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RESEARCH AND DEVELOPMENT SERVICES LEADING TO THE CONTROL OF ELECTRICAL PROPERTIES OF MATERIALS FOR HIGH TEMPERATURE RADOMES

LEON M. ATLAS
H. HENRY NAKAMURA

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OF ILLINOIS INSTITUTE OF TECHNOLOGY

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AERONAUTICAL SYSTEMS DIVISION

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AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report describes the third and final year of a research program under USAF Contract No. AF 33(616)-5929, Project No. 7371, "Applied Research in Electrical, Electronic, and Magnetic Materials," Task No. 73710 "Applied Research on Dielectric Materials." The work was under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. J. D. Latva acting as project engineer.

As in previous years, preparation of specimens and interpretation of electrical measurements were carried out at Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Illinois. Personnel contributing to this portion of the program were Dr. L. M. Atlas, project leader, Messrs. H. H. Nakamura and T. C. Parada who were responsible for preparation of most of the specimens, and Mr. J. K. Raney who explored the thermoelectric power of some of the compositions.

Mr. W. B. Westphal continued to direct the electrical measurement phase of the program at the Laboratory for Insulation Research of Massachusetts Institute of Technology under Air Force Contract No. AF 33(616)-5920.

ABSTRACT

High purity and doped alumina ceramics previously prepared on this program by cold pressing and sintering rarely exceeded 90% of theoretical density. Therefore hot pressing in argon was applied to pure aluminas prepared at ARF and to a commercial high purity product (Gulton Alucer MC). Densities in the range 3.85 g/cm^3 (for ARF alumina) to 3.97 g/cm^3 (for the Alucer MC) were readily obtained at 1650°-1750°C and 3000-3500 psi. Although the specimens were apparently rendered completely free of carbon by annealing in oxygen at 1500 to 1700°C, their dissipation factors were much higher than for sintered discs made from the same powders. These anomalously high losses appear to be caused by the absorption of impurity cations from the graphite hot pressing dies despite their low ash content.

With the objective of compensating the positive temperature variation of dielectric constant (k') characteristic of alumina regardless of its purity, compositions were formulated containing a titanate phase whose temperature variation of k' is negative. Attention was concentrated on $SrTiO_3$ and $SrTiO_3$-$BaTiO_3$ solid solutions of C.P. grade in the concentration range 8 to 20% by weight. At a level of 14% $SrTiO_3$, the k' of a titanate-alumina ceramic varied only 2.8% between 25 and 500°C at 10^6 c/s and 1.0% at 4 x 10^9 c/s as compared to 5.5 to 6.8% for high purity aluminas.

The stable coexistence of Al_2O_3 and $SrTiO_3$ on firing suggests a eutectic system which is actually pseudo binary because of the dissociation of the titanate. This eutectic was approximately located in the composition interval 65-70% $SrTiO_3$, and near 1625°C.

Ceramics having the composition 12% $SrTiO_3$-88% Al_2O_3 were evaluated under four point flexural loading at room temperature, 500°C, and 1000°C. Although the test specimens had 10% total porosity, application of Knudsen's equation demonstrated that the potential strength of the composite material was about the same as that of a commercial high alumina ceramic of the same porosity and grain size. The strength decrement with rising temperature (up to 1000°C) was also similar for both materials.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

WILLIAM G. RAMKE
Chief Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

I. INTRODUCTION

This report concludes a three year investigation of polycrystalline aluminum oxide as a dielectric material for use at high temperatures. Such studies of alumina ceramics have been by no means rare in the past ten years, and their results have been reported in the literature in detail (see for example the Laboratory for Insulation Research, Ref. 1, Cohen, Ref. 2, and Florio, Ref. 3). However, repetition of previous work by this program was avoided by a shift of emphasis away from conventional high alumina ceramics (containing a maximum of about 99.8% Al_2O_3) to specially prepared very pure aluminas having less than 100 ppm of foreign ions. Since it has been known for some time that improving the purity of alumina lowers its electrical losses, measurements made on the very pure materials of this program give a good indication of the potentialities of polycrystalline alumina as a dielectric.

If electrical losses are raised by the presence of impurities, the question arises: which of the common contaminants (aside from the alkalis whose effects are well known) have the most deleterious action? This problem was studied by introducing known concentrations of Si, Ti, Ca, Mg. Fe, and Cr into high purity powders before they were fabricated into ceramics. The results of electrical loss measurements on these ceramics were analyzed by multiple regression methods, and the individual effect of each impurity ion was characterized by its partial regression coefficient and by the product of its individual correlation coefficient and standardized partial regression coefficient. It was determined by this approach that Si had by far the greatest effect followed successively by Mg and Ti and finally by Ca, Cr, and Fe which behaved similarly.

Not only is it desirable that a dielectric have low losses, but for use in radomes, it would be of particular value if it also had a low temperature variation of dielectric constant (k'). Measurements of k' at low and intermediate frequencies (10^2 to 10^6 c/s) showed that dk'/dT was indeed very sensitive to the concentration of impurity ions - particularly of Mg. However, it was soon discovered that these variations were not really changes in the dielectric constant of the bulk material but were instead produced by the measuring technique, which was the commonly employed method of using the sample as the dielectric of a capacitor. Unfortunately, this technique usually assumes that the dielectric is homogeneous, whereas the actual situation may more closely approximate a thick central core sandwiched between two very thin resistive outer layers. The observed exponential rise of k' with T is therefore actually caused by an interfacial polarization whose effects diminish with rising frequency. Consequently, at 10^6, 10^7 c/s or higher, dk'/dT was found to be quite unaffected by impurities in the concentration range 0.1% or lower. These results clearly showed that close control of the temperature variation of k' could not be achieved with minor concentrations of

additives. The determination of the nature and concentration of admixtures that could effectively control the dk'/dT of alumina formed a major objective of the third year of the present program.

