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EXPLORATORY DEVELOPMENT OF HIGH TEMPERATURE CIRCUIT ANALOG RADAR ABSORBING MATERIALS (CA-RAM)

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Whittaker Corporation

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13. ABSTRACT

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Thermal expansion measurements of numerous candidate matrices have been performed. X-ray diffraction studies have been performed to determine crystallographic changes in the candidate matrix materials due to thermal treatment and/or modifications.

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WRD personnel involved in the program included Mr. R. L. Van Auken, Project Engineer; Mr. J. E. Hilzinger, thermal property determinations; and Mr. S. Freske, X-ray diffraction studies. Mr. V. A. Chase served as Program Manager.

This report covers the period 1 July 1971 to 30 June 1972.

This technical report has been reviewed and is approved.

S. R. LYON
Project Monitor

FOR THE COMMANDER

ROGER J. AUSTIN, Major, USAF
Acting Chief, Metals and Processing Branch
Metals and Ceramics Division

ABSTRACT

The objective of this program is the development of high temperature circuit analog radar absorbing materials, designs and prototypes. Material development efforts have involved silica fiber reinforced ceramic composites based on a chemically reacted aluminum phosphate ($AlPO_4$) ceramic matrix. Matrix development has involved approaches to achieve thermal expansion compatible with the fibrous reinforcement and matrix, while maintaining satisfactory mechanical and electrical properties over an ambient to 1600°F range. Maintaining simplified fabrication processing characteristics for the composites has been emphasized.

Matrix formulations have been developed which appear capable of meeting these requirements. Extensive thermal expansion measurements of numerous candidate matrices have been performed. X-ray diffraction studies have been performed to analyze crystallographic changes in the candidate matrix materials due to thermal treatment and/or modifications.

Dielectric constant and loss tangent values have been measured on ceramic matrices and silica fabric reinforced composites up to 1600°F. Scanning electron microscope analysis of the microstructure of both the ceramic matrices and silica fiber reinforced composites was performed before and after exposure to 1600°F.

Composite fabrication processing studies were performed for five ceramic matrix materials. A composite characterization study was performed which included properties before and after thermal aging. Flexural properties were determined versus temperature both before and after thermal aging. Composite panels were subjected to 165 db acoustical vibration at 1600°F. Panels were fabricated and delivered to Arthur D. Little Co. for free space electrical testing.

TABLE OF CONTENTS

FIGURES

Page

FIGURES (continued)

TABLES

SECTION I

INTRODUCTION

Radar absorber materials (RAM) incorporating the circuit analog (C-A) design have proven to be a most effective method of achieving radar cross section reduction over a broad frequency band while maintaining a high strength-to-weight ratio of the structure. However, currently these materials are based on fiber reinforced plastics and their upper temperature limit for long term service is approximately 600°F. In order to provide a structural RAM system that will perform in excess of 1000°F, it is necessary to provide both a C-A ribbon material and a compatible electrical and structural material that will withstand this temperature environment. This program is concerned with the development of the high temperature composite materials for use with temperature resistant C-A ribbons presently being developed under a separate contract. The RAM material developed must withstand temperatures to 1600°F combined with high acoustical vibration.

The basic approach under this program involves the development of fiber reinforced ceramic composites based on a chemically reacted ceramic matrix. These composite materials possess temperature resistance, electrical and structural properties which make them extremely attractive for RAM applications. In addition, they eliminate the fabrication problems and sensitivity to failure from impact and thermal shock that is typical of most monolithic ceramic materials.

The ceramic matrix development effort was based on aluminum phosphate ($AlPO_4$) prepared by the reaction of ortho-phosphoric acid (H_3PO_4) and aluminum hydroxide [$Al(OH)_3$] . This material is unique in that composites may be prepared in a manner very similar to thermosetting plastic materials. After curing to only 600°F, aluminum phosphate systems may be used as high as 3000°F. In addition, it exhibits a low dielectric constant and loss tangent which are stable over a wide temperature and frequency range.

