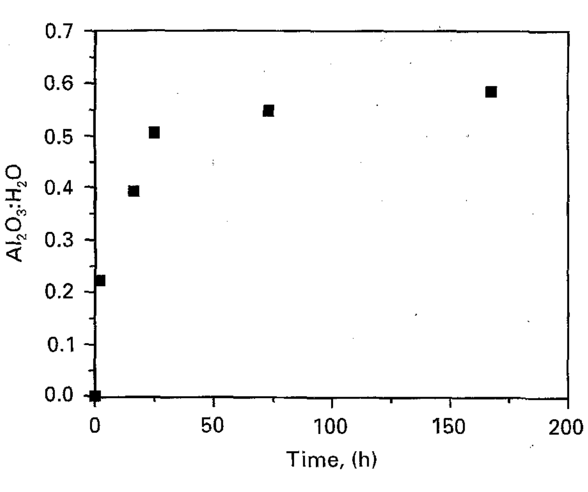

Figure 2 Water absorption curves for γ alumina in an atmosphere of 100% humidity at 293 K.

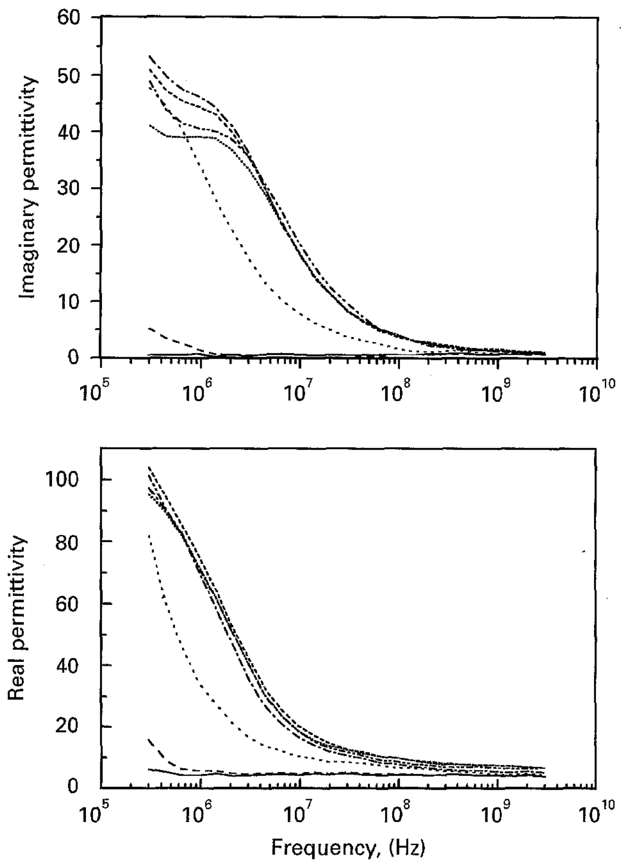

Figure 3 Dielectric spectra for γ alumina as a function of time of exposure at 50% relative humidity. Key: (—) 0 hours, (– –) 2 hours, (---) 17 hours, (———) 2 days, (————) 5 days, (–––) 14 days, (----) 36 days.

