JOURNAL OF MATERIALS SCIENCE 1 (1966) 186-198

A Review of the Recent Literature on the Dielectric Properties and Sintering of Alumina

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1. Introduction

This review of recent literature has been made with particular reference to the application of polycrystalline sintered alumina to radome problems.

A radome may be described briefly as a protective housing for radar receiving and transmitting equipment. The shape, design, and material of construction will depend upon the particular environmental conditions. In general, the material should be homogeneous with respect to permittivity and dielectric loss at all temperatures. As speeds of aircraft and missiles have increased, the temperatures encountered have passed beyond the limit of organic radome materials. Thus, the usefulness of these materials has decreased and attention has therefore been directed to materials capable of withstanding the higher temperatures. Alumina is such a material.

A very comprehensive survey of the radome field has been made by Pedigo [1], of the Coors Porcelain Co. He describes the manufacturing and testing of radomes from Coors aluminas AD99 and AD995; mechanical properties, tensile and flexural strength, dielectric properties, impact capacity, thermal shock, and rain erosion are discussed. Details of radome design and development during and since World War II are described in "Radar Scanners and Radomes" [2]. The biannual symposia on electromagnetic windows held at Ohio in 1962 and 1964 [3, 4] are also valuable sources of general information on American progress in radome development and design.

Details of stagnation temperatures of missiles are given by Ireland and Tarrants [5], e.g.

Mach 2.7	550° F	300° C
Mach 5.0	2000° F	1100° C
Mach 10	4500 to 6000° F	2500 to 3300° C

They mention aluminas, pyroceram, beryllia, and slip-cast fused silica, and comment on the serious problem of rain erosion damage of ceramics.

2. Alumina and Other Materials

The most up-to-date reference works on properties of refractory materials are reports by Burnett [6], and by Hague *et al* [7]. These reports cover a vast collection of materials ranging through oxides, carbides, nitrides, etc. Such properties as specific heat, thermal conductivity, elasticity, density, etc. are detailed with source references. Another excellent survey is one by Smiley *et al* [8] who deals almost entirely with mechanical properties; over 1200 references are listed. A review which deals with mechanical and dielectric properties of miscellaneous ceramics, particularly relevant to radomes, is by Koenig and Smoke [9]. Alumina is described as becoming increasingly important; magnesia is of less importance because of fabrication difficulties.

A survey of electroceramics has been made by Singer [10] who reviews alumina as well as the less well-known ceramics. Mention is made of Lucalox, steatite, forsterite, quartzite, and seawater magnesia; a brief discussion is given of thin wall, half-wave length, and sandwich radomes.

Beryllia has very desirable aerospace properties but suffers from serious rain erosion, particularly at high temperature [11]. It has been used as a radome material [12] and the authors claim that under carefully controlled conditions, BeO of 45,000 lb/in^2 flexural strength can be made; this strength is comparable with that of alumina. A number of references [3, 4, 13] to beryllia radome development is referred to in the paper. The literature on the preparation, fabrication, and properties of beryllia is extensive and several reviews have been published recently [14, 15]. Other inorganic materials of interest in radome construction include magnesium spinel [16], silica [17, 18] and silicon nitride [19].

An excellent survey of properties of alumina, with a comprehensive index to all literature on electrical and electronic properties, has recently been issued [20]; 92 commercial, sintered, polycrystalline alumina ceramics are reported upon, ranging in purity from 80 to 100%. The Aluminium Company of America (ALCOA) have produced another useful survey [21] of the electrical and mechanical properties of aluminas, together with X-ray data for the α, δ, γ, η, θ and χ forms. Alumina has been extensively studied in the field of high temperature ceramics and as a dielectric material; the discussion of these aspects is dealt with in later sections.

3. General References on Dielectrics

The literature has been abstracted with particular reference to dielectrics and low power sinusoidal fields.

Birks [22], Kingery [23], McPhee [24], Kuffel [25], Hochschild [26], Drexler [27], Bauman [28], and Anderson [29] have published introductory articles on dielectrics. Von Hippel's [30, 31] two books are excellent from the point of view of measurement of dielectric properties, as well as giving a good grounding in the theory. The series of books, "Progress in Dielectrics", also contains excellent reviews of the areas of dielectric polarisation and absorption [32, 33], although they are generally concerned with relatively simple systems.

Instrumentation, and measurement of dielectrics, are dealt with in papers by Westphal [34-37]; data are given for multicrystalline bodies of Al_2O_3, BeO, MgO, Mg_2SiO_4, Ta_2O_5, BN, glass ceramics, and silica glass. Microwave losses are due partly to the charge transfer responsible for low frequency conductivity and to the vibration spectra of infrared absorption. Both effects are increased by the addition of impurities. McPhee [24] also mentions that dielectric properties are much more sensitive to impurities, forming techniques, and firing procedures than mechanical properties.

4. Effects of Impurities on Dielectric Properties

4.1. Commercial Ceramics

Almost all papers dealing with measurement of dielectric properties of ceramics deal indirectly with the effect of impurities, because, in the extreme, no material can be said to be absolutely free from impurity effects arising from fabrication procedures, etc. A number of papers on ceramics other than alumina will be mentioned.

