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274 183

DEVELOPMENT OF REFRACTORY CERAMICS THAT CAN  
BE PROCESSED AT TEMPERATURES CONSIDERABLY  
LOWER THAN THEIR MAXIMUM PROCESSING TEMPERATURE

Quarterly Progress Report  
Contract No. NOW 61-0211-C-2  
1 December 1961 - 1 March 1962  
School of Ceramics  
Rutgers, The State University

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NAVAL WEAPONS

DEVELOPMENT OF REFRACTORY CERAMICS THAT CAN BE  
PROCESSED AT TEMPERATURES CONSIDERABLY LOWER THAN THEIR  
MAXIMUM USE TEMPERATURE

1 December 1961 - 1 March 1962

Prepared under Navy, Bureau of Weapons  
Contract NOW 61-0211-c

Quarterly Progress Report No. 5

School of Ceramics  
Rutgers, The State University  
New Brunswick, New Jersey

ABSTRACT

A study was initiated on the densification mechanisms of high alumina bodies that utilized the presintering process in their fabrication. Evidence is presented that the initial or presintering fire promotes the formation of phases that act as potent fluxes for the alumina in the final fire. A program is set up to determine the nature of the phases formed in the initial firing.

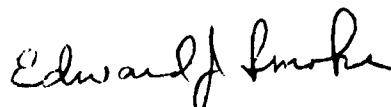
An initial attempt to utilize the devitrification mechanisms for producing a high quality refractory composition is reported. A 92% alumina composition was flame sprayed resulting in a glass that contains some alumina crystals. Differential thermal analysis and X-ray analysis indicated that a devitrifiable glass was produced.

High alumina bodies in the  $Al_2O_3$ -MgO system will be investigated in order to determine and control the densification of alumina. Experimental work will be carried out in a high temperature resistance furnace capable of reaching temperatures in excess of  $2000^\circ C$  in an extremely short time interval. Firings will be carried out in atmospheres of vacuum, dry hydrogen, and helium.

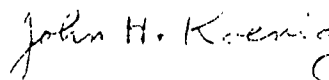
PREFACE

The undersigned constitute the planning committee for this project. Professor E. J. Smoke is project leader. The experimental work has been carried out by Mr. Peter Fleischner and Mr. Chester Ringel.

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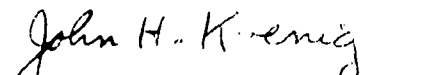


Edward J. Smoke  
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March 1, 1962

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## I. PRESINTERING STUDY

### A. Introduction

Most high quality industrial bodies as well as those prepared for research purposes contain appreciable void space exhibiting bulk densities between 75 and 92% of their true density. This quality is sufficient for most applications, however, there are applications in which this quality is not in a suitable range, such as for radome applications. Under earlier Navy sponsored research, the objective was to increase the percentage of true density to 100%. An alumina composition was developed which exhibited 99% of its true density. This was accomplished by a presintering process in which the composition was first prepared and fired conventionally in rod form at a diameter of 0.100 inch. These were ground to a controlled particle size distribution including sufficient fines for slip casting. Radome shapes up to 60 inches in height and 16 inches in diameter were prepared and some blanks weighing up to 150 pounds were fired to this quality. Under the present Navy sponsored contract, bodies containing 94%  $Al_2O_3$  - 3%  $MgO$  - 3%  $SiO_2$  have been produced with the utilization of the presintering process that mature at 2600°F and possess high strength, good electrical properties, and excellent refractoriness. Bodies of the same composition prepared conventionally were not matured at 3060°F and possessed lower strengths and refractoriness.

The explanation for the superior bodies produced utilizing the presintering process is that by presintering the raw materials, all reactions, gas evolution, and the like, take place before the final firing, so that a true densification can take place, unhindered by any reactions in the final firing operation. However, recent studies under this present Navy contract have shown that other mechanisms may come into play in the densification of a "presintered" body. Figure 1 on page 3, density vs firing temperature of an alumina body fabricated conventionally and fabricated with the utilization of the presintering process and Figure 2 on page 4, "density vs soaking time" of the same body show two distinctly different plots. The density of a conventionally fabricated body increases continuously with an increase of soaking time and also with an increase in the firing temperature. This type of curve is indicative of a diffusional mechanism type of sintering. In this type of sintering, matter transport is attained by diffusional means which are strongly dependent upon time and temperature. Densification will take place to a greater extent with an increase in time and temperature, and density will increase to its theoretical value if conditions are optimum. From the above considerations, it is assumed that the densification of a conventionally fabricated alumina body of this composition is realized through diffusional mechanisms. The two figures show a different plot of density vs time and temperature for an alumina body utilizing the