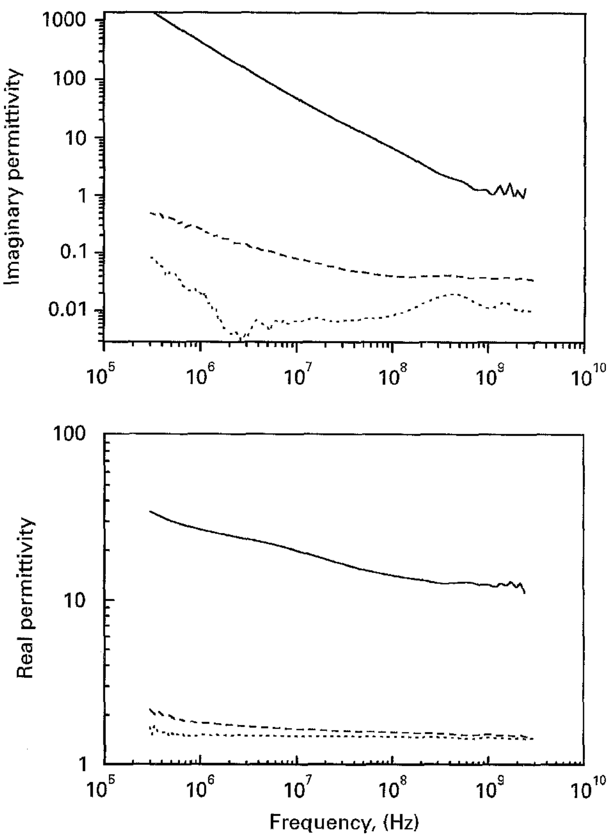

Figure 4 Dielectric properties of (—) 'wet' γ alumina after boiling in water for 1 h and its dehydration at (––) 373 and (----) 473 K.

3.2. Dehydration of 'wet' γ-alumina

A sample of γ-alumina boiled in water for 1 h, designated 'wet' γ-alumina with a mole ratio of $H_2O:Al_2O_3$ of 5.6:1 was prepared. The value of ε″, Fig. 4, is much greater than 1000 at 300 kHz indicative of a d.c. conduction process, which can be attributed to the formation of a continuous film of water between particles and masks contributions from other relaxation processes. The 'wet' γ-alumina was dried overnight at 373 K and then at 473 K and shows a massive reduction in both ε′ and ε″, Fig. 4. Gravimetric analysis indicates water contents of 0.5:1 and 0.4:1 for $H_2O:Al_2O_3$ at 373 and 473 K respectively. The γ-alumina hydrated for 24 h sorbed 0.5:1 of $H_2O:Al_2O_3$ and exhibits a high dielectric permittivity, whereas dehydrated alumina with a similar water content has a dielectric permittivity of below 2. The log–log plot, Fig. 4 for the most highly hydrated sample obeys the power law $\varepsilon'(\omega) \propto \omega^{-0.92}$ which implies a conduction type of mechanism. The surface of the particles at this point may be assumed to have in excess of a monolayer of sorbed water molecules.

The sorbed water can exist in tightly bound forms which do not have a significant dielectric signal, generate hydroxide which relaxes in the kilohertz region, form a loosely bound-physically absorbed conducting surface layer or a gel like structure in which case they exhibit a dielectric relaxation process in the mega hertz region.

3.3. Dielectric relaxation properties of BAY, GIB and BOE

The gravimetric analysis of BAY, GIB and BOE, Table I, are in reasonable agreement with the theoretical formulae except for BOE, which retained a large excess of water. The dielectric permittivity and losses of these materials, Fig. 5, are relatively low and decrease to high frequency. A correlation between the measured water content and the magnitude of ε′ and ε″ appears to exist. The water contents of these

TABLE I Water content of various aluminas

Oxide	Weight $\%H_2O$		$Al_2O_3:H_2O$	
	Actual	Theoretical	Actual	Theoretical
Gelatinous Boehmite	47.9	18.7–24	1:5.2	1:1.15
Bayerite	31.3	34.6	1:2.6	1:3.0
Gibbsite	36.7	34.6	1:3.9	1:3.0