Westphal [34-37] and Von Hippel [31, 38] have published many hundreds of tables of dielectric constant and loss tangent data for numerous compounds, inorganic and organic. The paper by Von Hippel and Westphal [38] includes a study of the loss characteristics of a "pure" ceramic of high and low density and of a ceramic of commercial purity (95.78% Al_2O_3). They show that the average loss factor k'' ($k'' = k' \tan \delta$) of the crystal is lower than that of the dense "pure" ceramic Coors AD99 (99% Al_2O_3) of 95.4% density. They suggest that the low density pure ceramic, Armour, 85.2% density and 99.8% Al_2O_3, was superior to single crystal alumina probably because poor contact between grains inhibited conductance. They also report that the commercial ceramic, Coors Al-200, proved to be so lossy that k' tripled by interfacial polarisation between room temperature and 500° C at 10^2 c/s. Other tables of dielectric properties have been published by Hall, Sanderson *et al* [39].

A similar paper dealing with the measurement of dielectric properties of alumina, mullite, aragonite, calcite, and barium sulphate is by de Keyser [40].

Kirillova [41] has examined the electrical properties of mullite ($3Al_2O_3.2SiO_2$) porcelains in detail. His general conclusions are that mullite, free from amorphous phase, has very low dielectric loss at 10^6 c/s and that tan δ depends upon the amount and composition of amorphous phase whose formation is due to impurities. Alkali oxides, which promote the formation of alumina-containing silicate glasses, have an appreciable effect on tan δ.

An interesting comparison of the dielectric properties at 2 to 25 Mc/s (25° C) of commercial aluminas including Coors, Wesgo, Gladding McBean, French Town Almanox, GECo (Lucalox) is made by Newlan [42]. Fused silicas, pyroceram, and beryllias are also covered. Newlan found that tan δ and dielectric constant (k') varied widely for similar compositions. The dielectric constant of Western Gold & Platinum Co (Wesgo) aluminas increased from 9.9 to 10.6 (pure sapphire) over the density range 3.70 to 3.85 g/cm^3. (No analytical data are given.) Tan δ for most of the commercial aluminas increased in a non-linear manner with temperature. Tan δ

for Lucalox, it was found, increased from 0.001 at 20° C to 0.0035 at 350° C for 215 Mc/s, and thereafter remained fairly constant up to 800° C. The manufacturers [43] claimed a dielectric constant of 9.9 and tan δ of 0.000025 at 20° C and 9720 Mc/s, density 3.98 g/cm^3 and purity 99.9%.

Other workers have examined aluminas in a similar way. Bowie [44] has measured dielectric constant and loss tangent of a US Stoneware product and Frenchtown 4462; the latter contained manganese dioxide, but its composition and density were not given. The dielectric constant (3000 Mc/s) was 8.7 up to 250° C and 8.9 at 850° C. The US Stoneware alumina was 95% alumina (density not given) and had k' of 8.2 and 8.4 at 250 and 800° C respectively. Tan δ values varied from about 0.001 to 0.1 over the temperature range 800 to 1400° C. Tierney *et al* [45] fabricated alumina from two samples of commercial (unnamed) 99.99% powder, as well as from their own powder produced by hydrolysis of carefully purified aluminium isopropoxide. The best electrical properties (k' and tan δ measured at 60 to 10^5 c/s at 100 to 500° C) were obtained for samples sintered in a graphite crucible induction heated in argon. When sintered in an alundum tube furnace the specimens were consistently bad. No details of density were given.

Florio [46] has measured both single crystal (Linde sapphire) and polycrystalline aluminas. Dielectric constant and tan δ were measured only at low frequencies (10^2 to 3×10^5 c/s) and at 900 to 1300° C. The polycrystalline alumina used was very impure (Fe 0.1%, Si 0.1%, Na 0.08%, Mg 0.1%, Ca 0.1%), and it was concluded that the observed dielectric losses were predominantly due to free electron conduction mechanisms. Bogoroditskii and Polyakov [47] prefer to attribute the variations in dielectric loss of alumina ceramics to the formation of β-Al_2O_3 formed during oxidising calcination.

Parallel UK testing of commercial alumina ceramics has been carried out for the Ministry of Aviation [48, 49]; the British Ceramic Research Association is at present evaluating aluminas [50]. A symposium [51] was held recently to discuss the results.

The effect of water on the dielectric properties of alumina has been shown to be important. Tucker, Gibbs *et al* [52-55] have investigated the effect of humidity and sorbed ionic species (Na^+, H^+) upon electrical conductivity and dielectric loss of single crystal alumina. A peak in the dielectric loss versus temperature curve has been attributed to desorption of material [53]. It has been suggested that impurities can act as plugs along dislocation lines [54, 55].

Cohen [56] has reviewed electrical conductivity measurements of single crystal and polycrystalline alumina with particular reference to the discrepancies between measurements made by different authors.