Attention was directed from the very start to the alkaline earth titanates which have a negative temperature variation of k' above their Curie points. If these compounds could be fired with alumina without losing their identity, the negative slope of the titanate could conceivably be balanced against the positive variation of the alumina. Early experiments showed that although there was an interaction between alumina and magnesium titanate, this fortunately did not occur with $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$. Moreover, as predicted, additions of these compounds to alumina did result in a striking reduction of dk'/dT. More surprising was the fact that when the mixtures were formulated with C.P. grade titanates, their dissipation factors were comparable to those of commercial high alumina ceramics even at 500°C.

The promising electrical capabilities of titanate-alumina ceramics at high temperatures led to a brief study of their mechanical properties and melting relations. Unfortunately, mechanical strength measurements were rendered somewhat ambiguous by the fact that the test bars had a total porosity of 10%. However, an attempt was made to overcome these textural difficulties mathematically, and the resulting corrected strengths were found to be very similar to that of a high alumina ceramic.

Porosity difficulties were by no means limited to titanate-alumina composites; they plagued the pure alumina phase of the program from its very inception. Sintering pure alumina prepared by dissolving the metal and calcining the precipitated hydrous oxide was never successful in fabricating ceramics with densities above about 92% of theoretical. Moreover, high sintering temperatures (1800-1950°C) created a marked tendency toward catastrophic secondary recrystallization, and many specimens displayed crystals exceeding one mm in diameter. Cutler (Ref. 4) has recently made a considerable improvement in the sintering of very pure alumina by calcining the aluminum chloride and sulfate directly to the oxide. The resulting powders have been sintered to 95-96% of theoretical density at temperatures as low as 1675°C. However, the approach in the present program was to hot press the pure oxide in graphite dies of low ash content surrounded by an inert atmosphere. Although high densities were obtained, other difficulties arose which will be described in the next section.

II. HOT PRESSED PURE ALUMINA CERAMICS

The Laboratory for Insulation Research (Ref. 1) has measured the dissipation factors of both sintered, and hot pressed alumina ceramics prepared by the Kearfott Company. It was found that the hot pressed material had losses more than an order of magnitude greater than those of the sintered ceramics, thereby demonstrating that although hot pressing might solve the density problem, it would also raise several new ones.

Nevertheless, hot pressing experiments were undertaken in the hope that the cause of the high electrical losses might be discovered and eliminated. The most obvious source of these losses in the Kearfott specimens was the finely divided carbonaceous particles which are characteristically disseminated in ceramics hot pressed in a graphite mold. Introduction of the carbon - which appears to be deposited from a vapor phase - might be prevented by hot pressing in a vacuum or an inert atmosphere. An additional precaution might be the use of a molybdenum or other metallic liner as a barrier. Alternatively, the carbon once formed might be removed by a sufficiently long period of annealing in oxygen. The second procedure has the advantage that it is simpler than vacuum hot pressing, and eliminates possible contamination from the metallic liner. In addition, an oxygen annealed specimen is likely to have fewer lattice defects than one hot pressed in a vacuum and not subsequently annealed. On the other hand, vacuum firing is an effective removal process for even slightly volatile impurities. A compromise procedure was actually used; this consisted of carrying out the hot pressing in a flowing argon atmosphere which has some purifying action, and subsequently annealing the specimens in oxygen.

All experiments were conducted in molds made from National Carbon Company AUC graphite, which is specified as having maximum and average ash contents of 0.08 and 0.03%. Ceramics were formed from two different aluminas - ARF powder (prepared by the solution of 99.999% Al and precipitation of the hydroxide) and Gulton Alucer MC, whose analyses are shown in Table I. These materials were first cold pressed in the graphite dies and loaded into an induction furnace which could be sealed. The furnace was first evacuated at room temperature (with no load applied to the die), and then filled and swept with argon, after which the powders were compressed at 3000 to 3500 psi and heated to 1650 to 1750°C. As the pressure was relieved by compaction of the powders, it was manually restored until the rate of pressure drop fell to a minimum.

Despite precautions to eliminate CO from the furnace atmosphere, the hot pressed products not only had black outer surfaces where they touched the graphite mold, but also displayed a gray interior. Before further heat treatment, they were ground to the required dimenions - which necessitated removal of the surface layers to a depth of about 1/16 inch. The gray specimens were then weighed and heated in a stream of flowing oxygen at 1500°C overnight or at 1500-1700°C for about seven hours. As a result of this oxidation, the specimens were bleached throughout except for a slight yellow stain which betrayed the presence of iron in the form of Fe^{3+}. The decolorization was accompanied by a loss of weight: 0.1% for the ARF Al_2O_3 powder and 0.01% for the Alucer MC. The density of the final oxygen annealed product also depended on the type of alumina powder used. ARF powder yielded a maximum density of 3.84 g/cm^3 when pressed at 3000-3500 psi and 1700-1750°C; whereas the Alucer was easily densified to 3.97 g/cm^3 at 3000 psi and 1650°C. Moreover, secondary recrystallization occurred

Table I

SPECTROGRAPHIC ANALYSES OF ALUMINA POWDERS AND CERAMICS

Element Conc (ppm)	ARF Powder	Gulton Alucer MC*	Hot Pressed ARF Powder	Sintered ARF Powder	Hot Pressed Alucer MC	Sintered Alucer MC
Si	12	< 50	250	10	100	20
Fe	20	< 20	40	50	150	400
Mg	18	-	6	20	18	45
Cr	1	50	< 2	5	< 2	5
Ca	1	10	250	30	250	30
Cu	1	2	< 0.2	< 0.2	< 0.2	< 0.2
Zn	-	< 10	-	-	-	-
Pb	-	70	-	-	-	-
Na	< 10	100	-	-	-	-
Ga	< 30	< 30	< 30	5	40	200

* Given by Gulton Industries Inc.

to a much greater extent in the ARF alumina, frequently culminating in specimens containing irregularly shaped crystals more than one mm across. These ceramics were so weak that grinding to the required dimensions was virtually impossible.