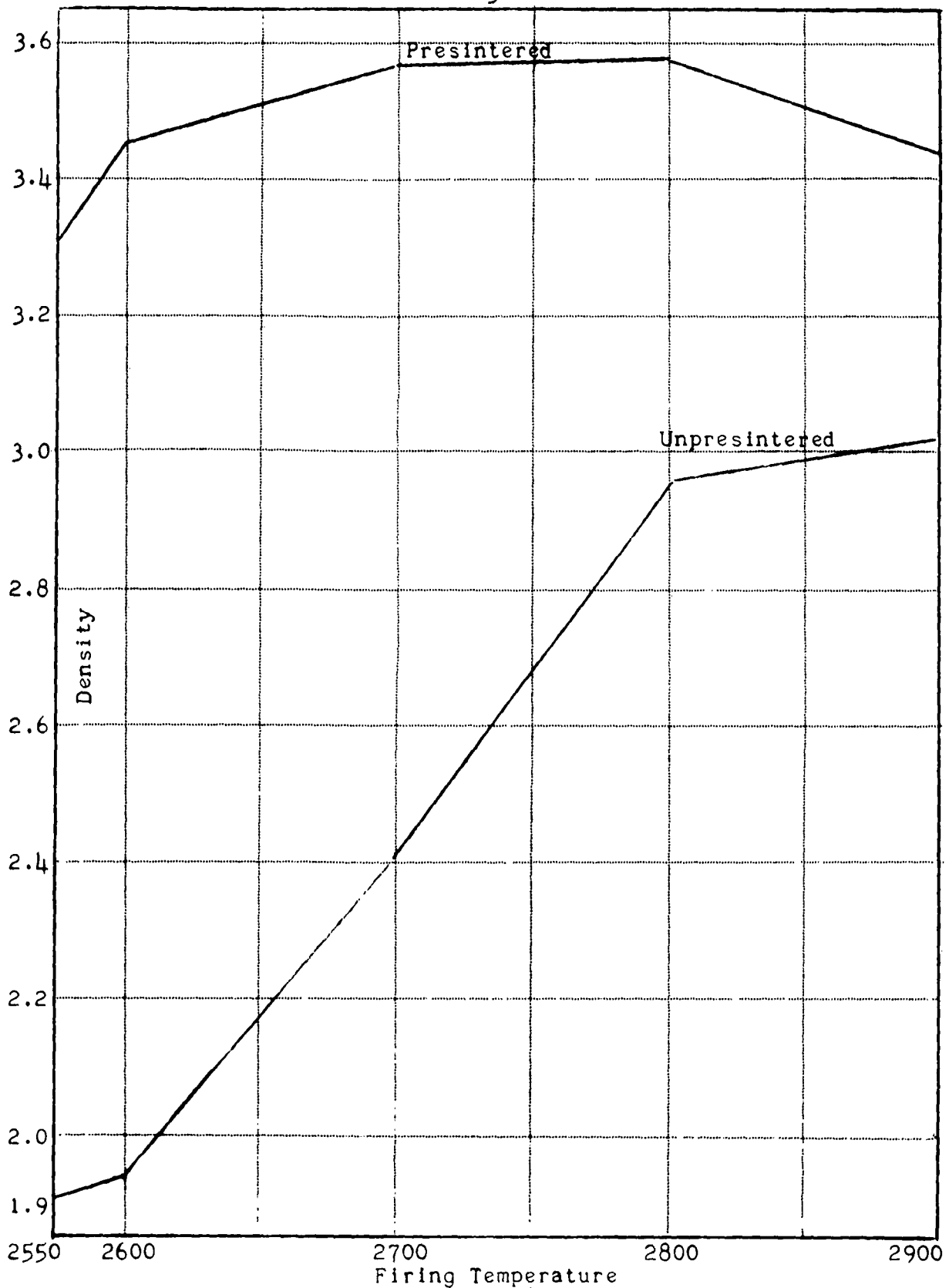


Figure 1  
DENSITY VS FIRING TEMPERATURE

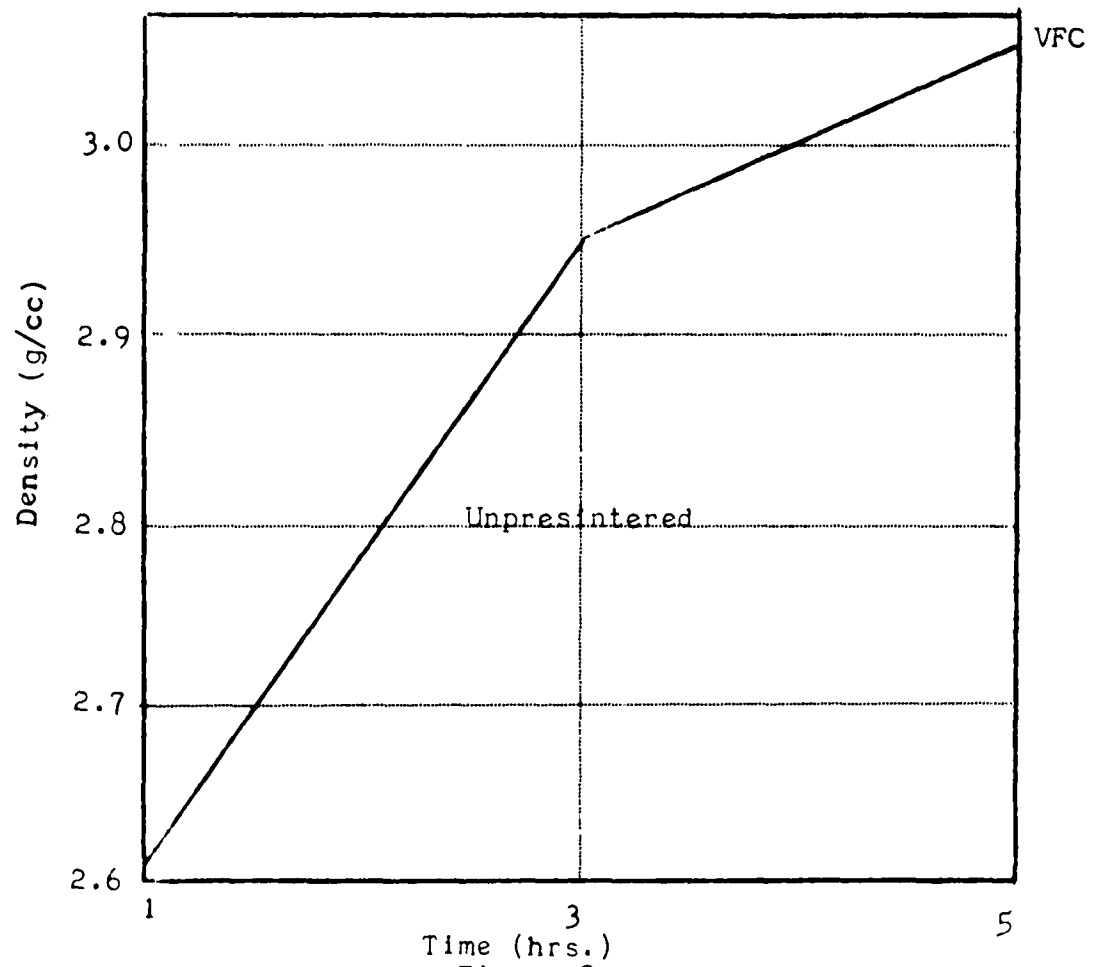
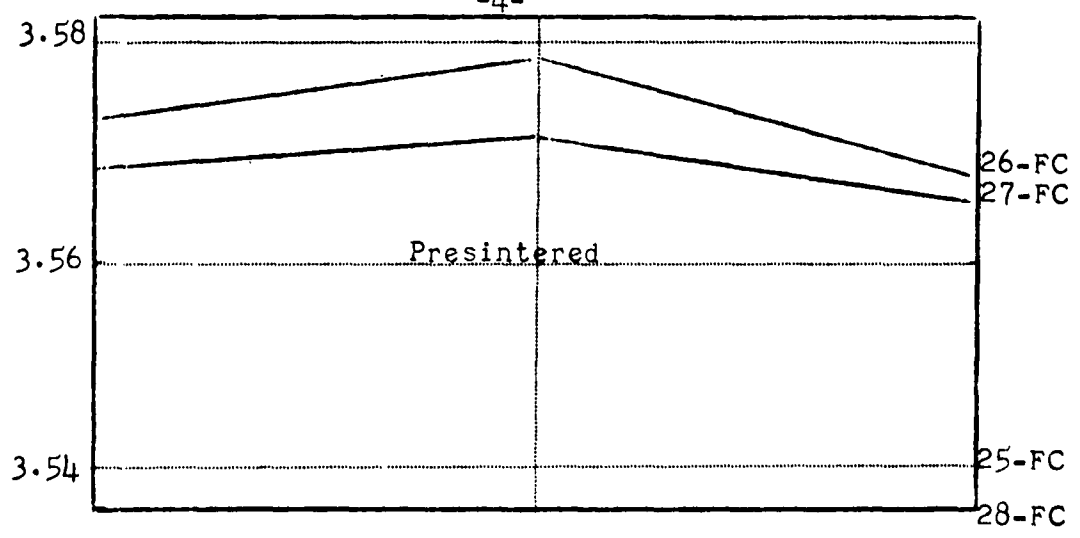


Figure 2  
DENSITY VS SOAKING TIME

presintering process in its fabrication. As seen, the density increases initially to a maximum value, at which time there is an intermediate leveling off of the values for a period of time, and finally the density decreases for an increase in time and firing temperature. This type of density curve is indicative of densification through the incorporation of a glassy or eutectic liquid phase. Here the initial increase of density is associated with the formation of a fluid glass or liquid eutectic phase which fills the voids and pulls the individual grains together by capillary action. The leveling off of the density is associated to that period of time or temperature range where all the voids are filled with glass and the particles are in closest contact and the fluidity of the glass or the eutectic liquid is of a comparable value over the range of time and firing temperature. The resultant decrease in density is associated with an increase in the viscosity of the glass or eutectic liquid such that it would tend to form spheres instead of coating all the grains, or the decrease in density may be associated with gas bubbles being formed within the glass. From the above considerations, it is assumed that the densification of an alumina body, containing silica and magnesia fabricated using the presintering process, is realized through a glassy bond or liquid type densification.

