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Comparison of the hydration behaviour of various aluminium oxides powders – A dielectric relaxation study



David Hayward, Richard A. Pethrick*

WestCHEM, Department and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

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ABSTRACT

Dielectric measurements are reported for alpha and gamma alumina powders exposed to moisture for various periods of time, temperatures and dried in air for various times. The observed behaviour reflects the nature of the surface oxide, topography of the oxide and is influenced by their ability to change as a consequence of thermal treatment. This study highlights the importance of the nature of the surface oxide on the processes of moisture penetration in aluminium bonded structures.

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1. Introduction

Electrochemical Impedance [EIS] and Dielectric Relaxation Spectroscopies [DRS] are powerful tools for the monitoring of moisture ingress into thermally aged adhesive bonded structures [1]. High frequency microwave techniques allow the detection of changes in the thickness of the adhesive bond, location of voids and the presence of kissing bonds [2–5]. Hydrothermal ageing of aluminium epoxy adhesive bonds are accompanied by significant changes in the dielectric characteristics of the joint [2]. Water has a large dipole and is easily detected even at relatively low levels within the bond line and can bind itself to polar groups in the matrix or segregate into nanoscale voids [6]. Interaction of moisture with the adhesive will produce plasticization, lowering the glass transition temperature [T_g] which aids further moisture uptake and modifies the mechanical properties of the joint.

Hydrothermal ageing of a typical metal joint occurs in three stages; initial moisture uptake at the edge of the joint in both the exposed adhesive and oxide layers. This stage is usually reversible and it is possible to recover much of the original strength of a joint by careful heat treatment [2]. The second stage is the non-reversible moisture absorption in which the adhesive is swollen and hydration of the oxide occurs. As these processes proceed the mechanical strength of the joint is lost. Finally, hydration of the oxide layer and swelling reach a point at which total bond failure occurs.

For high strength joints, oxides are often carefully grown on the surface of the adherent to enhance the 'lock and key' contribution

to the bonding mechanism. The dielectric technique has the ability to probe the changes in the interfacial oxide layer and allow identification of the stage in the ageing process when moisture ingress has become critical.

The nature of the surface oxide which is created depends on method of preparation; acid etching, grit blasting, etc. Differences in the structures of various acid grown oxides have been extensively studied [7] and produce differences in bond durability [8–13]. The bond strength depends on the balance between the adherent interacting with the adhesive through physical and chemical interactions and contributions from the 'lock and key' mechanism which depends on the nature of the oxide created [14–16]. Enhancement of the bond strength can be achieved by the use of suitable surface treatments [13,14].

Dielectric analysis has shown that catastrophic bond loss is often associated with extensive hydration of the surface oxide converting a stable oxide to a less stable form. The precise nature of the oxide on the adherent is usually not well defined however the analysis clearly indicates that significant changes are occurring [2,10–12].

The oxide Al_2O_3 created by pre-treatment of aluminium will be a mix of the oxide and various hydroxides and is best described as a combinations of gibbsite ($Al(OH)_3$), gamma alumina ($\gamma-AlO(OH)$), and alpha alumina ($\alpha-AlO(OH)$). γ alumina has a tetragonally deformed spine1 lattices and usually a higher surface area and is weaker than that of α alumina.

High frequency dielectric analysis indicates that water in these systems exists in a number of forms [18]:- (i) '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 [17,18]; (iii) water in the hydrated

* Corresponding author.

E-mail address: r.a.pethrick@strath.ac.uk (R.A. Pethrick).

surface layers which relaxes at about one megahertz; (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 alumina; (v) water which is condensed on to the surface and forms a conducting path around the particles and appears as a high value of dielectric loss [ϵ''] and is associated with ionic conduction.

The aim of this paper is to explore where there are differences between the dielectric signatures of α and γ aluminium oxides when absorbing moisture and whether or not they behave the same on thermal processing – drying. Earlier studies have probed the dielectric behaviour of alumina granules to absorb water and identified dipole processes at ~ 1 kHz and associated with water absorbed onto the surface [17,18].

2. Experimental

2.1. Materials

The aluminium oxide powders used were obtained from Degussa UK and had a particle size between 10–80 μm allowing easy separation by filtration when exposed to moisture. The powders were used as received and are representative of the richness of environments likely to be found in a real bonding situation [18,19].

2.2. Dielectric measurements

Dielectric measurements were carried out over the frequency range from 10^{-3} Hz to 65 kHz using an automatic measuring bridge which consisted of a Solatron 1250A Frequency Response Analyser (FRA) incorporated in a Nova Control Dielectric Spectrometer and has been described previously [20,21]. The frequency range from 10^{-3} Hz to 65 kHz has been shown to be characteristics of the oxide behaviour [17,18]. The cell was constructed from two polished aluminium bars 2×4 cm, separated by a polyethylene spacer to ensure a constant electrode separation was maintained. The treated powders were packed into the cell and measurements were performed at room temperature ($\sim 20^\circ\text{C}$). The cell thickness was measured at several points and the average found to be $0.17 \text{ mm} \pm 0.05 \text{ mm}$.