Bussey [57] of the Radio Standards Physics Division of NBS has recently published a note on measurement and the effect of humidity on dielectric properties. For a glass ceramic, it is shown that relative humidity and surface contamination alter the apparent loss, presumably by lowering the surface resistivity of the specimen, but Bussey suggests that measurements can be made at low relative humidity (< 30%) without the need for corrections.

4.2. Pure Alumina Ceramics

The only papers and reports which deal directly with the problem of impurity effects on dielectric properties are those of Atlas *et al* [58-62], extending over the period 1959-61. The work is part of a larger programme leading towards the construction of radomes capable of operating over a wide range of temperatures. (A further goal was the accumulation of information showing how alumina compositions and fabrication variables influence loss tangent and dielectric constant.)

The initial phase of the work [58] was the preparation of a very high purity alumina ceramic, and then the preparation of ceramics containing trace concentrations of common impurity ions, alone and in combination. They report that a pure alumina was prepared from 99.999% aluminium, which was first converted to chloride then, using ammonia, to the hydroxide. The product was fired to 1400° C to produce α-alumina. The spectroanalysis was, in ppm: Si 35, Mg 21, Fe 10, Ca 6, Ni 5, Cr 3, Cu 2, Ag 1. Controlled additions of impurities were milled in with polystyrene balls in a polythene jar, but the alumina was not analysed before firing. A binding agent of 10% polyvinyl alcohol (PVA) was used before pressing at 7 to 10 ton/in.^{2} in steel dies. After drying in air the compacts were fired at 1900° C in argon (RF heater), and subsequently heated at 1900° C for 1 h in air or superheated steam. They say that attempts were made to increase density by cycling, but final maximum densities obtained ranged from 2.96 to 3.42 g/cm^3 (theoretical maximum is 3.974).

A comparison between the electrical properties of sapphire, a Kearfott alumina, and ceramic A6 is made by Atlas *et al* [58].

It is worthy of note that the cleaning treatment of diamond ground discs for dielectric measurement involved a wash with dilute aqua regia, followed by boiling in water, then drying at 900° C in air and sometimes even at 1900° C in oxygen, hydrogen, or steam for 20 to 24 h.

The second part of the work by Atlas and Nagoa [59] describes in detail the batch analyses of the calcined aluminas used; twenty-three batches were analysed for Si, Ti, Fe, Cr, Mg, Ca, Ni, Cu, Co, Ag. They report that close control of chemical compositions was very difficult to maintain. Contamination of the discs was a serious problem and consequently it was decided to accept whatever composition came from the furnace and analyse the electrical data by the use of statistical methods. Various binders were tried: aluminium chloride, PVA, and an acrylic resin. PVA was eventually chosen. In the later period of the programme, firing was carried out in a Zircoa gas-oxygen furnace, the specimens being fired in air at 1930 to 1960° C for an unspecified time. However, the highest densities obtained were still only about 3.7 g/cm^3. Atlas and Nagao suggest that hot pressing might be used to attain theoretical density, but they point out that carbon from graphite dies would be undesirable. A preliminary experiment showed them that alumina hot pressed in argon yielded a white product. They also propose the addition of aluminium metal, based upon the reasoning that: (a) it will create oxygen defects in the alumina structure, thus accelerating sintering rates; and (b) some of the mobile aluminium may diffuse into the pores and subsequently be converted to the oxide. They say that the fired alumina bodies had grain sizes varying from 15 to 110 μm with most of the residual porosity at the grain boundaries. Introduction of carbon monoxide into the furnace caused the formation of grains of up to 2 mm in size. The "pure" alumina ceramics prepared were often yellow in colour and this was attributed to the presence of Fe^{2+} (and/or Ni^{2+}) and Fe^{3+} impurities. Additions of 100 ppm Si^{4+} prevent discolouration, and these workers suggest that the pure white colour of commercial aluminas was a result of the almost universal presence of SiO_2 as a major impurity. Density data showed that low concentrations of most of the impurity ions exerted no significant densifying action. MgO, however, they say, has a definite effect (although this is not directly obvious from an examination of the data presented).

According to these workers, analysis of the fired alumina ceramics proved to be the most serious problem of all. It was not uncommon for analysis of Ca and Mg to give values varying by ± 200 to ± 400%. Fe, Ti, and Cr were also troublesome and very often gave analyses 200 to 300% higher than the amounts actually introduced. Atlas and Nagao discuss in considerable detail the effects which the impurities, Si, Mg, Ca, Ti, Fe, and Cr, have on the dielectric properties. They found that Si caused the greatest rise in tan δ and Mg, Ti, Ca, Cr, and Fe had progressively decreasing effects. Electronic conduction was considered to be the primary loss mechanism operating at 500° C and 10^5 c/s. From the almost linear form of the k'' versus frequency graph, it was possible for the authors to calculate the dielectric conductivity, σ, using the equation

$$\sigma = \frac{fk' \tan \delta}{1.8 \times 10^{12}} \text{ ohm}^{-1} \text{ cm}^{-1}$$

and to calculate the energy of activation of conduction by plotting log σ against $1/T$. The plots were not linear, which suggested the existence of more than one conduction mechanism. The highest value of activation energy was given by Mg (2.0 eV) compared to 1.2 to 1.3 eV for Si, Ti, and Fe.