Electrical evaluation of hot pressed and oxidized specimens prepared from both powders showed considerably higher losses than occurred in comparable sintered specimens (Table II). Incomplete carbon removal cannot be held responsible for these results because the more porous (and presumably more permeable) ceramic pressed from ARF alumina also had the higher losses.

Table II

DIELECTRIC LOSSES OF HOT PRESSED AND SINTERED ALUMINAS

Ceramic Material	Tan δ 30°C, 10^6 c/s	Tan δ 250°C, 10^6 c/s	Tan δ 500°C, 10^6 c/s
Hot Pressed Alucer MC	0.00008	0.0025	0.039
Sintered Alucer MC	-	0.0004	0.013
Hot Pressed ARF Alumina	0.00002	0.029	0.13
Sintered ARF Alumina (range for several batches)	0.00025-0.00028	0.00006-0.00013	0.00048-0.0038

On the other hand, measured values of tan δ correlate well with surprisingly high levels of Si found in the hot pressed ceramics. The source of the Si as well as Ca and Fe was most probably the graphite pressing molds and plungers; all three of these impurity ions are major components of graphite ash. Considering the low ash content of the AUC graphite used, the high impurity concentration found in the hot pressed product gives evidence of extensive and rapid migration of the Si, Fe, and Ca out of the graphite and into the alumina.

A note of caution about spectrographic analyses of fired ceramics might well be interjected at this point. It has been observed during this program and by other investigators (Ref. 5) that impurity concentrations spectrographically determined in fired ceramics are commonly much higher than in the original batch powders. As an example, the

concentrations of Ca, Mg, and Fe apparently found in deliberately doped ceramics (crushed to powder and analyzed by the Harvey method) (Ref. 6) were in some cases two or three times higher than was originally introduced into the batch powders. Analyses based on a set of ceramic standards have generally been much more reliable. Two hypotheses to account for the analytical discrepancies between loose powders and fired ceramics are: (a) the effect is caused by differences in the rates of impurity volatilization from a ceramic and a loose powder; (b) there may be a significant change in the background radiation level which is used as the datum for impurity line intensities in the Harvey method. As yet there has been no experimental support for either of these hypotheses.

III. COMPENSATED ALUMINA CERAMICS

A. Dissipation Factors of Compensated Aluminas

Extensive measurements on alumina ceramics containing 0.1% or less of various impurities conclusively demonstrated that the high frequency dielectric constant was insensitive to low concentrations of foreign cations. Therefore, to gain control over the temperature variation of k', attention was focused on the formulation of internally compensated alumina ceramics. The promise of this approach was first suggested in WADC TR 59-300 Pt II, which showed that alumina and a compound having a negative dk'/dT ($CaTiO_3$) could be fired together without interaction. The resulting ceramic containing 10% of $CaTiO_3$ did have an almost invariant k' up to 250°C at 10^6-10^7 c/s. However, its dissipation factor at elevated temperatures was high (0.13 at 500°C and 10^6 c/s). The problem of excessive losses was attacked from two different points of view: (1) improving the purity of the titanate compound, and (2) lowering the concentration of titanate required for adequate compensation by using a compound having the highest practicable negative slope of k'.

1. Effect of Titanate Purity on Electrical Losses

Foreign ions introduced into a $CaTiO_3$-Al_2O_3 ceramic by way of the titanate compound can raise the dissipation factor as effectively as they do in pure alumina. Furthermore, a deficiency of Ca^{2+} below the stoichiometric ratio $CaO.TiO_2$, can reduce some Ti^{4+} ions to Ti^{3+}, which also contributes to electrical losses. These deleterious effects might be significantly reduced by the use of stoichiometric titanates having low impurity levels - particularly with respect to Si. This possibility was examined by formulating batches with a C.P. grade $SrTiO_3$ which, in contrast to the 0.86% SiO_2 of technical grade $CaTiO_3$, contained less than 0.03% of SiO_2, ZrO_2, Fe_2O_3, MnO_2, MgO, V_2O_5, CuO, BaO, Na_2O, Al_2O_3, and CaO. Moreover, the C.P. compound had a molar SrO/TiO_2 ratio of about 0.99 as compared to 0.97 for technical $CaTiO_3$.

Ceramics were prepared by wet milling the C.P. titanate with Gulton's Alucer MC. The dried pulps were somewhat fluffy, and had to be tempered with carbon tetrachloride to prevent lamination during pressing. Cylinders and discs were pressed at 10,000-15,000 psi and fired in a gas-oxygen furnace in a stream of flowing oxygen. Although a temperature of 1750°C was used in early phases of the program, it was later found that lowering the temperature to 1600-1650°C resulted in less oxygen loss and lower porosities. Ceramics fired at 1650°C were generally light cream in color with a very pale green or blue discoloration occurring locally. Porosity tended to increase with the $SrTiO_3$ concentration; 6% was the minimum value achieved with a 14% $SrTiO_3$ composition (computed from a calculated theoretical density of 4.14 g/cm^3).

Benefits accruing from the use of a C.P. titanate are evident in the tan δ values of Table III. For example, it may be noted that additions of up to about 17% of $SrTiO_3$ produce ceramics whose dissipation factors (at 10^6 c/s and 500°C) are about the same as that of pure Alucer, and at worst, only twice as high as measured for Coors AD 99 alumina. In contrast, the use of technical grade $CaTiO_3$ results in losses an order of magnitude or more greater than are obtained with the C.P. titanate.

Thus far, attention has been centered on ceramics in which the alumina component was the relatively pure but very fine Alucer MC. The question naturally arose whether the use of a good ceramic grade of alpha alumina powder would cause an excessive rise in tan δ. This question was resolved with the aid of a mixture formulated with Alcoa T61 alumina reground by the Champion Spark Plug Company. Table III shows that for a 10% $SrTiO_3$ composition, losses were about the same for ceramics prepared with both Alucer and T61 aluminas.