3. Results and discussion

3.1. Comparison of α and γ alumina

Samples of α and γ alumina were immersed at room temperature in deionised water for one hour and then dried in an air oven for 10 days. The dielectric loss curves (ϵ'') versus frequency, Fig. 1 [A] exhibits large values below 10 Hz indicative of a Maxwell Wagner Sillers [MWS] type of loss [22–24]. Hydrated aluminium ions under the action of the slowly changing applied field will migrate to the electrodes and produce large MWS polarization effects. Both oxides exhibit a MWS process but at different frequencies reflecting the different structures from which they arise. The MWS loss can be modelled provided the structure of the hetero-phase is known [22–25]. Model studies of conducting inclusions in a less conducting phase [25] have shown that in the ideal situation the structure of the material can be obtained from this data. In the current situation, the oxide surface will be more conducting than the particles and this situation has been modelled using a benzoic acid doped styrene-butadiene-styrene triblock phase [24]. However the heterogeneous and richness of structure of the surface oxide makes such modelling impossible at this time.

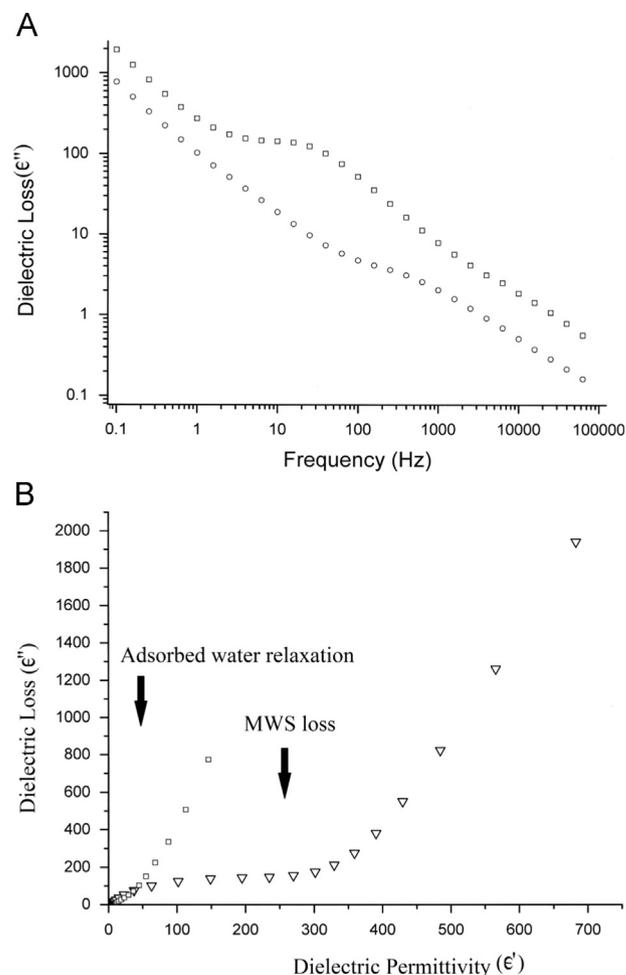


Fig. 1. Dielectric loss (ϵ'') [A] and dielectric loss (ϵ'') versus dielectric permittivity (ϵ') – Cole–Cole plots [B]. Key:- [A] \square – α -alumina-immersed at room temperature (r.t.) in H_2O for 1 h then dried in air for 10 days; \circ – γ -alumina-immersed in r.t. H_2O for 1 h then dried in air for 10 days; [B] Δ – α -alumina; \square – γ -alumina.

The Cole–Cole complex plane plot [26] in which the dielectric loss (ϵ'') is plotted against the dielectric permittivity (ϵ'), Fig. 1[B] indicates that at high frequency, both materials display a common feature indicative of water interacting with surface hydroxyl groups, shown as the small relaxation feature closer to the axis of the plot. At lower frequency, the α alumina exhibits a larger feature which reflects a large MWS loss and indicates the conduction is easier at the interface with α alumina than with γ alumina. The α alumina is stable at all temperatures and has a trigonal structure with Al ions in 2/3 of the octahedral interstitial positions. These dense particles are less able to trap hydrated aluminium ions, whereas the γ alumina is a defect cubic spinel structure which can trap the mobile hydrated cations and as a consequence will have a lower surface conductivity and a smaller MWS feature.

3.2. Influence of measurement conditions on the data obtained

The measurement applies a voltage across the electrode system and has the potential of inducing electrochemistry and hence change in the oxide. Observations were made using 4, 1 and 0.1 V, Fig. 2. The oxidation–reduction potential for aluminium is, $E^\circ = 2.30 \text{ V}$ [27] and corresponds to the electrochemical process:- $\text{Al} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3 + 3\text{e}^-$. Whilst at high frequency the time for polarization is very short and hence changes in the nature of the oxide will be unable to occur, at low frequency where the field changes will take of the order of seconds or longer, electrochemistry can occur and will

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