Polarisation effects are discussed in some detail. It is stated that dispersion of k' is approximately proportional to tan δ at 10^6 c/s and 500° C and therefore to the electronic conductivity of the bulk ceramic. The anomalous behaviour of Mg^{2+}, which leads to greater dispersion of k', may be attributed to the greater mobility of this smaller ion. Interfacial polarisation is suggested as a loss mechanism, which in the case of Si^{4+} occurs because of enhanced electron mobility at the grain boundaries, a mechanism which is also proposed by Pappis and Kingery [63]. Atlas and Nagao [59] suggest that increase of dielectric constant, k', with temperature is a function only of the alumina, and that impurities have practically no effect on the temperature coefficient of k'. They suggest that a ceramic based on alumina, but containing a second material with negative temperature coefficient, might be a solution to the difficulty. Compositions of alumina with $CaTiO_3$ and $SrTiO_3$ were calculated from Lichtenecker's equation. Preliminary experiments showed them that tan δ was very high, 0.04: this may be acceptable, since Pyroceram has tan $\delta = 0.1$.

The final report [60] in this series by Atlas *et al* describes attempts to hot press some of the "pure" alumina and also a Gulton Alucer MC Alumina. Reference is made to the higher dielectric loss of hot-pressed aluminas (compared to sintered aluminas), which is attributed to the presence of a small amount of carbon. Westphal [35] lists one with 0.1% of carbon but whose tan δ increased only from 0.0003 to 0.001 over 700° C at 10^{10} c/s. The carbon is described as being finely divided, but its chemical form is not stated. Atlas and Nakamura [60] suggest that vacuum hot pressing might overcome the increase in dissipation factor; but, because of experimental difficulties, they say they finally compromised by hot pressing in a flowing argon atmosphere. The final products were always grey in colour, but this could be removed by firing in oxygen at 1500° C overnight, or at 1700° C for 7 h. The final density achieved was never more than 3.84 g/cm^3, and was often accompanied by excessive grain growth, whereas the Alucer alumina always gave 3.97 g/cm^3. The dielectric measurements showed that the hot-pressed aluminas were lossier than cold pressed and sintered products. This they attributed partly to the increase of Si, Ca, and Fe impurities which migrated from the graphite to the ceramic. The investigations into titanate-alumina ceramics were continued and the temperature variation of k' at 4×10^9 c/s was studied for several mixtures. It was found that additions of $SrTiO_3$ were successful in lowering the temperature coefficient of dielectric constant. This report concludes with a summary of the three years work carried out, nearly all of which is published in the open literature [61, 62].

A very recent investigation of dielectric loss in alumina is reported by Snow and Cutler [64]. They studied dielectric loss in sapphire and single crystal MgO over the frequency range 0.2 to 100 kc/s for the temperature 25 to 800° C. They report that the loss was dependent on the atmosphere, and it could be reduced by either rinsing in ether or by using dry argon in the sample chamber. These losses are believed to be due to physically adsorbed water. Broad loss peaks observable at 540° C in air were attributed to chemisorbed water; the relaxation time obeyed the equation

$$\tau = \tau_0 \, e^{\Delta H/RT}$$

where ΔH was 1.4 eV for both MgO and sapphire, and $\tau_0 = 1.6 \times 10^{-14}$ sec for MgO and 0.53×10^{-14} sec for sapphire. Peaks which could be explained on the basis of relaxation of cation vacancy-impurity complexes were not observed. Although the major portion of this work is concerned with loss data for MgO, it has important implications with regard to the dielectric behaviour of alumina.

4.3. Alumina-based Ceramics

Kato, Okuda *et al* [65, 66] have also investigated alumina porcelains as high frequency insulators. In the first paper, they describe their examination of three starting aluminas derived from the following: ammonium alum; Bayer process α-alumina; and Norton 38:900 alumina. The basic object of the investigation was to obtain an alumina replacement for the steatite and forsterite porcelains that are at present used for high frequency insulation. Kato and Okuda required a low temperature (1400° C) sintered ceramic and therefore made additions of 2% of each of MnO_2 and TiO_2 (Cutler *et al* [67] having already demonstrated that the sintering of aluminas could thus be modified). The Japanese workers showed that aluminium titanate was formed, although it was not detected by X-ray diffraction; they also assumed that manganese spinel ($MnO.Al_2O_3$) was formed. Physical properties, bending strength, and thermal conductivity were determined in addition to the dielectric constant and loss (at 1 Mc/s). The densities in general were low, 3.4 to 3.7 g/cm^3, and dielectric properties varied considerably. The best values for dielectric loss were shown with the Bayer alumina, the decomposition (alum) alumina being particularly bad. They attribute the poor values to the aluminium titanate.