One undesirable feature of the ortho aluminum phosphate material is the crystalline inversion which occurs at various temperatures, similar to an α - β quartz inversion occurring at approximately 1140°F. This inversion is reversible and is associated with linear dimensional change of approximately 1.5%. Large mismatches between thermal expansion/contraction of the matrix and fibrous reinforcement can result in internal stress concentrations which lead to degradation by creep and static fatigue of the reinforcement. A major effort during the matrix development phase was toward the attenuation or elimination of these inversions and the development of ceramic matrices having thermal expansion compatibility with silica reinforcement. Approaches investigated for alleviating the crystalline inversion problem included low thermal expansion fillers and the use of reactive additives to distort or change the basic ortho aluminum phosphate crystalline structure. Lithium-aluminum-silicate additives proved to be the most successful class of materials. The overall expansion of the aluminum phosphate was reduced by the negative thermal crystalline inversions were eliminated, apparently by high temperature reaction of the aluminum phosphate matrix and additive. A secondary benefit of the additive was realized by an increase in strength of the matrix.

During the matrix material development and screening studies testing was performed which included thermal expansion, mechanical, electrical and physical properties, thermal aging studies, water solubility, microstructure studies and X-ray diffraction analysis.

As a result of the preliminary screening and evaluation, the following five matrices were selected for further evaluation:

$AlPO_4$

$AlPO_4$ + 25% Silica

$AlPO_4$ + 35% Petalite

$AlPO_4$ + 35% Spodumene

$AlPO_4$ + 50% Spodumene

Composite fabrication studies utilizing glass and silica fabric reinforcement were conducted and have resulted in the development of a reliable process for producing high quality laminated composites.

Physical, mechanical and electrical properties were measured on silica fabric reinforced composite specimens before and after aging at temperatures up to 1600°F for time durations up to 200 hours. Extended aging at 1600°F had little effect on the physical and electrical properties of the material. However, the mechanical properties at ambient temperature are considerably lower after the 1600°F exposure. This reduction in mechanical properties is attributed to degradation of the reinforcement and occurs within one hour after exposure at 1600°F, but stabilizes and remains constant throughout the remaining 200-hour duration.

Panels (12" x 12") were fabricated for acoustical vibration and free space dielectric testing. The acoustical vibration testing was performed at Wyle Laboratories for the five most promising candidate material systems. While all panels cracked during the acoustical vibration tests at 1600°F, it appeared that a large factor contributing to the cracking was due to stress caused by expansion of the metal mounting frame.

Panels were prepared and submitted to Arthur D. Little Co. for free space dielectric measurements. A trade-off study will then be performed to select the three most promising material systems to be carried into Phase II which involves RAM panel development.

SECTION II

PHASE I PROGRAM OUTLINE

The objective of this program is the development of a ceramic composite having desirable electrical properties, thermal stability and other characteristics which are adequate for high temperature circuit analog RAM applications. The program consists of three major phases which are designated as: (I) Basic Materials Development and Characterization, (II) Development and Characterization of RAM System, and (III) Development and Fabrication of Prototype RAM Composite Parts.

Due to the classified nature of Phases II and III this report contains only the program outline for Phase I, which is unclassified.

PHASE I - MATERIALS DEVELOPMENT AND CHARACTERIZATION

Task A - Materials Systems Development Characterization

The purpose of Task A is to perform a basic materials and process study of the following chemically reacted $AlPO_4$/quartz fiber reinforced candidate materials systems:

- Lightweight geometric core (honeycomb, egg crate, etc.) sandwich.
- Woven fabric reinforced solid laminate.
- Woven reinforced 3D composite.

During the course of this study specimens shall be prepared having various densities, matrix contents, and porosities. To this end the following individual studies are to be conducted:

1. The alleviation and/or elimination of the $AlPO_4$ berlinite inversion by investigating reactant ratios, bond site substitutions, bond site reductions, and thermal treatments and additives for reconstructive phase transformations.