Thus, by presintering the raw materials there is now a wholly different type of densification mechanism taking place in

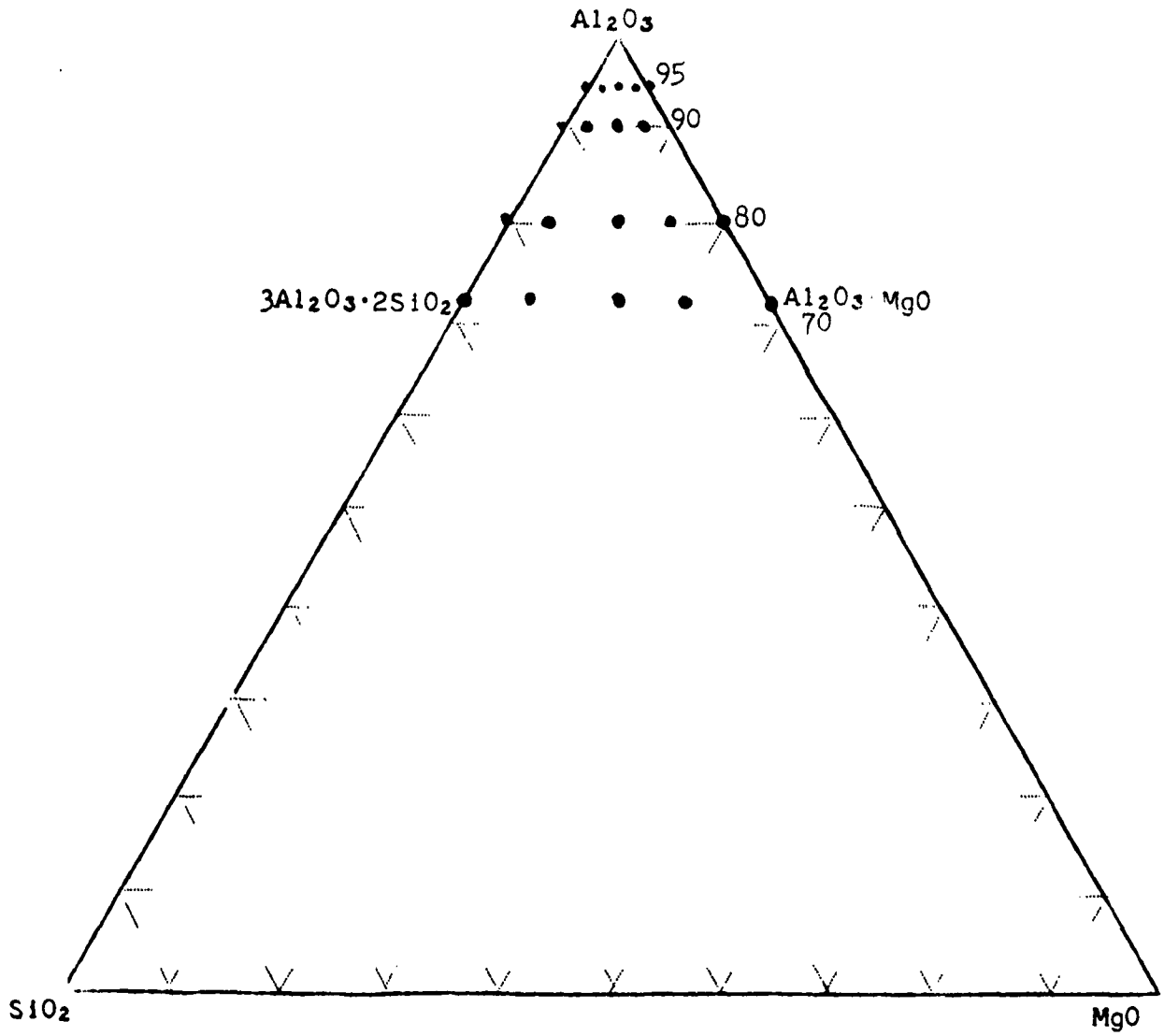
the final firing than took place in conventionally fabricated bodies of the same composition. This has led to the speculation that the "presintering" fire enables the formation of a fluid, low melting glass in the final fire; or "presintering" enables the formation of a potent flux for the alumina such to form a low melting liquid in the final firing.

The object of this study is to determine the dependence in the initial fire of: raw materials, firing temperature, phase formation, grain size, density, phase distribution, and sintering mechanisms, upon the resultant body achieved in the final firing operation. From this study it is hoped to determine the effect of relative amounts of various phases formed in the presintering fire that give rise to the beneficial phase formations in the resultant body.

#### B. Body Compositions

The body compositions were chosen such that the effect of the alumina, magnesia, and the silica could be noted with regard to their role in phase formations, maturing temperatures, grain size, phase distribution, density, and sintering mechanisms. The compositions chosen are within the  $Al_2O_3-SiO_2-MgO$  phase diagram shown in Figure 3 on page 7. As seen from the figure, the alumina content increases from 71.8% to 95% by weight, while the remainder of the body composition is added wholly as silica, magnesia, or, fixed ratios of silica and magnesia.

Figure 3  
COMPOSITIONS CHOSEN IN  $\text{Al}_2\text{O}_3$ - $\text{MgO}$ - $\text{SiO}_2$  PHASE DIAGRAM



In all the body compositions the alumina was added as A-14 aluminum oxide, Alcoa Corporation; the magnesia was added as magnesium carbonate, analytical reagent, Mallinckrodt Chemical Works; and the silica was added as supersil, No. 5 micron, Pennsylvania Glass Sand Corporation. The magnesium carbonate was fired to 2000°F and was found to contain 42.4% magnesium oxide.

<u>Body PF-71</u>	<u>2000 gm batch formula</u>
Al <sub>2</sub> O <sub>3</sub> -71.8%	1436.0 gms
MgO-0.00%	-
SiO <sub>2</sub> -28.2%	564.0
<u>Body PF-72</u>	
Al <sub>2</sub> O <sub>3</sub> -71.8%	1436.0
MgO-7.05%	332.5
SiO <sub>2</sub> -21.15%	423.0
<u>Body PF-73</u>	
Al <sub>2</sub> O <sub>3</sub> -71.8%	1436.0
MgO-14.1%	665.1
SiO <sub>2</sub> -14.1%	282.0
<u>Body PF-74</u>	
Al <sub>2</sub> O <sub>3</sub> -71.8%	1436.0
MgO-21.15%	997.6
SiO <sub>2</sub> -7.05%	141.0

<u>Body PF-75</u>	<u>2000 gm batch formula</u>
Al <sub>2</sub> O <sub>3</sub> -71.8%	1436.0 gms
MgO-28.2%	1330.2 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -00.0%	-
<u>Body PF-81</u>	
Al <sub>2</sub> O <sub>3</sub> -80%	1600.0
MgO-00%	-
SiO <sub>2</sub> -20%	400.0
<u>Body PF-82</u>	
Al <sub>2</sub> O <sub>3</sub> -80%	1600.0
MgO-5%	235.8 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -15%	300.0
<u>Body PF-83</u>	
Al <sub>2</sub> O <sub>3</sub> -80%	1600.0
MgO-10%	471.6 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -10%	200.0
<u>Body PF-84</u>	
Al <sub>2</sub> O <sub>3</sub> -80%	1600.0
MgO-15%	707.4 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -5%	100.0
<u>Body PF-85</u>	
Al <sub>2</sub> O <sub>3</sub> -80%	1600.0
MgO-20%	943.3 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -00%	-