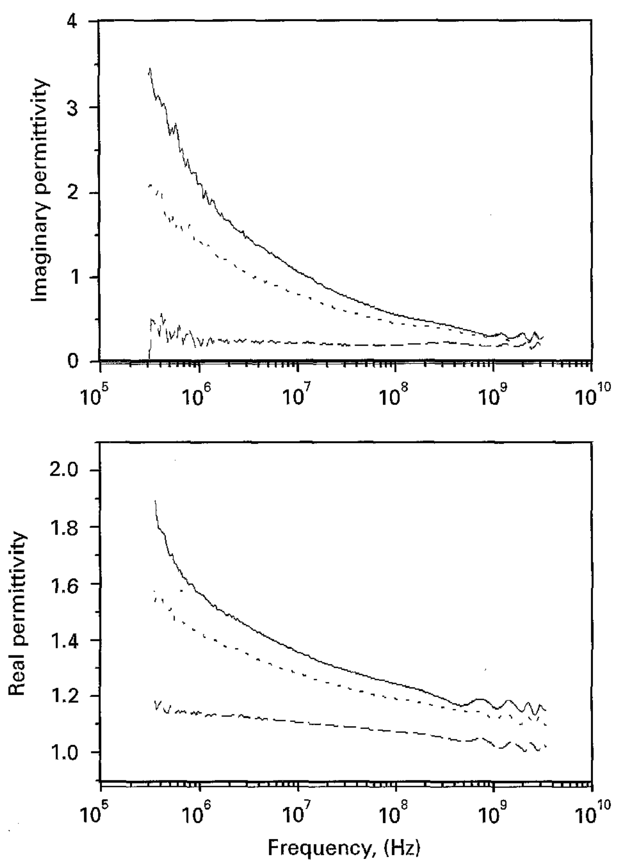

Figure 5 Comparison of the dielectric characteristics of the three different forms of aluminium oxide. Key: (—) Boehmite % H_2O–47.9%, (– – –) Bayerite % H_2O–31.3%, (-----) Gibbsite % H_2O–36.7%.

materials are considerably higher than those for the most hydrated γ-alumina but the values of ε′ and ε″ are much less. These results suggest that 'water' is locked into the matrix, resulting in a negligible dielectric response, similar to the effect of dehydrating the 'wet' γ-alumina which is surprising in view of the especially high water content of BOE.

3.3.1. Hydration of BAY, GIB and BOE

These materials were exposed to water vapour at 50% relative humidity, Fig. 6. The dielectric permittivity shows a broad response which increases in intensity with sorption. Compared to hydrated γ-alumina there is a more gradual decrease in the locus of the dielectric process at high frequency. The dielectric loss similarly shows a broad response, which increases with the level of sorption. At higher levels of sorption there is a marked increase in the lower frequency loss spectrum, with little change at higher frequencies indicating the absence of water trapped in capillaries.

GIB, shows a similar loss spectrum to BAY, Fig. 6, and there is evidence of an increase at low frequency in the dielectric permittivity on long exposure. For BOE, ε′ and ε″ increase at low frequencies at high sorption levels, Fig. 6.

The gravimetric changes with exposure for the three materials, Fig. 7, are Fickian, in contrast to that for γ-alumina. Dramatic changes in the dielectric ressponses on hydration are produced by small increase