2. Use of Titanates Having a High Negative Temperature Variation of Dielectric Constant

Despite the almost negligible losses apparently created by introducing C.P. grade titanates into aluminas, several advantages would be gained by reducing the concentration of compensating phase to a minimum. Among these advantages might be listed a lessening of the oxygen dissociation problem and, as will be shown later, of the concentration of liquid phase that begins to form near 1625°C. The first step toward raising the negative dk'/dT of the compensating phase was to replace $CaTiO_3$ (-0.18/°C at 150°C) (Ref. 7) with $SrTiO_3$ (-0.74/°C at 150°C) (Ref. 7). A further increase might be obtained by raising the Curie temperature of the titanate - ideally to a point just below the minimum use temperature of the dielectric. Such an upward displacement of the Curie point can readily be achieved by forming solid solutions of $SrTiO_3$ and $BaTiO_3$. Unfortunately, as dk'/dT increases, it also becomes more variable with T; consequently, compensation of the linear positive slope of the alumina cannot be obtained for wide temperature intervals. A

Table III
DISSIPATION FACTORS OF TITANATE-ALUMINA CERAMICS

Compensating Compound[1]	Tanδ 10^6 c/s		Tanδ 8.5×10^9 c/s
	250°C	500°C	500°C
10% $CaTiO_3$[2]	0.0029	0.13	0.02
8% $SrTiO_3$[3]	0.00019	0.0039	0.00025
8% $SrTiO_3$ + 0.5% SrO	0.00021	0.0030	0.00045
10% (50% $BaTiO_3$- 50% $SrTiO_3$)	0.0010	0.0036	-
10% (30% $BaTiO_3$- 70% $SrTiO_3$)	0.0018	0.022	-
10% $SrTiO_3$	0.00074	0.0095	-
10% $SrTiO_3$ in T61 alumina[4]	0.0090	0.012	-
12% $SrTiO_3$	0.0003	0.007	-
14% $SrTiO_3$	0.00055	0.010	-
17% $SrTiO_3$	0.00045	0.011	-
20% $SrTiO_3$	-	0.027	-
100% Alucer	0.00038	0.013	-
Coors AD99	0.0029	0.0052	0.0001o

(1) These compounds were used in conjunction with Gulton Alucer MC except where otherwise stated.

(2) TAM regular commercial grade.

(3) TAM C.P. grade.

(4) Alcoa T61 alumina reground by Champion Spark Plug Company

possible solution to this problem might be to spread out the sharp Curie point to a broader range by incompletely reacting the two end members of the titanate solid solution. This approach was followed by preparing alumina compositions containing mechanical mixtures of the two titanates (50% $BaTiO_3$-50% $SrTiO_3$ and 30% $BaTiO_3$-70% $SrTiO_3$). It was found that firing these formulations, which had titanate concentrations of 8 and 10%, did result in incomplete solutions of the two end members. X-ray

diffraction patterns showed the presence of alpha alumina and a titanate compound whose diffraction lines appeared as bands ranging in spacing between the values given by $SrTiO_3$ and $BaTiO_3$. Although preparation of the graded solid solution was successful, it was found that a given concentration of this inhomogeneous phase was even less effective for compensating the alumina than $SrTiO_3$ alone.

B.   Dielectric Constants of Compensated Aluminas

The fact that titanate additions effectively compensate the positive dk'/dT of alumina is clearly demonstrated by the 10^6, 10^7 c/s measurements listed in Table IV and the microwave curves of Figure 1. Ideally, the variation of k' with T should be about the same in both frequency regions for materials having very low losses. While this condition has been approached fairly closely in the present situation, conductivity losses are still sufficient to produce anomalous variation of k' at 10^6-10^7 c/s. Therefore, the microwave data, obtained by cavity measurements at about 4×10^9 c/s, give the more reliable measure of the true dk'/dT of the bulk sample material. The microwave curves of Figure 1 show two important features: (1) the average slope of the k' vs T curves diminishes to zero as the $SrTiO_3$ content increases; (2) the originally linear curve of alumina departs from linearity with a $SrTiO_3$ addition. The latter effect is caused by the characteristics of the curve for $SrTiO_3$ alone, and by the increasing effect of losses produced by the titanate at the higher temperatures. Nevertheless, the variation of k' between 25 and 500°C given by a 14% $SrTiO_3$ composition is only about 1% as compared to 5.5% for very pure alumina. Extending the upper temperature limit to 860°C only raises the total variation to about 4% with 14% of $SrTiO_3$ and 2.6% with 20% of $SrTiO_3$.

The behavior of graded $SrTiO_3$-$BaTiO_3$ solid solutions as compensating compounds is shown in Table IV. No improvement in compensation over an equal concentration of $SrTiO_3$ is indicated. Nevertheless, the general approach of using a complex compensating phase or phases should not be abandoned; it appears to be the only means of overcoming the non linearity that is produced by using a simple compound such as $SrTiO_3$.