The second paper [66] deals with the effects of certain oxide additives on the electrical properties of alumina ceramics. $Mg(OH)_2$, Co_3O_4, Fe_2O_3, Cr_2O_3, TiO_2, and MnO_2 were chosen because they appeared to exert the most satisfactory effects on sintering [67-69]*. The alumina used as a basic material was the Bayer

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*References quoted by Kato *et al* [66].

process material examined earlier [65]. They describe how the additives (2 to 5 %) were mixed by a wet method and then dried. Paraffin wax (6 %) was used as a binder before pressing at 1500 lb/in.^{2}; the product was then fired in a gas oven for 30 min at temperature. At the levels of the additions, they report that the sintering rates were in the order

$$MnO_2 > TiO_2 > Co_3O_4 \simeq Fe_2O_3 \simeq Mg(OH)_2$$

(The result for $Mg(OH)_2$ may seem to be in contradiction to Coble's work [70], but it must be remembered that the Japanese work was carried out at very high concentrations of MgO.) X-ray diffraction studies showed that free MgO was absent, spinel ($MgO.Al_2O_3$) and alumina only being detected. For the titania compositions only TiO_2 was detectable up to 1400° C, but beyond this temperature β-aluminium titanate ($TiO_2.Al_2O_3$) was observed. Manganese was detected as manganese spinel; and the workers also found that Fe_2O_3 and Cr_2O_3 both form solid solutions, thus causing the alumina lattice to expand. Their dielectric properties are not particularly enlightening because of experimental difficulties encountered during measurement. TiO_2 and Fe_2O_3 exerted little effect on dielectric constant; MnO_2 additions were claimed to be particularly beneficial to the electrical properties but little else could be deduced from the dielectric loss values obtained.

A very recent study of alumina-based bodies produced by liquid phase sintering has been made by Barr, Montgomery and Long [71]. Alcoa A-14 alumina was sintered with $Mn_2P_2O_7$, and $Mg_2P_2O_7$; tragacanth or methocel was used as a binder. Discs were cold pressed at 5 to 7½ ton/in.^{2} before firing in electric kilns (atmosphere not given). Of the two additives, $Mg_2P_2O_7$ was found to yield the better ceramic for possible high temperature radome use. An 80 % Al_2O_3: 20 % $Mg_2P_2O_7$ composition showed significant improvement of dissipation factor at all test frequencies; at 100 kc/s, $\tan \delta = 0.0001$. A 60:40 composition was extensively examined at 9375 Mc/s and it proved to be at least as good as an unnamed 98 % alumina ceramic examined simultaneously. However, these authors say they observed a marked improvement in loss tangent when the ceramic containing pyrophosphate was dried. They attribute the water absorption to the porosity of the bodies, but do not mention the possible water erosion problem, which is so important for a radome ceramic.

Floyd [72] studied the effects of secondary phases on dielectric properties of alumina. He reports that very small changes in the composition of secondary phase can exert large differences in dissipation factors measured at 10^6 c/s and 25° C. The secondary phase fluxes $BaO.SiO_2$, $CaO.MgO.SiO_2$ and $SrO.SiO_2$ were investigated, and Floyd suggests that the feldspars formed (e.g. $BaO.Al_2O_3.2SiO_2$) caused high dielectric loss because of their thermal expansion mismatch. In a later paper [73], the preparation of alumina bodies of density ~ 3.7 g/cm^3 and purity ~ 95 % Al_2O_3 is described; and dielectric loss factors (10^6 c/s) measured as a function of grain size are given. The lower purity body showed no dependence of loss factor on grain size.

A rather more fundamental approach to the effects of fabrication variables on dielectric properties has been made by Tallan and Detwiler [74]. According to them, measurements of dielectric loss on Linde sapphire revealed a characteristic loss peak which depended upon the previous history of the sample, e.g. exposure to air, H_2, HCl. Later, Tallan and Graham [75] suggested that the dissipation factor maximum of sapphire is attributable to dipolar relaxation involving a mobile cation.

A paper by Filatov [76] is concerned with the effect of porosity on $\tan \delta$ and k' (8 Mc/s) for a clay ceramic (not a pure alumina). He reports that, with increasing porosity (from 10 to 20 %), $\tan \delta$ and k' increased in strong fields but decreased in weak electrical fields. He attributes increased loss at high field strengths to ionisation of the gas filling the pores. References have already been mentioned which contain data relating dielectric constant and $\tan \delta$ with density (therefore porosity) of high density alumina, e.g. Von Hippel and Westphal [38] compare the two theoretical relationships between porosity and dielectric constant with the empirical Lichtenecker equation [23].

M. B. Smyth [77] has reviewed all the theories of dielectrics, and concludes that low loss ceramic bodies should have a crystal phase which has low $\tan \delta$, and which can dissolve metal ion impurities.

A study which is directly related to the radome problem has been made by Smoke *et al* [78]. They describe how alumina ware was prepared by slip casting alumina (Alcoa A14) together with additions of magnesia and silica. It was found that k' (measured by Q-meter) decreases as

Al_2O_3 is replaced by MgO or SiO_2. The effect is greater for SiO_2 because spinel ($MgO.Al_2O_3$) has $k' \sim 7.0$, but SiO_2 has $k' \sim 4$. A typical radome ceramic, matured at 1600° C, had a modulus of rupture 35,000 lb/in.^{2}, $k' = 8.8$, loss factor 0.007, and density 3.66 g/cm^3. A later report [79] deals with the development of low temperature (1550° C) fired alumina bodies.