2. Different available weaves for the fused silica tapes and cloth.

3. Incorporation of negative thermal expansion fillers and/or reactive fillers with the base $AlPO_4$ matrix.

4. The determination of thermal and chemical stability of the compositions and material combinations.

Task B - Preliminary Screening Tests

1. Physical Properties:
    - Density
    - Microstructure
    - Porosity
2. Structural Integrity:
    - Room temperature flexural strength and modulus.
    - Room temperature flexural strength and modulus after exposure to 1600°F for 10 hours and after thermal cycling from room temperature to 1600°F.
3. Thermal Integrity:
    - Weight loss after exposure to 1600°F for 5 hours.
    - Dimensional change after exposure to 1600°F for 5 hours.

Task C - Characterization Studies

1. Determination of physical properties before and after exposure to 1100°F and 1600°F for time durations of 1, 10, 50, 100 and 200 hours:
    - Density
    - Porosity
    - Microstructure
    - Weight loss
    - Dimensional changes
    - Thermal expansion
    - Thermal shock resistance
2. The determination of dielectric constant and loss tangent at X band for each of the following conditions:
    - At least four points between room temperature and 1600°F during heating and cooling.
    - After exposures for 100 and 200 hours at 1600°F.
3. Determination of flexural strength and modulus for the following conditions:
    - Room Temperature
    - 1100°F

- 1600°F
- At room temperature and 1600°F after exposures of 1, 10, 50 and 100 hours at 1600°F.

4. The determination of air impedance values for each of the candidate materials to evaluate their potential for being transpirationally cooled.

Task D - Process Optimization Study and Prototype Panel Development

1. Conduct process development studies to fabricate 12-inch square panels from each of the candidate materials. This study will establish the reproducibility of each candidate system and the comparative ease with which they can be prepared.

2. The preparation of 12-inch square sample plates for free space dielectric constant and loss tangent measurements made at room temperature, 500°F, 1000°F and 1600°F before and after exposures to 1600°F for 100 hours.

3. The preparation of 12-inch square sample plates for direct impingement acoustical vibration testing at room temperature and elevated temperatures up to 165 db at frequencies of 200 and 1000 cps before and after aging at 1600°F.

Task E - Trade-Off Studies

A trade-off analysis will be performed and with the concurrence of the AFML project officer the selection of three candidate materials will be made for evaluation during Phase II of this program.

SECTION III

TECHNICAL DISCUSSION

This Interim Technical Report covers the work performed on Tasks A, B, and C of Phase I outlined in Section II.

1. MATRIX STUDIES

The matrix study included the addition of chemically reactive additives and low expansion additives to the basic $AlPO_4$ mix. Prior to conducting the additive study, a process was established whereby 4-inch square by 1/4-inch thick tiles of the candidate material system could be prepared. Some preliminary work had indicated that many of the additive systems which would be investigated are chemically reactive with the phosphoric acid, aluminum trihydrate, and the additive being incorporated. Many of the more reactive systems, such as β-eucryptite and magnesium hydroxide, exothermed immediately on contact with the acid at temperatures well below 0°F. It was decided, therefore, to prepare the $AlPO_4$ (phosphoric acid plus aluminum trihydrate 100% reaction ratio) in a partially reacted form (B-staged). This is performed by mixing the $AlPO_4$ and aluminum trihydrate and allowing it to react at room temperature for one hour. At this point the initial exotherm is completed and the mix returned to room temperature. Following this initial reaction, the $AlPO_4$ mix is treated for 1 hour at 150°F, 1 hour at 200°F, and 1 hour at 250°F. The resulting material is hard and extremely brittle. It is then broken into small pieces and ball milled to a fine powder.