C.   Melting Relations in the System $SrTiO_3$-Al_2O_3

Since optimum electrical compensation requires an appreciable concentration of $SrTiO_3$ in an alumina ceramic, it is important to establish melting relations between the two compounds. Although there has been much work published on $SrTiO_3$ and Al_2O_3 separately, nothing was found on mixtures of these two oxides or on the general system SrO-TiO_2-Al_2O_3. It should be noted at this point that the join $SrTiO_3$-Al_2O_3 does not form a true binary system because of the dissociation of the titanate. However, oxygen loss does not appear to be extensive enough in air to change melting relations significantly; therefore, for

Table IV

DIELECTRIC COMPENSATION OF ALUMINA BY TITANATE COMPOUNDS

Compensating Compound[1]	Concentration Wt %	Min. k' 10^6, 10^7 c/s 25 to 500°C	Max. k' 10^6, 10^7 c/s 25 to 500°C	% Change of k', 25-500°C
Pure ARF alumina (A8)		8.85 (25°)[2]	9.45 (500°)[2]	6.8
Coors AD 99		9.30 (25°)	9.85 (500°)	5.9
30% $BaTiO_3$- 70% $SrTiO_3$	8	10.30 (25°)	10.75 (500°)	4.4
$SrTiO_3$	8	10.55 (25°)	10.90 (500°)	3.3
30% $BaTiO_3$ 70% $SrTiO_3$	10	10.20 (25°)	10.65 (500°)	4.4
50% $BaTiO_3$ 50% $SrTiO_3$	10	9.90 (25°)	10.30 (500°)	4.0
$SrTiO_3$	10	10.45 (25°)	10.85 (500°)	3.8
$SrTiO_3$ (in T61 alumina)	10	10.15 (25°)	10.50 (500°)	3.4
$SrTiO_3$	12	10.57 (150°)	10.70 (500°)	1.2
$SrTiO_3$	14	11.92 (150°)	12.25 (500°)	2.8
$SrTiO_3$	17	12.5 (250°)	12.65 (25°, 500°)	1.2
$SrTiO_3$	20	13.05 (275°)	13.40 (25°)	2.7

[1] Compensating compounds were used in conjunction with Gulton Alucer MC except where otherwise stated.

[2] Temperatures in parentheses are those at which k' assumed its minimum and maximum values in the range 25 to 500°C
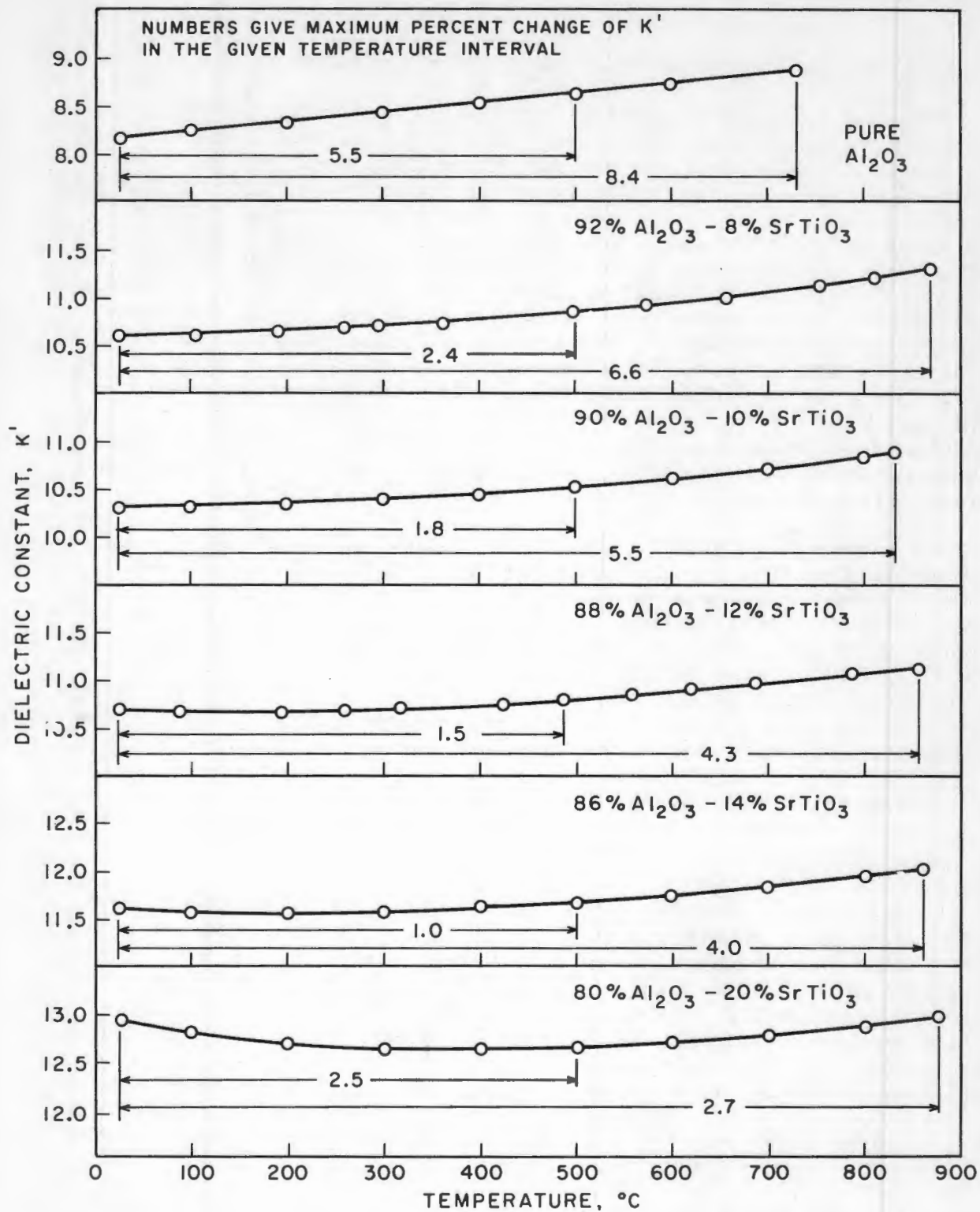
FIG. I TEMPERATURE VARIATION OF K' AT 4×10^9 C/S FOR Al_2O_3 – $SrTiO_3$ COMPOSITIONS.

purposes of this program, the dissociation was ignored.