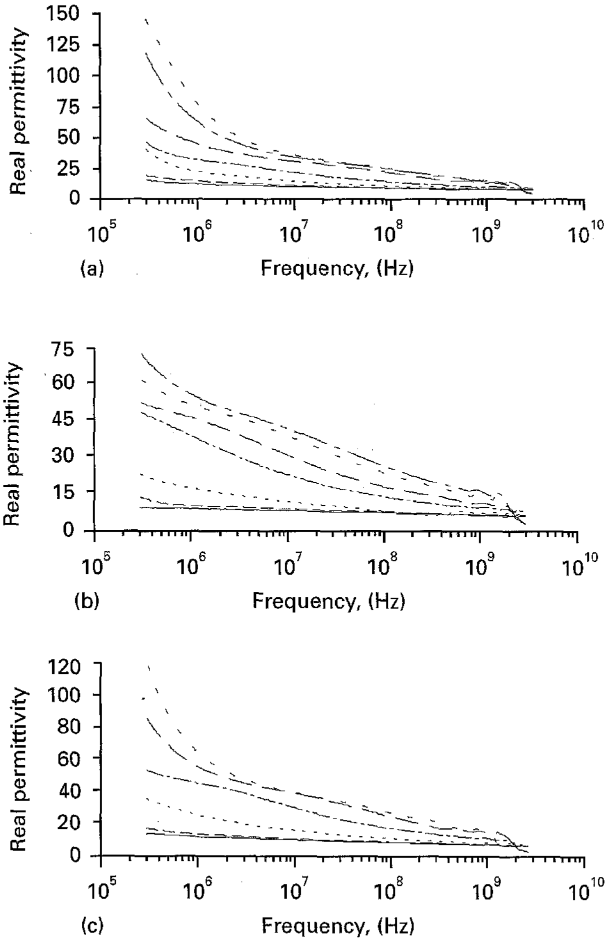

Figure 6(a) Water uptake by Bayerite at 50% relative humidity and 293 K. Key: (—) 0 h, (– – –) 4.5 h, (–·–·) 21.5 h, (– - –) 48 h, (– –) 72 h, (– –) 7 days, (– · –) 16 days. (b) Water uptake by Boehmite at 50% relative humidity and 293 K. Key: (—) 0 h, (– –) 17 h, (–·–·) 24 h, (– - –) 47 h, (– –) 8 days, (– –) 21 days, (– – –) 37 days. (c) Water uptake by Gibbsite at 50% relative humidity and 293 K. Key: (—) 0 h, (– – –) 4.5 h, (----) 21.5 h, (– - –) 48 h, (– –) 7 days, (– – –) 24 days.

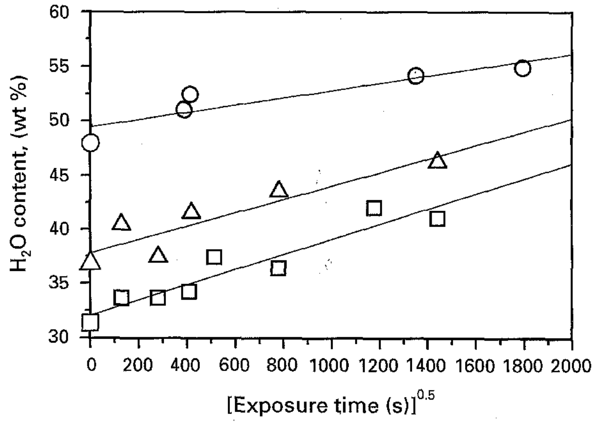

Figure 7 Variation of the water uptake with time for the three oxides. Key: (○) Boehmite, (□) Bayerite, (△) Gibbsite.

in the overall water content. The relationship between the dielectric constant and the exposure can be expressed as a plot of the change in the amplitude of ε′ at 400 kHz i.e. a measure of all the dipoles contributing above 400 kHz, against the square root of exposure time, Fig. 8, for BAY. The initial sorption produces little effect and the slope of the dielectric increment increases to give an almost linear region. Similar

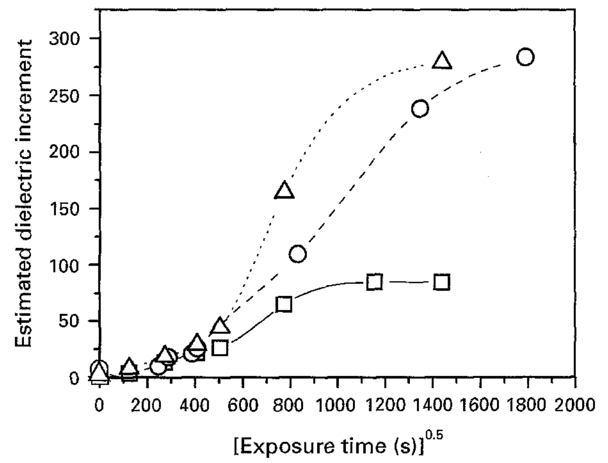

Figure 8 Variation of the dielectric increment at 400 kHz with time for the three oxides. Key: (○) Boehmite, (□) Bayerite, (△) Gibbsite.