<u>Body PF-91</u>	<u>2000 gm batch formula</u>
Al <sub>2</sub> O <sub>3</sub> -90%	1800.0 gms
MgO-00%	-
SiO <sub>2</sub> -10%	200.0
<u>Body PF-92</u>	
Al <sub>2</sub> O <sub>3</sub> -90%	1800.0
MgO-2.5%	117.9 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -7.5%	150.0
<u>Body PF-93</u>	
Al <sub>2</sub> O <sub>3</sub> -90.0%	1800.0
MgO-5.0%	235.8 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -5.0%	100.0
<u>Body PF-94</u>	
Al <sub>2</sub> O <sub>3</sub> -90.0%	1800.0
MgO-7.5%	353.7 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -2.5%	50.0
<u>Body PF-95</u>	
Al <sub>2</sub> O <sub>3</sub> -90.0%	1800.0
MgO-10.0%	471.6 gms MgCO <sub>3</sub>
SiO <sub>2</sub> -00.0%	-
<u>Body PF-51</u>	
Al <sub>2</sub> O <sub>3</sub> -95.0%	1900.0
MgO-00.0%	-
SiO <sub>2</sub> -5.0%	100.0

A 11

Body PF-52

Al<sub>2</sub>O<sub>3</sub>-95.0%

MgO-1.25%

SiO<sub>2</sub>-3.75%

Body PF-53

Al<sub>2</sub>O<sub>3</sub>-95%

MgO-2.5%

SiO<sub>2</sub>-2.5%

Body PF-54

Al<sub>2</sub>O<sub>3</sub>-95.0%

MgO-3.75%

SiO<sub>2</sub>-1.25%

Body PF-55

Al<sub>2</sub>O<sub>3</sub>-95.0%

MgO-5.0%

SiO<sub>2</sub>-0.0%

2000 gm batch formula

1900.0

58.95 gms MgCO<sub>3</sub>

75.00

1900.0

117.9 gms MgCO<sub>3</sub>

50.0

1900.0

176.85

25.0

1900.0

235.8

-

C. Presintering Process

The raw materials were weighed and then mixed in a twin shell blender for one hour. Upon completion of mixing, the batch was placed in a Lancaster muller mixer where 27% by weight of a 2% Superloid solution was mixed in the batch. Then the batch was granulated by passing through a micropulverizer to attain an extrudable granular distribution. The extrusion was performed without de-airing through a 1/8 inch diameter die. These thin bars were dried overnight and then broken into 1/2 inch lengths. The batch was then divided into five equal parts, each part placed in mullite saggars and fired to one of several predetermined temperatures. The temperatures selected were: 2000°F, 2600°F, 2700°F, 2800°F, and vitrification, in seven hours with a one hour soak at each temperature. The bars were removed from the kiln and ground for 24 hours in an alumina pebble mill with alumina balls. The mill batch was as follows: 100% bars, 600% balls, and 50% water. The milled slurry was then passed through a 325 mesh screen and allowed to dry. After drying, the batch was pulverized by passing through a micropulverizer, then mixed wet in a Lancaster muller mixer with 5% by weight of a 2% Superloid solution. The wet batch was passed through a 20 mesh screen and pressed into discs one inch in diameter at 11 tons pressure using a hand operated hydraulic press. These discs were fired to 2500°F, 2600°F, 2700°F, 2800°F, and vitrification in seven hours with a one hour soak at each firing temperature.

D. Investigational Procedure

The following investigational procedure will be used in this study:

Upon completion of the initial, or presintering fire the thin bars of each composition are to be investigated. An X-ray analysis will be performed to determine the phases present, including solid solutions. Microscopic determinations will be performed with the use of polished sections to determine grain size, shape of grains, and phase distribution. Density and moisture absorption will be determined by conventional means.

Upon completion of the grinding operation, the material will be investigated microscopically to determine fragment size and effect of grinding upon phase distribution.

Upon completion of the final firing, the discs of each composition are to be investigated. An X-ray analysis will be performed to determine the phases present, including solid solutions. Microscopic determinations will be performed with use of polished sections to determine grain size, shape of grains, and phase distribution. Density and moisture absorption will be determined by conventional means.

E. Conclusions

From this study it is hoped that various conclusions can be reached. By determining what phases are formed in the presintering fire, it should be possible to determine the effect of

various phases upon the sintering characteristics of alumina. Once the effect has been shown, it should now be possible to present an accurate description of the densification mechanisms taking place in the final firing operation. If these densification mechanisms can be traced to beneficial phase formations, it may be possible to achieve the beneficial results of presintering by modifying the presintering operation to reduce time and temperatures involved and make the process more economical.

#### F. Progress of Study

All compositions have been weighed, mixed, extruded, dried and fired to 2000°F, 2600°F, 2700°F, and 2800°F in seven hours with a one hour soak at the maximum temperature. Density measurements, X-ray, and microscopic analysis of the presintered bars has just recently been started and these results will be incorporated in future reports.

## II. DEVITRIFICATION STUDY

### A. Introduction

There are two principal approaches to prereacted materials. One is presintering, which is presently being investigated, and the other is devitrification. Devitrification involves the melting of the total composition followed by rapid quenching to maintain the glassy or random structure, reducing this frit to a

fine particle distribution, fabricating specimens from the powdered frit by conventional methods, then firing. During this subsequent conventional firing of these specimens, the principal crystalline phase devitrifies to form the crystalline phase in the specimens. This prereaction procedure results in very intimate mixing of the composition, actually on an atomic basis. This procedure has been used successfully at this research center with a number of rather low melting compositions whose principal crystalline phases are ternary compounds, including some lithium aluminosilicates, lead aluminosilicates, magnesium aluminosilicates, boron phospho-silicates, etc.

This procedure has also been used successfully to produce a glass containing up to 94% barium titanate. However the advantageous ferroelectric properties are so diluted by the 6% additives necessary to produce the frit that a procedure was devised to make a glass of 100% barium titanate. In order to accomplish this, very high temperatures are necessary and since the barium titanate is a pure compound the quenching operation must be extremely rapid to maintain the glass or random structure. These requirements have been met by flame spraying directly into distilled water. Another requirement is that the particle size must be such as to flow through the flame spray gun, to be completely melted, and be cooled rapidly enough so that crystallization does not occur within the particles.

Since the type of composition of interest to this present effort is more refractory than the barium titanate, it was decided to attempt to utilize the procedure used for the pure barium titanate. It was anticipated that it will be difficult to maintain all of the alumina content of the high alumina type compositions presently under study in the glassy state because of its very high melting temperature. However, if a considerable amount could be retained in the glassy state for subsequent controlled devitrification, improvements should be realized. The object of this phase of the effort is to prereact a high alumina composition for the devitrification process to determine its potential for lowering the firing temperature of a refractory high frequency insulator.

B. Procedure

The compositions selected for evaluation is that prepared by presintering and used for the earlier radome work as observed in Report No. 4, N-onr-404(03). This composition was selected because of its superior properties and the object is to determine whether any improvement as to quality, lower firing temperature, etc., could be realized.