The fact that dielectric mixtures of Al_2O_3 and $SrTiO_3$ showed no apparent change in phase assemblage on firing suggested that the system had a pseudo binary eutectic, and that other compounds and extensive solid solution phases were not stable. The temperature and composition location of the eutectic point was investigated by observing the deformation of pyrometric cones composed of various mixtures of $SrTiO_3$ and Al_2O_3. Compositions were prepared containing 10, 20, 30, 40, 50, 60, 65, 70, 75, and 80% of C.P. $SrTiO_3$ in Alucer MC alumina. Using a polyvinyl alcohol binder, these mixtures were formed into cones, mounted on alumina plaques, enclosed in an alumina muffle, and fired in a gas-oxygen furnace. Most consistent results were obtained by maintaining the maximum temperature of the experiment for about one half hour before the furnace was shut off. The onset of liquid formation could be detected by a bending over of the cone tips. With increasing liquid concentration, the cones deteriorated to a point where they almost completely vanished - having soaked into the porous plaques.

By means of the cone technique, the eutectic composition was approximately located at a point between 65 and 70% $SrTiO_3$, and the eutectic temperature was tentatively fixed near 1625°C. Thus it has been established that liquid formation will commence in an alumina compensated with $SrTiO_3$ at about 1625°C - in contrast to approximately 2040°C for alpha alumina. While it is true that the titanate-alumina mixture has a melting range of possibly 250°C - in contrast to the sharp transformation point of pure alumina - the mechanical properties of the mixture are likely to deteriorate rapidly above the solidus temperature.

D. Flexural Strength of $SrTiO_3$-Al_2O_3 Ceramics

1. Introduction

Dissociation of oxygen during firing has thus far prevented the fabrication of low porosity $SrTiO_3$-Al_2O_3 ceramics whose flexural strengths might be directly compared to that of alumina. However, there is little doubt that continued research on this family of dielectric materials will uncover firing conditions under which dense ceramics can be prepared. At this stage, however, useful information can still be derived from measurements of porous specimens because porosity and grain size effects can be at least approximately compensated mathematically. Moreover, although absolute strength is very sensitive to both of these textural characteristics its temperature variation is more likely to be dependent mainly on composition.

Measurements of flexural strength were carried out under four point loading by the technique described by Bortz and Firestone (Ref. 8). Briefly, this consists of using a specimen in the form of a flat sided dog bone having two perforations at each widened end. The bending force is

applied to pins inserted in these openings, and the specimen ruptures in the narrowed central gage section. The function of the pin system, which is located along the neutral axis of the specimen, is to minimize positive strength errors caused by friction effects. The stress which produces failure is then given by:

$$\sigma = S = \frac{3\,Pa}{bd^2} \tag{1}$$

where P is the applied load
  b is the width of the gage section measured normal to the direction of the applied load
  d is the thickness of the gage section measured parallel to the applied load
  a is the distance between the axes of the two pins at the same end of a specimen
  S is the bend strength of the material.

2. Preparation of Specimens

Perforated dog bone specimens were prepared from a 12% C.P. $SrTiO_3$-88% Alucer MC Al_2O_3 mixture by the following sequence of operations:

a. The titanate and Alucer were wet milled together in polyethylene containers with plastic balls, and the pulp was dried by evaporation in an oven.

b. The mixed powder was blended with an aqueous solution of polyvinyl alcohol as a binder and cold pressed at 10,000 psi into rectangular plates measuring about 4-1/4 x 1-1/4 x 1/4 inches.

c. After drying at about 100°C, the unfired plates were ground to form the tapered gage section, and two holes were drilled at each end.

d. The specimens were loaded into a sagger constructed from Alfrax B1 bricks and covered with alumina grain. In order to prevent the non shrinking granular alumina from entering the openings in the sample, they were filled loosely with a paste composed of Alucer and water. During firing, this filling shrank even more than the bars; therefore, they did not create dangerous stresses in the perforation area.

e. The sagger was fired in a gas-air furnace to a maximum temperature of 1600°C, which was reached in about 20 hours and maintained for an additional 4 hours. The product had a density of only 3.49-3.58 g/cm³ in contrast to 3.88 g/cm³ obtained for 14% $SrTiO_3$ discs fired to 1600°C in a gas-oxygen furnace.

f. On the assumption that the low density might be caused by oxygen dissociation, the firing was repeated, but this time with oxygen flowing

through the sagger.

After two refirings, first at 1580 and then at 1565°C, a mean density of about 3.68 g/cm³ was achieved. However, this still corresponds to a total porosity of 10%.

3. Measuring Techniques

Flexural strength measurements under four point loading were carried out at 25°, 500°, and 1000°C in a Kanthal wound furnace. The load transmitting apparatus was constructed of Inconel X except for the pins which were of Renē 41. Specimens were inserted in the furnace at the measuring temperature and allowed to equilibrate for about 10 to 20 minutes before being loaded to failure. . Longer equilibration times up to an hour or more were tried with no significant change in results. Groups of seven or eight $SrTiO_3$-Al_2O_3 specimens were broken at each temperature. For comparison purposes, groups of twenty alumina specimens (Wesgo Al 995) were evaluated at room temperature and at 1000°C.

Results presented in Table V clearly show the weakness produced by the 10% porosity of the titanate-alumina ceramic. Another factor in this weakness is grain size: the titanate composition had about double the average grain size of the Wesgo Al 995. However, these effects can be roughly eliminated, and the titanate composition mathematically reduced to the same condition as the Al 995 by means of Knudsen's relationship (Ref. 9):

$$S = kG^{-a} e^{-bP} \qquad (2)$$

where S = strength
k, a, and b are constants
G is grain diameter
P is volume fraction of porosity.