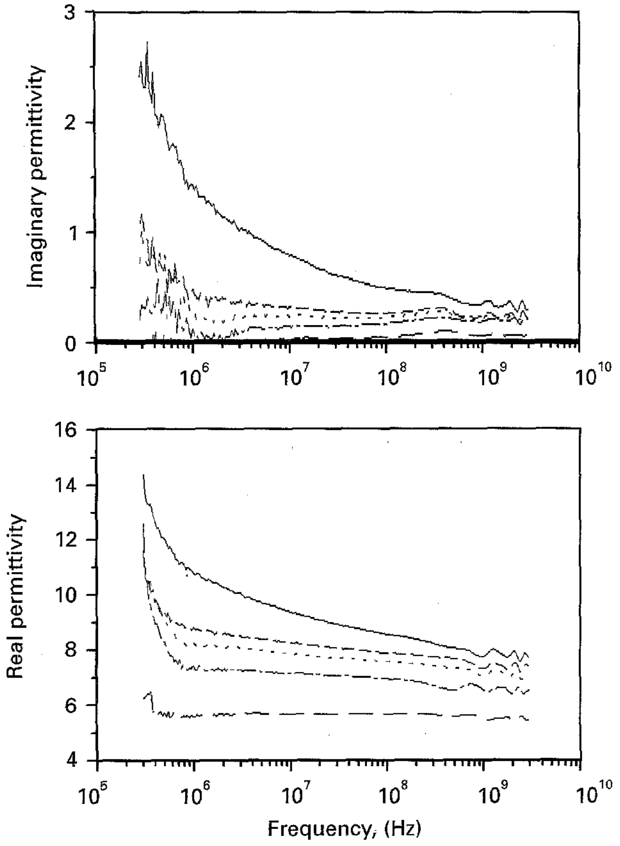

Figure 9 Dielectric spectra for Bayerite during the dehydration process. Key: (—) 2 h at 373 K (32.3%), (– – –) 2 h at 423 K (32.1%), (---) 2 h at 473 K (29.9%), (———) 2 h at 523 K (21.7%), (–·–) 2 h at 773 K.

behaviour is observed with GIB and BOE, Fig. 8. Since these materials have been dried at 423 K before use, the initial sorption would replace water desorbed from the material. Desorption would leave an interactive surface which would strongly bind the newly sorbed water. After this stage further sorbed water would be less tightly bound and would more effectively contribute to the dielectric increment.

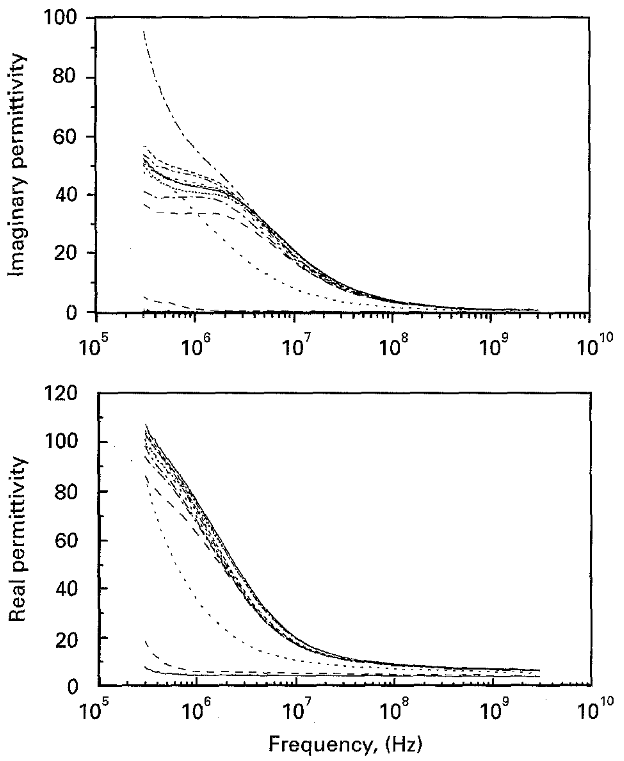

Figure 10 Dielectric spectra for $H_2N(CH_2)_3Si(OC_2H_5)_3$ coupled alumina as a function of time at 50% relative humidity. Key: (—) 0 h, (–·–) 2 h, (–··–) 3.5 h, (-----) 1 day, (— —) 5 days, (------) 7 days, (---) 12 days, (–·–) 13 days, (—) 14 days.