Pyroceram type ceramics, called sitals by Mashkovich [80], have been the subject of recent studies by this author.

5. High Power Windows

The use of high-temperature electroceramics finds many applications other than the limited fields of radomes and insulation. One of these is in the manufacture of windows for high power klystrons (microwave generators); for this particular application, dielectric loss (which may cause heating and mechanical failure) and the ability to form a vacuum-tight joint are important. A considerable amount of work is being carried out on alumina ceramics for klystron windows and the problems encountered are often relevant to radomes. The application of ceramics to valves is discussed by Moulson and Popper [81]. Increasing interest is being shown in the mechanism of failure of high power windows [82, 83].

At Stanford University [84, 85], studies are being made of the failure of klystron windows. The major cause of failure (100 kV electron bombardment) is internal damage, and the likely mechanism is gas discharge within pores in the ceramic, which in this study was Coors AD94. The windows, although translucent, often had filamentary type opaque inclusions present. Failure by multipactor induced thermal stress is believed to play an important role in the breakdown of sapphire and polycrystalline alumina high power windows [86]. The term "multipactor" refers to secondary electron emission resulting from electron bombardment of the dielectric. The phenomenon is particularly important in high power klystrons. It has been shown by Preist [87] that there are two separate mechanisms of heating, one requiring the presence of the magnetic field and the other one not requiring it. Both involve energy exchange between the electric field and the window by free electrons which concentrate on the surface of the window and multiply by the multipactor process.

A number of commercial firms in this country are working on contract for the Ministry of Defence. EMI [88] have recently published the results of their work. Reports have been issued by The Plessey Co Ltd, dealing with the fabrication of an alumina developed by them for manufacture of windows (e.g. reference 89). Other reports covering the period 1962-64 [90], deal with experimental work on the sintering of alumina alone, and with added sintering agents, and these will be discussed in the section on sintering.

A very recent article [91] on alumina referred to a material with a purity of 99.7%, grain size 3 to 4μm and density ~ 3.9. It is called SPK special grade E37, and is made by Süd-Plastik und Keramik of Feldmühle AG. The source of alumina and the method of fabrication are not given, but the small grain size suggests that it is hot pressed.

A particular aspect of the problem of impurity effects which does not appear to be mentioned by anyone is the effect of any temporary binder. Nearly all papers concerned with sintering and the fabrication of alumina by cold pressing mention the use of temporary binders, including carbowaxes, paraffin wax, polyvinyl alcohol, polyvinyl-propylene and acryllic resin. In the author's view, binders should be considered as a fabrication variable. The fact, that they are fired out at some stage before final densification occurs, does not mean that there are no after-effects produced by their initial presence. These effects could be important particularly if the dielectric properties and micro-structure are to be controlled.

6. Sintering and Fabrication of Alumina

An excellent survey of the literature on sintering has been made by Wilder [92–94], who covered the period 1937-59; in what follows, only the literature which has appeared since 1959 will be mentioned.

Mangsen *et al* [95] have studied the hot pressing of Linde A alumina and found that

$$\frac{dD}{dt} = \frac{3P}{4\eta}(1 - D)$$

where: D = relative density; P = pressure, dynes/cm^2; η = viscosity. At 1520° C and 1820 to 2000 lb/in^2, $D = 1$. Gibbs, Baker, Beauchamp and Miles [96] describe the sintering of Johnson & Matthey alumina of 99.99% purity. In this study the specimens were cold pressed and sintered in air at 800 to 1900° C to yield a final density of only 90%. Crandall, Chung and Gray [97] hot pressed Norton 38-900 alumina at 1650° C in a graphite mould coated with boron nitride. The grain size was controlled to ~ 12 μm with densities ranging from 3.87 to 3.98 g/cm^3. Much of this work is supported by funds from the US Army [98]. Hot pressing of Linde A (0.3μm), Linde B (0.05μm), and Norton 38900 (5 to 10μm) aluminas has been reported by Felten [99]; but within the range of temperature examined, none of the powders produced a body of density greater than 78.5% of theoretical.

In 1961, Kuczynski [100] extended his theory of sintering by studying the effect of oxygen on the sintering of alumina. Sintering rate was accelerated probably because of the increased concentration of point defects in the surface layers due to O absorption. In 1962, Coble [101] and St Pierre and Gatti [102] were issued patents for making transparent polycrystalline alumina bodies, and in 1963 Lucalox* was announced [103]. Transparent alumina is made by cold pressing a size-graded alumina containing ~0.1% MgO. The powder is pressed at 5 to 35 ton/in.^{2} to yield a green body of density $\nless$ 35%. The body is then pre-fired in air at 1000 to 1200° C, before being fired in hydrogen at 1900° C for 17 h. A detailed investigation of the effects of the firing atmosphere was presented later [104]. Coble found that N_2, Ar, and He were not good, and high density could be achieved with H_2 or O_2; earlier work by Walker [105] gave similar results. The patent [101] mentions that magnesium spinel ($MgO.Al_2O_3$) is formed during sintering of Lucalox alumina bodies, but White [106] claims that spinel is not found on the grain boundaries, suggesting solid solution of magnesia. This is supported by some recent work by Jorgensen [107].