The high alumina body of composition 91.9% Al<sub>2</sub>O<sub>3</sub> - 6.0% SiO<sub>2</sub> - 2.1% MgO was prepared from the following raw materials:

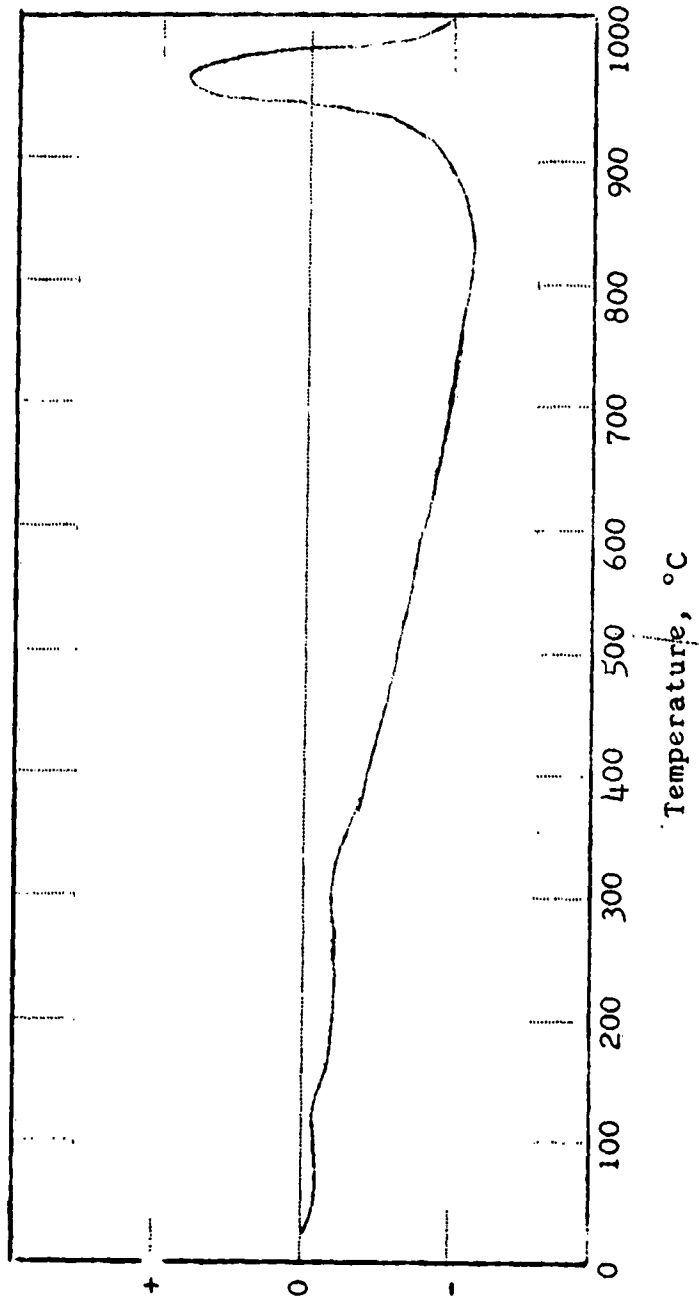
Aluminum Oxide - 90%	A-14, Alcoa Corporation
Talc - 6%	Montana No. 1736
Clay - 4%	Victoria Ball Clay, United Clay Mines

The ingredients were weighed and mixed for one hour in a twin shell blender. Upon completion of mixing, the batch was placed in a Lancaster muller mixer where 27% by weight of a 2% Superloid solution was mixed into the batch. The batch was then granulated by passing through a micropulverizer to attain an extrudable granular distribution. The extrusion was performed without de-airing through a 1/8 inch die. These thin bars were dried overnight, broken into 1/2 inch lengths, placed in mullite saggars, and fired to 2800°F with a one hour soak at the maximum temperature. Upon cooling the bars were removed from the kiln and broken by impaction into particles minus 325 mesh and plus 400 mesh, and particles that pass through 400 mesh. These batches were passed through a Metco, Type 2D Thermo Spray Gun into distilled water for rapid quenching. The flame sprayed particles were dried and classified into two particle size groups, those that pass 325 mesh and those that pass 400 mesh. Differential thermal analysis and X-ray analysis were performed upon the particles. Discs were prepared and fired to 2700°F, 2800°F, and 2900°F with a one hour soak at each temperature. Bulk density and moisture absorption measurements were performed conventionally.

### C. Results

The results are shown in the table below and in Figures 4 and 5 on pages 18 and 19. X-ray analysis show that a complete glass was not attained. Considerable alumina has either not