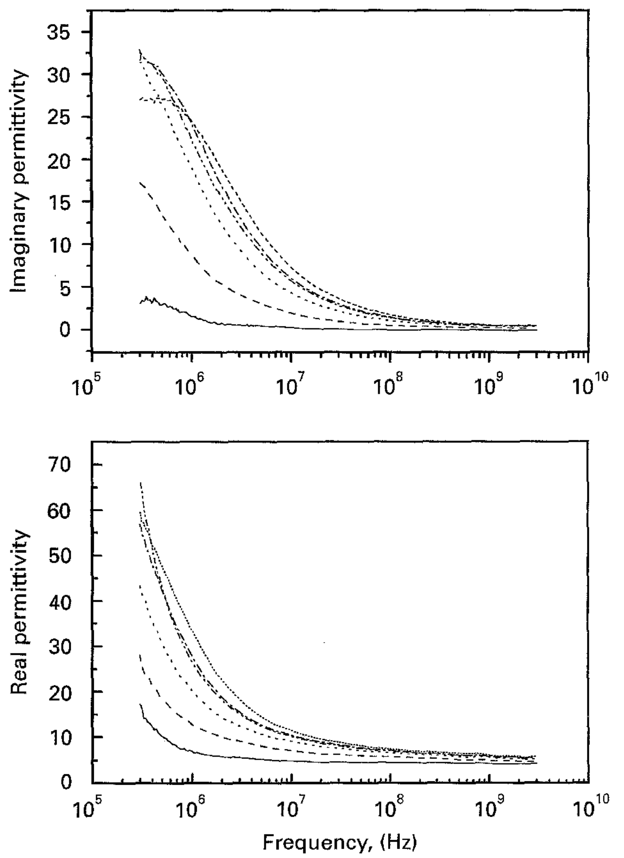

Figure 11 Dielectric spectra for $CH_3Si(OCH_3)_3$ coupled alumina as a function of time at 50% relative humidity. Key: (—) 0 h, (– – –) 2 h, (----) 20 h, (–·–) 7 days, (–··–) 8 days, (······) 28 days.

3.3.2. Dehydration of BAY, GIB and BOE

Heating of hydrated BAY, GIB and BOE indicates that even after 2 h at 373 K a large decrease in ε' and ε'' is observed, Fig. 9, and continues to decrease on further heating and GIB and BOE exhibit similar behaviour.

3.4. Silyl coated alumina

Coating the surface of alumina metal components with silyl compounds is known to provide protection from the effects of water vapour. Samples of dried γ-alumina coated with silane coupling agents; γ-aminopropyl–triethoxysilane and methyl–trimethoxysilane were used as model systems, Fig. 10. Changes in the dielectric properties of the silylated samples during exposure to water vapour, Fig. 10 indicated that exposure for 17 h of the uncoated sample shows evidence of a maximum at *ca.* 3×10^6 Hz, Fig. 3, the coated samples show a loss maximum at *ca.* 10^6 Hz, with **no indication of the lower frequency tail.** Adsorption measurements showed that the uptake of water after 8 days at 50% relative humidity was 4% for the uncoated γ-alumina compared to only 1% for the uncoated samples and are clear evidence for the decrease in reactivity to water of the silylated coated material.

The dielectric data indicates that the silyl overlayer hinders the formation of the hydrated layer and inhibits the development of the more complex oxide hydroxide layer which occurs with the unprotected oxide.

4. Conclusions

The dielectric response in the mega hertz region for these hydrated aluminas is not quantitative, the dominant process being associated with water in a loosely bound form associated with hydroxide-oxide layers. Water in these systems exists in a number of forms:-

(1) 'silent' water which does not have a dielectric signature and is trapped in the oxide as a hydrate.
(ii) water can react with the oxide to form a hydroxide which has a distinct dielectric relaxation centred at 10 kHz and associated with OH rotation.
iii) water in the hydrated surface layers which relaxes at about a megahertz and is the dominant feature in these studies.
(iv) water which is trapped in capillaries or voids and will relax at about 12 GHz, and does not make a significant contribution to the dielectric properties of the aluminas in this case.
(v) water which is condensed on to the surface and forms a conducting path around the particles and appears as a high value of ε'' and is associated with ionic conduction.

These studies have indicated the complexity of the processes occurring on hydration of the oxide. Formation of this phase is inhibited by coating the alumina with a silyl coupling agent.

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