The additives, which are dry powder ingredients, were then blended with milled B-staged $AlPO_4$. This powder blend is then placed in the tool shown in Figure 1 and molded under heat and pressure. On heating to 250°F - 300°F the $AlPO_4$ phase melts to a liquid before completing its final reaction. After 1 hour at 350°F the molding is allowed to cool and removed from the tool. The molded tile is then placed in an air circulating oven and final cured up to 600°F for two hours.

Except for a few additives, which are discussed later on in the report, this process proved to be quite adequate for preparing optimum tile specimens for each of the matrix systems.

a. Crystalline Inversion Studies

The alleviation and/or the elimination of the $AlPO_4$ berlinite inversion was investigated by: (1) varying the reactant ratios of the $AlPO_4$, (2) additives to promote bond site substitutions, (3) additives to reduce the number of reactive bond sites to give a different crystalline structure, and (4) thermal treatments to the additives and matrix ingredients to reconstruct the phase transformation. The inversion characteristics of the $AlPO_4$ system vs. temperature are illustrated on the next page.

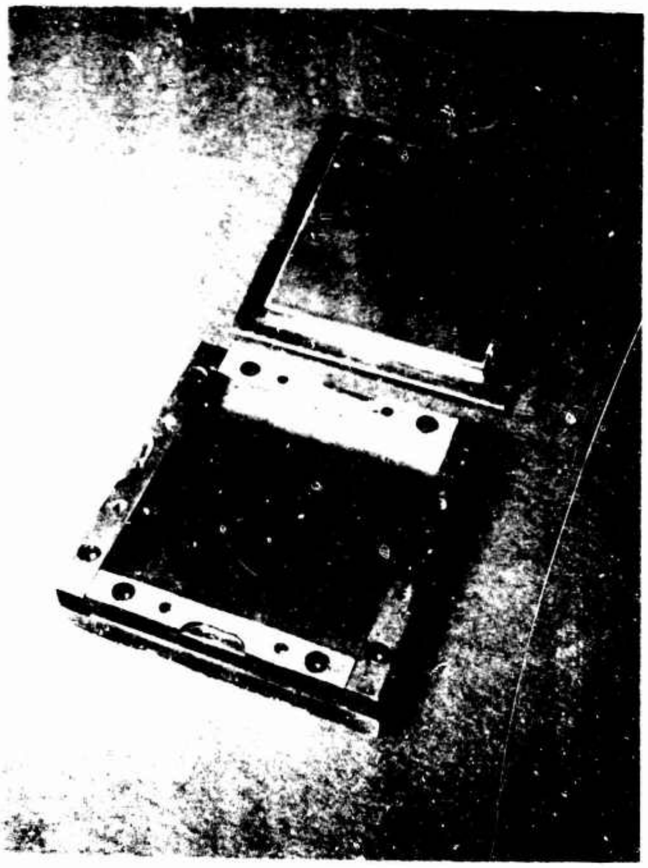

Figure 1. 4-Inch x 4-Inch Tile Fabrication Tool

$\boxed{AlPO_4}$

$$\text{Berlinite} \xleftrightarrow[(1499^\circ \pm 7^\circ F)]{815^\circ \pm 4^\circ C} \text{Tridymite} \xleftrightarrow[1877^\circ \pm 90^\circ F]{1025^\circ \pm 50^\circ C} \text{Cristobalite} \xleftrightarrow[>2912^\circ F]{>1600^\circ C} \text{Fused } AlPO_4$$

$$\beta \xleftrightarrow[(1087^\circ \pm 4^\circ F)]{586^\circ \pm 2^\circ C} \alpha \qquad \beta \xleftrightarrow[(199.4^\circ \pm 5^\circ F)]{93^\circ \pm 3^\circ C} \alpha_1 \xleftrightarrow[(266^\circ F)]{130^\circ C(?)} \alpha_2 \qquad \beta \xleftrightarrow[(410^\circ \pm 9^\circ F)]{210^\circ \pm 5^\circ C} \alpha$$

Figure 2 shows a typical thermal expansion curve of the normal ortho $AlPO_4$ matrix. The reversible α - β berlinite inversion, which peaks at 1140°F, is a major concern due to the large difference in thermal expansion of the matrix and reinforcing fibers.