Aldred [108] has reviewed commercial alumina ceramics (Morgan, Lodge Plug and KLG) and presents some data on physical properties. Bruch [109] examined sintering kinetics and paid particular attention to the effect of green density upon porosity and fired density. Mention is made of unpublished work by St Pierre and Gatti, claiming to have produced 100% dense alumina from Linde A without any additions; Coble has suggested that there was sufficient MgO in the furnace refractory used by St Pierre and Gatti to account for the densification. A further review of sintering theory has also been made by White [110], covering the literature into 1962.

In 1963, Paladino and Coble [111] investigated the effect of grain boundaries on diffusion processes occurring in alumina. They report finding oxygen ion diffusion to be enhanced by grain boundaries, and conclude that kinetic processes in polycrystalline alumina below a certain grain size are controlled by the bulk diffusion of the cation. Furthermore, it has been shown that in single crystal alumina the electrical conductivity is too high to be related to either anion or cation diffusion, and is electronic. Johnson and Cutler [112, 113] have investigated the shrinkage during the sintering of alumina, as well as the kinetics. They conclude that shrinkage is best described by a grain boundary vacancy diffusion model for the temperature range 1200 to 1600° C. These workers describe the examination of a number of alumina powders:

Alumina	*Particle Size* (*μm*)
Gulton Alucer MC	0.2 to 0.5
Alcoa A14 (elutriated)	3 to 5
Alcoa A14 (as received)	1 to 20
Linde A	0.3 to 0.6
Linde C	0.5 to 1.0
High Purity (< 100 ppm)	0.3 to 0.5
High Purity + MgO	0.3 to 0.5

(The last two were prepared in the laboratory.) Neither analytical details nor densities of fired pellets are given.

Additional studies on the effects of MgO and TiO_2 on the sintering of alumina include Ringel's [114]. He found that alumina containing 0.25% MgO sintered more rapidly than a ceramic containing 2% MgO. Attempts to sinter, in vacuum, a pure alumina (source not given) to theoretical density failed. The sintering of alumina containing TiO_2 has recently been studied by Bagley and Cutler [115], and much earlier by Smothers and Reynolds [116] and Bron *et al* [117, 118].

The sintering of porcelains is being investigated by Oishi and co-workers [119-121], who are studying grain growth in various environments including vacuum, wet and dry H_2, CO, Ar and air. Dry hydrogen is found to be the most effective for densification, followed by CO, at temperatures > 1900° C. They have observed little difference between firings carried

*Stellox, an AEI material of similar specification, was announced in the February 1964 issue of *Engineering*.

out in air or in vacuum and propose a vacancy diffusion model. In the UK, Budworth *et al* [122] have examined a number of aspects of hot pressing of alumina and have used this technique for joining alumina.

The effects of impurities, porosity, and grain size on the mechanical properties of alumina are reported in a number of very recent papers [123-127]. Spriggs *et al* [125] say they found that very fine grain alumina was not as strong as predicted, but additional post fabrication treatment resulted in increased strength. Similar results are reported by Phillips and Di Vita [126]. Vasilos, Spriggs *et al* [128, 129] measured at 30 to 1500° C the elastic modulus of several hot-pressed Linde A aluminas of densities $> 98\%$ of the theoretical, and with grain sizes 10 to 250μm. The elastic modulus (55×10^6 lb/in.^{2}) was essentially independent of temperature. A useful survey of hot pressing of refractory oxides in general has been made by Poluboyarinov and Shal'nov [130]. Other references to hot pressing of alumina are given in papers by Coble and Ellis [131], Rossi [132], Rossi and Fulrath [133], and McClelland and Zehms [134]. Reviews on sintering include those by Cutler [135], Coble [136, 137] and Burke [138, 139]; Coble has reviewed most of the aspects of "activated" sintering mainly by reference to his own contributions, but Burke's reviews are more comprehensive. Kuczynski [140] issued a summary report of his sintering researches (1957-62), most of which has been published in the open literature [100, 141, 142].

Work was published recently by Jorgensen and Westbrook [143], who demonstrated that for NiO additions the impurity was segregated at the grain boundaries. Use was made of ^{63}NiO and autoradiographic techniques (but the technique is not applicable to Mg isotopes, because they are too short lived). The effects of additions of CoO, Fe_2O_3, and CaO, up to 0.1% wt, in sintering of Linde A were studied also. Manganese oxide (up to 0.5%) is reported by Keski and Cutler [144] to accelerate the sintering rate, but to cause a decrease on further addition. Grain boundary diffusion was considered to be the operative mechanism. Jorgensen [107] recently published further evidence for grain boundary controlled sintering in alumina containing MgO. A Japanese paper [145] reports, in abstract form only, that a relationship between rate of grain growth, grain diameter, volume fraction of pores and average pore diameter has been noted. The effect of 0.16% added MgO has also been studied. Amato *et al* [146] studied the sintering of alumina containing added MgO and SiO_2. The alumina, type P11OC1 (Degussa), had BET surface area 96 m^2/g and particle size 5 to 30 mμm. For aluminas sintered in hydrogen at 1500 to 1700° C, the densities were always higher when MgO or SiO_2 was present, but the chemical purity of the alumina is not mentioned.