The constant k in equation (2) may be eliminated by calculating S_1/S_2, where S_1 is the measured strength of test bars having a porosity of 10% and a grain size G_1, and S_2 is the calculated strength of the same material with a texture similar to that of Wesgo Al 995; i.e., with P = 2% and $G_2 = G_1/2$. Equation (2) then becomes:

$$\frac{S_2}{S_1} = \left(\frac{1}{2}\right)^{-a} \frac{e^{-0.02b}}{e^{-0.10b}} \qquad (3)$$

Using the value of 4 for b (calculated by Knudsen from Coble and Kingery's (Ref. 10) data for bend tests on sintered alumina) and 0.5 for the constant a (from the original Orowan-Petch (Ref. 11) treatment of grain size), S_2/S_1 becomes approximately 1.9. Multiplying the experimental room temperature strength of the porous titanate-alumina composition (13,800 psi) by the correction factor gives a value of about

Table V
FLEXURAL STRENGTH OF 12% SrTiO$_3$-88% Al$_2$O$_3$ CERAMICS[1]

Temperature °C	Flexural Strength (psi)			
	12% SrTiO$_3$[2] 88% Al$_2$O$_3$	Coef. of Variation (%)	Wesgo Al 995	Coef. of Variation (%)
25	13,800 (26,000)	15.1	27,900	13.1
500	13,700	18.6	-	-
1000	10,500 (20,000)	16.2	19,600	10.1

[1] All test bars broken under four point loading in the as fired condition.

[2] The test bars of the titanate-alumina composition had a porosity of 10% and a grain size approximately twice that of the Al 995. The parenthesized strength values have been calculated using Knudsen's (Ref. 9) relationship to reduce this ceramic mathematically to the same porosity and grain size as the Wesgo alumina.

26,000 psi for the titanate composition in a form similar to Wesgo Al 995. The similarity between this value and the one actually measured for Wesgo alumina (27,900 psi) implies that the potential flexural strengths of properly fired titanate-alumina dielectrics are comparable to those of commercial high alumina ceramics. Moreover, the compensated ceramic has about the same temperature variation of strength as alumina in short term experiments conducted over the range 25 to 1000°C. However, the catalytic influence of Ti ions on grain growth and sintering may well produce a considerable acceleration of creep and possibly of corrosion fatigue. Measurements of these properties should form an important part of any future research on titanate-alumina ceramics.

IV. COMMENTS AND CONCLUSIONS

Since this report completes the ARF alumina dielectric program on Contract AF 33(616)-5929, the following list of conclusions and comments embraces the entire project. Their purpose is to summarize the major observations and accomplishments of the program and to point out areas where additional research may be particularly desirable.

1. High purity alumina powders, containing less than 100 ppm of foreign cations, can be readily prepared by dissolving 99.999% aluminum metal in hot HCl and either: (a) evaporating and calcining the

chloride solution or (b) precipitating and decomposing the hydrated oxide. The surface area and particle size of the resulting powders are very sensitive to differences of calcining temperature in the range 1000 to 1300°C. The calcined precipitated alumina used in this program was a very fluffy powder composed of particles which were themselves aggregates of smaller grains. Consequently, cold pressed densities were very low and a maximum fired density of only about 92% of theoretical was attained at temperatures as high as 1950°C. Recently, Cutler (Ref. 4) has prepared very pure alumina by dissolving metal in HCl or H_2SO_4. He found that the directly calcined sulfates and chlorides were more easily densified than oxides derived from the hydrate. Cutler was able to prepare alumina ceramics with densities up to 95 to 96% of theoretical by long firing at temperatures as low as 1675°C; moreover, he noted that the density tended to decrease at higher firing temperatures.

2. Alumina ceramics formed by sintering high purity powders in flowing air have dissipation factors about an order of magnitude lower than commercial high alumina ceramics. As an example, the following values of tan δ were measured at 500°C; 0.2 at 10^2 c/s, 0.044 at 10^3 c/s, 0.0092 at 10^4 c/s, 0.0027 at 10^5 c/s, 0.00048 at 10^6 c/s, and 0.0002 at 10^7 c/s. Nevertheless, the dissipation factors generally remain about an order of magnitude higher than corresponding values obtained for single crystal sapphire. Since the purity of the sapphire is no greater than that of the ceramic, the difference in losses must be assigned to another cause - most probably grain boundary effects. Evidence in favor of this is given by Arrhenius plots of log conductivity (calculated from tan δ at 10^5 c/s) vs 1/T. Pure alumina ceramics display an activation energy of conduction of about 1.3 ev at 500°C, but the energy falls to a fraction of an electron volt at lower temperatures. Thus, there are at least two mechanisms producing losses, and the low activation energy of the low temperature process is strongly indicative of a surface effect. An example of one loss mechanism caused by grain boundary influence was observed in several samples of aluminas having very low Si concentrations. The effect appeared as a small relaxation peak in curves of the dielectric loss factor, k", vs frequency. This peak did not shift in frequency with temperature, and gradually diminished in height to zero at about 300°C. The lack of temperature dependence suggests a non activated electronic process such as the oscillation of conduction electrons between potential barriers at the grain boundaries. The existence of such a process makes it possible to estimate the electron mobility within a grain provided the grain diameter and measuring potential are known. Values of 11-15 cm^2/volt sec at room temperature were calculated by this method. Actually, these values represent maximum rather than true mobilities because the current carriers do not traverse the entire grain. Instead, they stop at some point short of the grain boundary in response to a space charge zone created by the piling up of like charges. However, experience with such semiconductors as germanium, silicon, and zinc oxide indicates that this potential barrier is no greater than 10^{-4} cm thick - less

than one-tenth of the grain diameters in the ceramics measured (Refs. 12, 13).