(1) Stoichiometry Studies of Reactants

A stoichiometry study was initiated to determine the effect of various reactant ratios on the $AlPO_4$ matrix. The stoichiometry study included investigations of 80%, 90%, 100%, 110%, and 120% stoichiometric acid ratios. These ratios were prepared into cured 4-inch square by 1/4 inch thick tiles and evaluated in the following manner: a portion of each tile was immersed in water to determine its solubility. Still another portion of the tile was ground into powder to determine its crystallographic structure using X-ray diffraction. The water immersion study, which consisted of a 24-hour immersion, showed very definitely that the 100% ratio was the only stable blend.

The reactants for this stoichiometry study were analytical grade 85% phosphoric acid which by analysis was actually 84.7% phosphoric acid, and aluminum trihydrate (RH730*). The stoichiometry study assumed the following reaction

$$H_3PO_4 + Al(OH)_3 \longrightarrow AlPO_4 + 3H_2O$$

The 90% ratio was porous and had a somewhat chalky texture. The 80% sample was even more porous and had very little integrity and could be flaked away with light rubbing. During the water immersion tests of these two samples they came completely apart into individual grains.

The 110% ratio was visually the best sample of the five that were prepared. Its integrity was excellent and by comparison it was much stronger than the other four ratios. Its surface appeared to have a glassy consistency and its interior was very dense. The 120% ratio was tacky on the surface after a 600°F cure. This is apparently due to the excess unreacted acid remaining in the tile. When exposed to the water immersion tests both the 110% and the 120% ratios were dissolved. Observations made during the immersion tests showed that the 120% ratio began to dissolve immediately and was complete within three hours. The 110% ratio took longer, but over a 24-hour period it too was completely dissolved.

Additional samples of the 110% acid ratio which had demonstrated good strength and toughness were prepared and slowly heated to 1000°F and cooled. The purpose was to complete any incomplete reactions and to remove by vaporization residual unreacted phosphoric acid from the tile. On examination the samples were found to be cracked in several places and could be easily broken by hand. The density was also lower and a slight porosity was observed. Apparently the toughness of the original sample after 600°F cure was due to the excess acid providing a binder effect. Removing the acid by higher heat treatment resulted in cracking and overall weakening of the tile. After these tests the following conclusions were made.