Some recent literature is contained in a number of 1964 theses [147-151]. Most of Bagley's work was briefly published in an earlier paper [115]. The work indicates that small additions of TiO_2 cause an increase in the density of alumina ceramics and also that the mechanism of sintering is dependent upon the particle size of the starting alumina. Additions to Linde A alumina (0.3 μm) of Na_2O in amounts 10 to 10,000 ppm stimulated exaggerated grain-growth; even an atmosphere of Na_2O was effective. No exaggerated grain growth was observed with high purity alumina except when the furnace atmosphere was not clean.

The Plessey Co Ltd [89, 90] have repeated much of Coble's work [70] using Linde A and an alumina prepared by the hydrolysis of aluminium isopropoxide [152]. The effects of small additions of NiO, LiF, Li_2O, ZrO_2, CeO_2, TiO_2, and MoO_3 on sintering were examined; NiO and MoO_3 were found to be advantageous to sintering. Pavlushkin [153] reports on the effects of 52 different oxides on the sintering of alumina. The main discussion gives particular emphasis to SiO_2, CaO, Fe_2O_3, MgO, and Na_2O. A considerable amount of work has been carried out by Philpott *et al* [154] of the Worcester Royal Porcelain Co, who have examined the sintering of several commercial α-aluminas containing various binders. The effects of forming pressure, source and amount of MgO (as nitrate, sulphate, and oxide), 0.1, 0.2, 0.3 wt%, were examined, but none of these parameters affected the final fired density. Use of a spray-dried PVA impregnated alumina*, pre-fired at 1400° C for 24 h before sintering to 1750° C in 24 h with $\frac{1}{2}$ h soak, produced a ceramic with a bulk density of ~ 3.9 g/cm^3. Permittivities of about 9.7 and tan δ of 0.002, (both at 1 Mc/s) were obtained. When large amounts of Mobilcer A binder were used, up to 0.1% residual carbon

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*Cera, 99.8% Al_2O_3; 0.3 m^2/g, 2–6μm (Information taken from British Aluminium Co Special Products data sheet 902, dated June, 1960.)

was detected by chemical analysis. They say that they found the carbon content to depend largely upon the firing conditions, but that they did not establish the true chemical form of the carbon. The authors note that they were unable to fabricate Linde A alumina by cold pressing, contrary to the experience of many workers.

The earliest reference to the sintering of Linde A alumina is contained in a report [155] summarising work carried out over the period 1946-49, and which is particularly concerned with the mechanical properties of ceramics. Two other commercially available aluminas were used, Alcoa T61 tabular and Norton 38900. The aluminas were cold pressed with a binder (Sohio Parawax in carbon tetrachloride), slip cast, and extruded (Mogul gum or corn starch, glycerine and phenol); specimens were fired for 3 h in gas/air or oxygen at 1700° C and 1830° C respectively. The effects of added aluminium chloride, aluminium fluoride, and magnesium fluoride were studied for amounts up to 5% in T61 alumina. It was estimated that 5% of MgF_2 produced 10% of spinel, thus masking the advantageous properties of MgF_2. With scattered exceptions the bulk density of the fired specimens decreased and the porosity increased with increase in the amount of additions. Linde A alone never exceeded a density 3.79 g/cm^3, and pre-sintering the alumina gave even lower densities; some data for the other aluminas are given below:

Material	Density Fired 1700°C	Density Fired 1830°C	Corresponding Crystal Size (μm)	
Linde A	—	3.79	—	85
T61	3.10	3.44	20	31
T61 Ground 8h/acid washed	3.43	3.68	11	74
Norton 38900	3.45	3.73	5	10

In addition to the literature on conventional sintering techniques and hot pressing, much general information is available in papers by Kingery [23, 156, 157], Ault *et al* [158] and Pincus *et al* [159]. The flame spraying process is particularly well covered in papers by Ault and Milligan [160-162] and Huffadine and Thomas [163].

Acknowledgements

The author wishes to thank the Ministry of Aviation and the Ministry of Defence (N) for permission to refer to work carried out for them.

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*See footnote on page 195.

Note Added During Proofing

Since this review was written, some additional reports [164-168] have been abstracted. They deal with a survey of ceramic materials for radomes [164], anisotropy in polycrystalline alumina [165], the effect of metal additions on grain growth in alumina [166]. A new approach in the evaluation of shrinkage during sintering (at 1400° C) of alumina is discussed by Daniels and Wadsworth [167]. Smoke *et al* [168] have investigated the sintering of alumina in H_2, O_2, A, and vacuum; they found that sintering in vacuum gave the best results, argon the poorest.

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