Figure 4  
DIFFERENTIAL THERMAL ANALYSIS OF  
FLAME SPRAYED 91.9% ALUMINA COMPOSITION



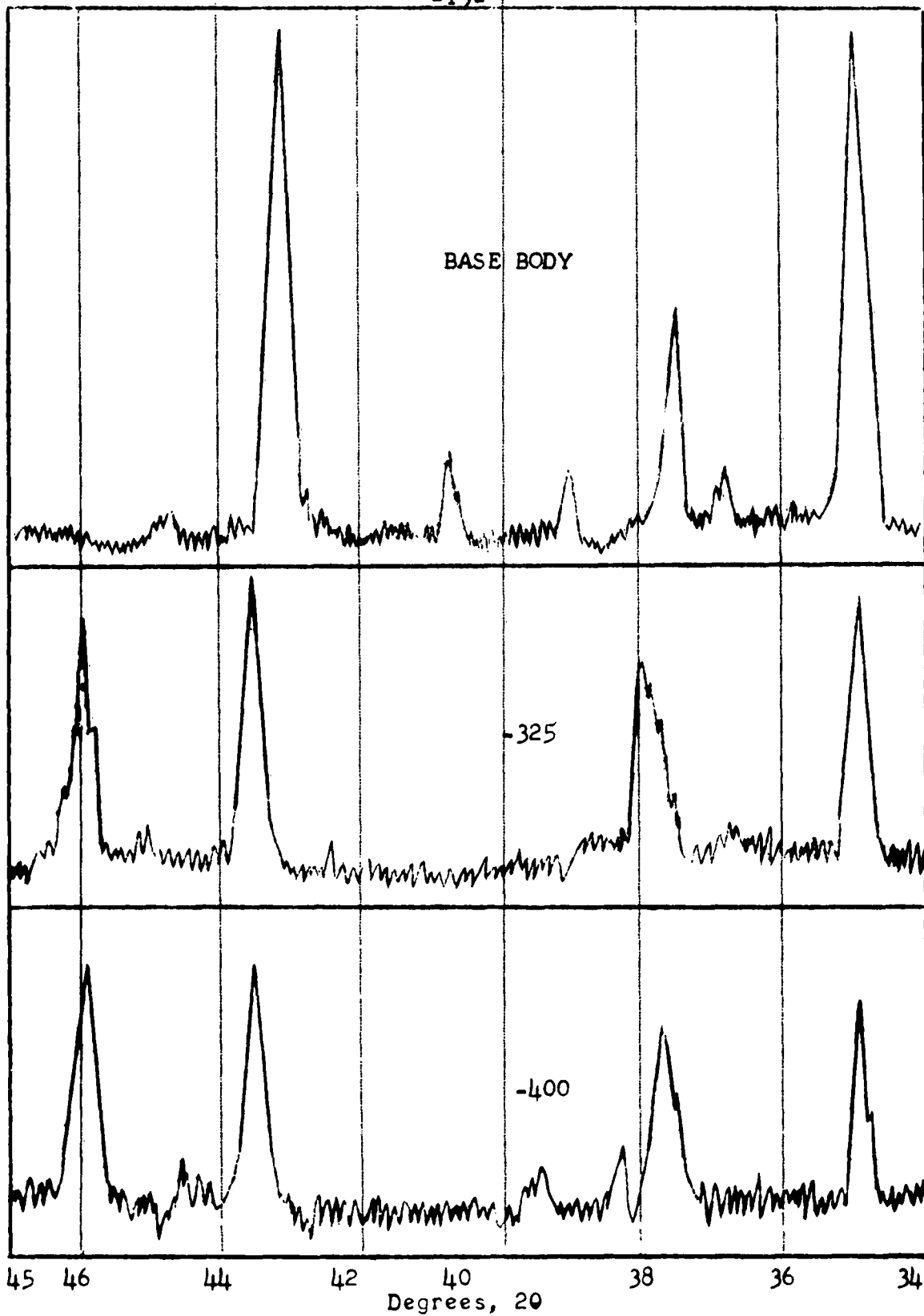
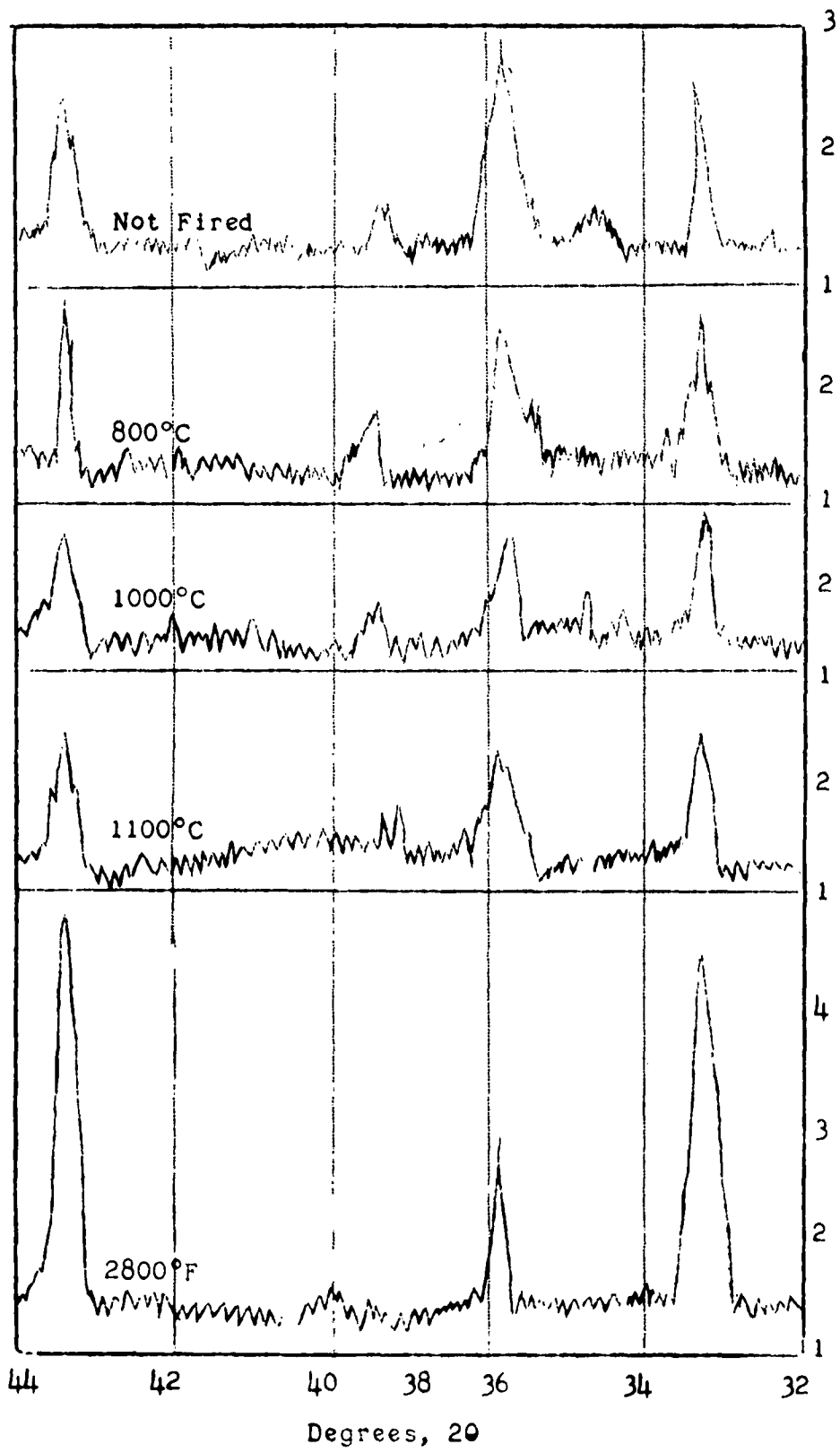


Figure 5  
X-RAY ANALYSIS OF FLAME SPRAYED BODY AND STANDARD



melted because the spray gun temperature was too low, or the rate of quenching was too slow and partial devitrification has resulted. This analysis indicates that as the particle size of the composition used to flame spray is decreased the crystal content in the glass decreases as evidenced by the decrease in peak height as the particle size decreases. Thus, with small enough particles and/or controllable parameters with the flame spray procedure, a complete glass should be obtained.

Differential thermal analysis exhibits an exothermic peak at 960°C. This indicates that devitrification mechanisms are occurring. X-ray analysis of the flame sprayed material, when heated in powdered form to 1470°, 1830°, 2010° and 2800°F, shows that the devitrification at the first three temperatures is incomplete, but is complete at the highest temperature. The intensity of the major peaks are approximately twice as high after the highest firing.

Table I  
Density and Moisture Absorption Results  
of Flame Sprayed Material

	<u>Moisture Absorption</u>	<u>Bulk Density</u>
2700°F	12.4%	2.55
2800°F	8.2	2.89
2900°F	3.8	3.27

The above table shows that the specimens possess a high moisture absorption, and subsequently a low bulk density, when fired in the range 2700°F through 2900°F with the minimum moisture absorption being 3.8% and the maximum bulk density being 3.27 at the highest temperature. It is believed that these results can be attributed to a poor particle size distribution and the spherical shape of the particles resulting in poor packing upon fabrication. In order to remedy this situation the particle size distribution must be altered for better packing. This will be a phase in the future program on devitrification.

D. Summary

This initial attempt at devitrification as a mechanism for producing a superior high alumina composition, has resulted in an essentially glassy structure, but containing some crystalline alumina. It is felt that by controlling the parameters of initial particle size, quenching rate, and flame temperature that a total glass can be attained. This glass devitrifies upon subsequent heating as evidenced by differential thermal analysis and X-ray analysis. However, specimens prepared did not possess optimum qualities in terms of density and moisture absorption. This is due to a narrow range of spherical particle sizes resulting from the flame spray process.

E. Future Work

1. Effort to control particle size.
2. Study of less refractory compositions utilizing the devitrification mechanisms.

### III. SINTERING STUDIES IN THE ALUMINA-MAGNESIA SYSTEM

#### A. Introduction

##### 1. Object

The overall objective of this research program is to lower the firing temperature yet retain all the desirable engineering properties including refractory of ceramic compositions for radome application. To the present alumina compositions containing up to 96% have been studied as bodies utilizing the "prereacted raw materials" technique. In this type composition the crystals are bonded by a glassy phase. The phase reported herein will be devoted to compositions in the range of 98 to 100% alumina in which the densifying mechanism is solid state sintering in the absence of a glassy phase.