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* Reynolds Aluminum

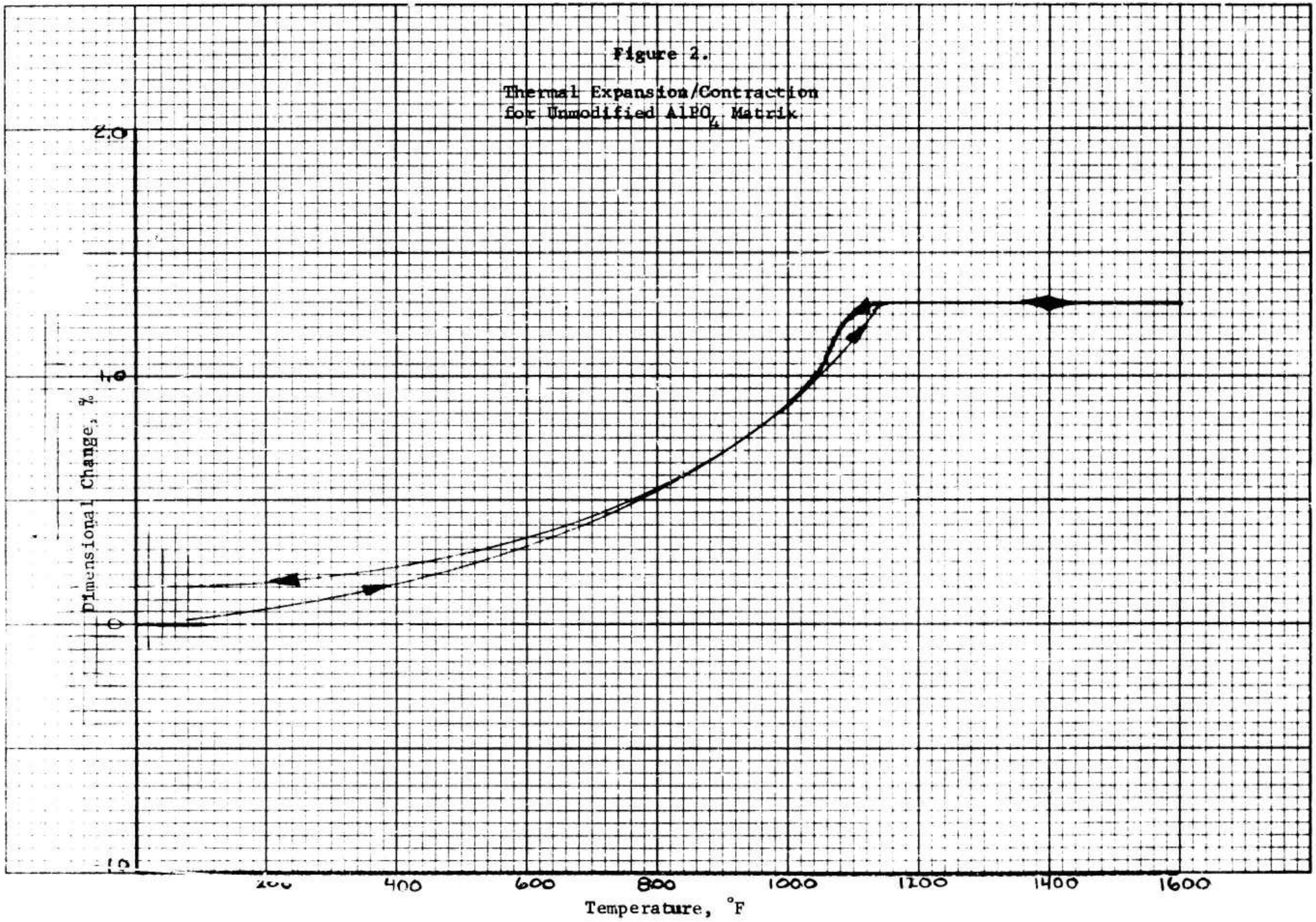

Figure 2.

Thermal Expansion/Contraction
for Unmodified $AlPO_4$ Matrix

1. There is insufficient bonding in the 80% - 90% ratios to withstand the effect of water immersion.

2. The 110% and 120% ratios contain an integral acid phase which is soluble in water, allowing a breakdown of the cured tile.

3. The 100% ratio is apparently completely reacted and stable in water after the 600°F cure.

With the exception of the work performed with substitution additives, the 100% reaction ratio for the $AlPO_4$ matrix was used throughout the remainder of the program.

(2) Negative Thermal Expansion Additives

Matrix additive studies were conducted by making various percent-by-weight additions of zero expansion and negative expansion additives to the basic $AlPO_4$ matrix. The purpose of this study was to attenuate as much as possible the berlinite inversion without sacrifice to structural, thermal, and electrical performance. A total of five additives were investigated: a 5 micron size silica powder (Min-U-Sil*), spodumene (Thermal Grain No. 3**), β-spodumene (Lithafrax 2121***), heat treated petalite (Lithafrax 2122***), and a very negative expansion lithium aluminum silicate (β-Eucryptite**). The percentages which were evaluated for each additive were 25% by weight, 35% by weight, and 50% by weight.

No problems were incurred in preparing specimens from the silica powder, the spodumene, and the petalite. They exhibited complete inertness to the $AlPO_4$ matrix and could be easily processed into the standard test tile.