3. Fabrication of ceramics by hot pressing ARF precipitated alumina (calcined at 1100°C) and Gulton Alucer MC resulted in densities of 3.84 and 3.97 g/cm^3 respectively. Both oxides were hot pressed in flowing argon; the former at 3500 psi and 1700-1750°C, and the latter at 3000 psi and 1650°C. The products were gray ceramics showing extensive grain growth. The gray color, caused by entrapped carbonaceous particles was completely eliminated from hot pressed specimens by oxygen annealing for a day at 1500°C or at 1500-1700°C for seven hours. Despite the fact that the pressing was carried out in graphite dies that were claimed to have an average ash content of only 0.03%, the cation impurity content rose from a concentration of less than 0.01% (in the ARF calcined precipitate) to levels close to 0.06%. Consequently, the dielectric losses of these ceramics were over ten times higher than those of the best cold pressed and sintered aluminas prepared from high purity oxides. As examples, tan δ (10^6 c/s and 500°C) for the hot pressed and oxygen annealed Alucer MC was 0.039, whereas for the originally purer ARF calcined precipitate it actually rose as high as 0.13.

4. Silicon ion impurities in alumina produce the greatest increase of tan δ of the group Si, Mg, Ti, (Ca, Fe, Cr) evaluated over the ion concentration range up to about 0.1%. The remaining impurities are listed in order of decreasing effect, and the last three are about equal in their behavior. Using the product of the individual correlation coefficient and the standardized partial regression coefficient as a measure of impurity influence, the relative effect of each ion at 10^6 c/s is Si (0.66), Mg (0.09), Ti (0.07), Ca (0.03), Fe (0.01), and Cr (0). At 10^2 c/s, the order is similar, but Mg becomes much more important: Si (0.40), Mg (0.23), Ti (0), Ca (0), Fe (0), Cr (0). The rising influence of Mg at low frequency reflects an increasing proportion of ionic conduction; Mg is probably the most mobile of the listed impurity cations. The dominant role of Si may be the result of a three fold action: (a) replacement of four Al^{3+} by three Si^{4+} (or introduction of an interstitial Si^{4+}) creates cation vacancies which form shallow trapping sites for positive holes; (b) the Si^{4+} ion itself, because of its excess positive charge, creates electron traps just below the conduction band; (c) a concentration of Si^{4+} ions at grain boundaries may form a very lossy vitreous or semi-vitreous layer.

5. Of the six cation impurities evaluated as possible sources of electrical loss, only Mg^{2+} was found to have a significant effect on the sintering of very pure alumina. Concentrations of less than 0.1% of Mg ion had an appreciable densifying action and produced ceramics having a semi-vitreous appearance.

6. Although low concentrations (0.1% or less) of impurities - particularly Mg - can produce drastic changes in experimental curves of dielectric constant vs temperature, this effect does not correspond to real changes in the value of k' of a bulk sample. The observed variations correlate with sample conductivity, and are due to an interfacial polarization in which charge carriers move between barrier layers formed at the measuring electrodes. The experimental variability, therefore, reflects the temperature variation of the number of free current carriers rather than of the dielectric constant. The strong effect produced by Mg^{2+}, especially at lower frequencies, is in line with its high mobility as an ionic charge carrier. Accumulation of these cations at an electrode creates a space charge zone which acts as the barrier layer. At higher frequencies (10^6-10^7 c/s) this effect diminishes in importance, and all of the aluminas, doped and pure, have a similar temperature variation of k' of about 6-7% from 25 to 500°C.

7. Control of the temperature variation of k' for a predominantly alumina ceramic was accomplished by introducing a compensating compound in concentrations ranging from 8 to 20%. $SrTiO_3$ was found to be an effective compensating phase at microwave frequencies for temperatures up to about 800°C. When fired with Al_2O_3 it remains as a stable compound and does not disappear through reaction or solid solution. At a titanate concentration of 14%, dk'/dT between 25 and 500°C is reduced from 5.5% observed for a pure alumina ceramic to 1.0%. Expanding the temperature interval to 25-730°C still results in the relatively small temperature variation of 2.8% as compared to 8.4% for alumina alone. Despite the high Ti concentration entailed by a 14% addition of $SrTiO_3$, dielectric losses are not excessive if a C.P. grade titanate is used in the formulation of the mixture. Under these conditions, tan   (at 500°C and 10^6 c/s) of a 14% $SrTiO_3$-86% Al_2O_3 ceramic is only 0.01 as compared to 0.0052 for Coors AD 99 alumina. A side effect of $SrTiO_3$ additions to alumina is an approximate 40% rise of the room temperature dielectric constant.

8. Mixtures of $SrTiO_3$ and Al_2O_3 form a pseudo binary system having a eutectic point at a composition between 65 and 70% $SrTiO_3$ and a temperature near 1625°C. Above this temperature, oxygen dissociation, which introduces porosity as well as electrical losses into the composite, takes on increasing importance. Ceramics of highest density are favored by low firing temperatures (1600-1650°C), minimum exposure at the maturing temperature, and maximum partial pressure of oxygen in the firing atmosphere. Once porosity has been introduced into a titanate-alumina ceramic it cannot be easily reduced; repeated firings produce only a limited improvement. The fabrication technique described earlier in this report might be improved by the following specific measures: (a) a ceramic grade of alumina which can be effectively pressed might be used in place of the fluffy Alucer; (b) the alumina and titanate might be sintered together and reground before pressing into the desired shape; (c) low concentrations (less than 0.1%) of Mg^{2+} might be incorporated to hold down grain growth.

9. Applying Knudsen's equation to porous flexural test bars of a 12% $SrTiO_3$-88% Al_2O_3 mixture gives promise that a fully densified and fine grained composite should have a bend strength very similar to that of a high alumina ceramic. Moreover, this simularity of properties extends to the temperature variation of strength - at least for short term experiments up to 1000°C.

Thus the alumina dielectric investigation closes with its major objectives for the most part accomplished but with at least two important problems as yet unsolved: (a) the fabrication of very dense high purity alumina ceramics having the low losses observed in somewhat porous cold pressed and sintered specimens; (b) the fabrication of titanate-alumina composites having porosities and grain sizes comparable to those of a good high alumina ceramic. Solution of these problems will make possible the development of ceramic radomes of superior loss and dielectric constant characteristics.

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