##### 2. Literature Review

Two theories have been proposed for solid state sintering, the plastic flow theory and the diffusion theory. Recent investigators have shown that the plastic flow theory does not completely explain sintering primarily because there is no explanation for the inability to remove a pore within the grain. If a pore is found at a grain boundary or found within a grain, the resultant sintering can be totally different. When the pore is located within the grain it is difficult, if not impossible, for removal and further densification is stopped. When the pore is located at the grain boundary it can be removed and the body can be further densified.

In the diffusion theory, densification is said to take place by means of vacancy movement. A vacancy is a missing atom or ion in the crystal lattice, and the movement of vacancies is equivalent, except opposite in sign, to the movement of ions. The driving force for both sintering and grain growth is the reduction in surface energy which is equivalent to a reduction in surface area per unit volume. Diffusion sintering is divided into three primary stages: initial, intermediate, and final. It has been well established by Kuczynski (1) that during the initial stage of sintering the source of vacancies is the neck area, the contact area between two adjacent spherical grains or particles. The initial stage of sintering is that period where the interparticle contact area increases from 0 to 0.2 of the cross sectional area of the initial particle. This stage of sintering is commonly called neck growth. The vacancy source for this stage is the neck area and the vacancy sink is the grain boundary. The initial stage of sintering ends when the neck surface becomes blunted due to neck growth. At this time grain growth begins because there is no longer a source of excess vacancy concentration at the neck. The intermediate stage of sintering occurs after grain growth has occurred. It is defined as a continuous pore channel coincident with three grain edges. This assumption has been partially verified by experiment. Upon shrinkage and densification, the continuous pore channel becomes condensed. Changes in the pore shape and pore distribution define the final stage of sintering.

There are two possible final stages of sintering, the previously mentioned condensed continuous pore channel and the other final stage results from discontinuous grain growth. In the first possible final stage of sintering the pores are located at the intersection of four grain corners; while in the alternate stage, the pores may be located at the grain corners and within the grain. Discontinuous grain growth is a phenomenon where large grains grow very rapidly at the expense of small grains. This phenomenon occurs when normal grain growth is inhibited by pores or other discontinuities at the grain boundary. Only few grains grow at this rapid pace resulting in a unidirectional grain boundary movement. In normal grain growth the grain boundary movement is of a equidirectional nature and occurs at a slower rate. It is the rapid unidirectional movement of grain boundaries that cause pores to be trapped within the growing grain. This gives rise to the second possible final stage of sintering. Once the pores are trapped complete densification of a solid state sintered body cannot take place.

In the theory of sintering using the diffusional processes there are three paths that vacancies can travel.

1. Evaporation condensation - vapor path.
2. Boundary or surface diffusion - vacancies travel along the surface of the grains or along the grain boundary.
3. Bulk diffusion - vacancies travel from their source through the bulk of the material and sink at the grain boundary.

Experimental results have shown that bulk diffusion is the predominant mechanism in sintering.

The primary sources and sinks for vacancies in the three stages of sintering are as follows:

	<u>Source</u>	<u>Sink</u>
1. Initial Stage	Neck	Grain boundary
2. Intermediate Stage	Continuous pore channel	Grain boundary
3. Final Stage	Isolated pores at grain boundaries	Grain boundary

Work has been done in the use of various atmospheres to aid the sintering process. Kucznski has shown that the diffusion coefficient of alumina is increased by many orders of magnitude with the use of a dry hydrogen atmosphere. It is thought that this is primarily due to the partial reduction of alumina and the subsequent formation of vacancies above and beyond those normally found at equilibrium. Coble (2) has applied this mechanism to prepare theoretically dense alumina. Kucznski also verified this theory by using wet hydrogen and observed no increase in the diffusion coefficient.

The effect of a small addition of MgO to alumina was established by Coble in the preparation of Lucalox. It was found that a quarter of a per cent of MgO was sufficient to inhibit secondary recrystallization (exaggerated grain growth) and thereby make it possible to obtain theoretically dense alumina.

These mechanisms have been studied and applied to a limited extent only. The objective of the present study is to attempt to produce pure or nearly pure alumina bodies which will be able to be used at temperatures considerably higher than their fabrication temperature. This will be accomplished by application of the solid state sintering mechanism and procedure.

## B. Procedure

### 1. Approach to Problem

The compositions to be investigated in the  $\text{Al}_2\text{O}_3$ -MgO system are: 100%  $\text{Al}_2\text{O}_3$ , 99.75%  $\text{Al}_2\text{O}_3$ , and 98%  $\text{Al}_2\text{O}_3$ . Small additions of MgO to alumina will tend to concentrate at the grain boundary because of the disordered state found there as compared to the ordered state within the crystal lattice. This makes it easier for small additions to stay at the grain boundary rather than the interior of the grain. Disagreement exists as to how MgO enters alumina in the region stated above. It may be that very small additions of MgO (1/4%) will enter as a solid solution and larger additions will form a spinel phase. If this is the case, the first two compositions will show the difference in the sintering characteristics of materials with and without a solid solution formed at the grain boundaries. The final composition is located in what is believed to be a region of spinel formation below the eutectic. The effect of a spinel phase at the grain boundary on the sintering of alumina will be compared to the effects of a solid solution, and to pure alumina. This comparison will include the following physical variables as a function of time and temperature:

1. Rate of grain growth.
2. Rate of densification or shrinkage.
3. Effect on exaggerated grain growth.
4. Diffusion coefficients.

This type of comparison should be applicable to many other oxides and may yield an insight into the sintering of many other solid state sintered compositions.

The effect of atmosphere on the sintering characteristics of alumina will be investigated for all three compositions mentioned. As noted in the first phase above, only a partial investigation of this effect has been carried out. Three atmospheres will be investigated; vacuum, dry hydrogen and helium. With this approach a comparison can be made of two effects; diffusion of gas in the pore phase, and the reduction of alumina. A comparison of the effect of a reducing atmosphere coupled with a fast diffusing gas molecule will be investigated using dry hydrogen. The effect of only a fast diffusing gas molecule will be determined by using helium gas. An ultimate effect in the diffusion rate of gases located within pores will be investigated with the use of a vacuum atmosphere. Finally, a comparison of these three atmospheres with data already published for the firing of alumina in air will be made. This investigation will show if there is any contribution by the diffusion rate of gases in pores to the overall rate of diffusion in  $Al_2O_3$ . For example, if the diffusion of gases found within the pores of a body contribute to

the overall diffusion coefficient it may be possible to produce theoretically dense pure alumina bodies which have not been obtained as yet. (Lucalox contains a small percentage of magnesia). This would mean that the rate of pore removal would be fast enough to overcome the initiation of exaggerated grain growth in pure alumina. In addition the combination of a reducing atmosphere, that will be able to create vacancies, and a fast diffusing gas molecule (dry hydrogen) will be compared to the other atmospheres, to determine the contribution of each factor above and in combination. It is expected that the study of various atmospheres on the diffusion of alumina will enable one to reduce the operating time and temperature in the fabrication of alumina bodies.

The combination of both phases namely composition and atmosphere under investigation, should result in a greater understanding and thus the ability to control the sintering process. The physical variables that will be determined as a function of temperature, time, atmospheres and additives are:

1. Grain growth.
2. Exaggerated grain growth.
3. Density and porosity.
4. Diffusion coefficients.

## 2. Raw Materials

Starting materials - Single crystal alumina with a particle size of  $0.3\mu$  will be used as a source of alumina. From the

preceding discussion it can be seen that if one starts with a raw material that has pores located within the grain these pores will probably not be removed during subsequent sintering. Therefore, the raw starting material must be free of voids. Single crystal alumina is a raw material that has few if any internal pores. The form of magnesia that will be used is a  $Mg(NO_3)_2$  solution. The addition of magnesia in this form and its subsequent fabrication into a body, will yield a uniform fine dispersion of magnesia in alumina.

The materials to be used are:

Alumina

Linde "A" alumina - Linde Company

Single crystal alumina

Purity - 99.99 + alumina

Grain size - 0.3 microns

Grain shape - spherical

Magnesia

"Baker's" magnesium nitrate crystals

Formula -  $Mg(NO_3)_2 \cdot 6H_2O$

Purity - 99.8% magnesium nitrate hexahydrate

C. Sintering Equipment

A photograph showing the set-up to be used for sintering is shown in Figure 1 on page 30. The set-up consists of the following equipment:

Figure 1  
EQUIPMENT FOR SINTERING STUDIES



- A. Power Stat - 15.6 KVA
- B. Ammeter - 0-50 Amps
- C. 10 KVA Transformer Output 1000 Amps, 10 Volts
- D. High Temperature Resistance Furnace
- E. Atmosphere Inlet Valve
- F. Atmosphere Outlet Valve
- G. Vacuum Valve
- H. MC-275 Oil Diffusion Pump
- I. Welch Duo-Seal Mechanical Vacuum Pump
- J. GPH-100A Discharge Vacuum Gauge
- K. GTC-100 Thermocouple Vacuum Gauge

1. Electrical components
  - A. Powerstat
  - B. 10 KVA transformer
2. Furnace
3. Vacuum equipment
  - A. Vacuum valve
  - B. Diffusion pump
  - C. Mechanical pump
4. Vacuum measuring equipment
  - A. Thermocouple vacuum gauge
  - B. Discharge gauge

The electrical power comes from the right side of the photograph to the furnace which in turn is attached to the vacuum system. The inlet and outlet valves on the furnace will be used to introduce, and remove continuously, atmospheres other than vacuum.

1. Electrical Components

The power source is 230 volts and 60 amps line current. This current is fed into a "Superior Electric Company Powerstat capable of carrying 15.6 KVA." The current then goes through a 0-50 amp ammeter to a 10 KVA transformer. The 10 KVA transformer is capable of delivering 1000 amps at 10 volts (Figure 1). This large amperage is necessary to heat up the molybdenum heating element in the furnace. The powerstat controls the current going into the furnace. The primary current going into the 10 KVA transformer is recorded on the 0-50 amp ammeter. The furnace temperature is controlled and varied by the powerstat.

## 2. Vacuum System

The vacuum system essentially consists of a mechanical vacuum pump backed up by an oil diffusion pump which is located below a vacuum valve which in turn, is attached to the bottom of the furnace (Figure 1). There are two pressure measuring devices for the system. A thermocouple gauge capable of measuring pressures between 1000 and five microns is located between the mechanical pump and the diffusion pump. The discharge gauge is located near the atmosphere outlet valve on the furnace and is capable of measuring pressures between 25 and  $10^{-3}$  microns.

The mechanical pump is capable of reducing the pressure in the system to about 25 microns. When the mechanical pump has reduced the pressure to less than a hundred microns the oil diffusion pump is turned on. The oil diffusion pump has a capacity of 275 liters per second and will take the system down to a pressure of about a tenth of a micron or less. A vacuum valve is located below the furnace. This valve will be open when vacuum firings are to be carried out and closed when other atmospheres are to be used. In this way the vacuum system can be protected in case of any hazard in the furnace and foreign particle entrapment in the vacuum system can be avoided.

## 3. The Furnace

The high temperature resistance furnace is basically the one described in the "Journal of the American Ceramic Society," Vol. 33, No. 1, January 1950, pages 25 and 26 by F. H. McRitchie and

N. N. Ault. We are indebted to Mr. Ault for his assistance in building this furnace. The furnace is shown in Figure 1.

It is a high temperature resistance furnace equipped for operation in vacuum, hydrogen, helium and other inert atmospheres. The heating element is a cylindrical sheet of molybdenum .005" thick. This is placed between 2 copper contact cones from where the electrical current enters. This cylinder has a gap of about 1/16" in order to sight directly on the specimens to be fired. The specimens are placed on molybdenum discs .005" thick and are suspended within the heating element by means of tungsten wire which is welded into the bottom of the top water jacket of the furnace (see Progress Report No. 2 of this contract for a sketch of the furnace).

The furnace shell is made of copper and is water cooled. The furnace interior is silver plated and radiation shields of molybdenum are located within the heating element near both upper and lower water jackets to maintain uniform temperature. Vacuum tight needle valves are placed on both the atmosphere inlet and outlet connections in order to maintain a vacuum when other atmospheres are not used. The furnace contains no insulating materials and therefore no problem arises in the outgassing of these materials under vacuum. In addition, since there is no insulating materials present, this furnace has a very fast current-temperature response. For example it is possible to heat this furnace to 2000°C in 30 seconds.

D. Fabrication

Magnesium nitrate solution will be added to Linde "A" alumina and a slurry formed. This slurry will be agitated for half an hour and then dried. The dried material is then remixed in an alumina mortar and pestal with sufficient water to produce a consistency capable of being press to discs. Discs 5/8 inches in diameter by 1/8 inches thick will be pressed at 50,000 psi. These discs will then be placed in small card bond boxes and placed in a desicator for storage. Two or three samples of each composition will then be placed in the furnace and brought up to 1000°C for half an hour to remove moisture. Then the samples will be brought up to the predetermined sintering temperature and held there for the length of time desired. Occasionally six samples of the same composition will be fired in order to determine the variation of temperature in the furnace and its effect on the properties that will be measured. Firings will be carried out at 1500, 1600, 1700 and 1750°C. At each of these temperatures the specimens will be soaked for 1, 3, 5 and 7 hours.

E. Physical Measurements

1. Density and Porosity

- A. Remove sample from furnace.
- B. Let samples cool in desicator.
- C. Weigh the samples.
- D. Boil for two hours in water.
- E. Determine wet and wet suspended weights.
- F. Calculate density and porosity.

2. Measure initial and final diameter of specimen and determine linear shrinkage.
3. Measure grain size, pore size, shape and location and exaggerated grain growth.
  - A. Prepare polished section for study under the microscope.
  - B. Determine average grain size by measuring at least 100 grains.
  - C. Determine pore size, shape, and distribution (about the grain).
1. From this measurement and (b) above exaggerated grain growth can be determined.

F. Analysis of Data

From the above determinations plots will be made of the following physical properties as a function of time, temperature, atmosphere and composition.

1. Density
2. Total porosity
3. Grain growth rate
4. Exaggerated grain growth.

From this data diffusion coefficients and activation energies for diffusion will be determined for the different atmospheres and compositions; density, total porosity, grain growth rate, and exaggerated grain growth will be determined and compared for the variables under investigation.

After the analysis of the above data, equations will be derived showing the relationships of atmosphere and composition on sintering of alumina. In addition these data will be used to broaden the understanding now known of solid state sintering and afford considerable knowledge in the control of the sintering process.

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