Unexpected difficulties were encountered with the β-spodumene and the β-eucryptite material. On contact with the acid they were found to be extremely reactive, causing immediate gellation. X-ray diffraction scans of these two materials indicated they were essentially identical in crystallography. Since the β-eucryptite material had the greatest potential for reducing the overall expansion of the $AlPO_4$ matrix, work concentrated on developing a process for the β-eucryptite whereby specimens could be prepared and tested. Initial attempts to block or inhibit this reaction by using water and organic solvent blends were partially successful but resulted in weak and poorly structured specimens.

Eventually a process was established whereby the β-eucryptite could be added to the $AlPO_4$ matrix with a minimal exotherm. It involved diluting the mixture 50% by volume with water. The water had the effect of blocking the reaction sufficiently to permit fabrication of the test tile. This excess water was removed by adjusting the molding cycle to permit evaporation of the water during the curing cycle.

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* Penn Glass and Sand Co.

** Foote Mineral Company

*** The Carborundum Company

Considering only the processibility, the systems containing silica, spodumene, and petalite were the easiest to prepare. They are sufficiently inert to allow mixing and curing without exotherm and they do not inhibit the degree of cure.

(3) Reactive Lattice Additives

A study was conducted to investigate additives which would be chemically reactive with the $AlPO_4$ and become an integral part of the lattice structure. The purpose was to form a compound with a discontinuous $AlPO_4$ network which would have the effect of alleviating or eliminating the $\alpha - \beta$ berlinite inversion. Investigations were conducted on magnesium hydroxide, lithium hydroxide, boric acid, lithium aluminate, and lithium metasilicate. Initial efforts involved a 10% stoichiometric substitution for each of these systems.

No particular difficulties were incurred in preparing specimens of the aforementioned substitution additives up to the 350°F cure. However, during the postcure to 600°F every one of the additives had spalled surfaces or had cracked severely. Modification to the fabrication process for preparing tiles and a long postcure up to 600°F was effective in reducing the degree of cracking. It was sufficient at least to obtain some specimens for thermal expansion measurement.

Generally there was a large shrinkage associated with the substitution additive that could not be controlled by processing. It became even worse when higher concentrations were used. No useful candidates were obtained during this study.

(4) Hydrated Aluminas

Another method of attenuating the $\alpha - \beta$ berlinite inversion is to reduce the number of bond sites in the $AlPO_4$ matrix. The method investigated to achieve the reduced number of bond sites was to convert the aluminum trihydrate to a dehydrated form through thermal treatments. Three treatments were investigated: heat treatment for 1 hour at 1472°F, 10 hours at 1472°F, and 1 hour at 752°F. During each thermal treatment weight loss was measured and the reactant ratios were adjusted to compensate for the remaining reactive sites. Stoichiometric ratios between the hydrated alumina and the phosphoric acid were calculated and tile specimens were prepared from each system. Both samples which had been exposed to 1472°F were soluble in water after the 600°F postcure. Apparently the resulting alumina was not sufficiently reactive with the acid to form an insoluble chemical bond. The aluminum trihydrate which was treated at 752°F yielded a very tough and dense specimen. During the water immersion tests it was not noticeably affected. The specimen was retained for thermal expansion testing and X-ray diffraction measurements.

b. X-Ray Diffraction Studies

The equipment being used in these studies is a Philips Type 12045B/3 X-ray diffraction unit in conjunction with a Philips Model 12206/7 electronic circuit panel. The output is fed to a Bristol strip chart recorder. A proportional detector is used, and is mounted on a goniometer which has been allowed to sweep at a rate of 1°/min, usually between $2\theta = 5^\circ$ and $2\theta = 90^\circ$. A copper target has been used exclusively in generating the radiation, with 35 KV applied to the tube, and a tube current of 15 mA.

Our powder diffraction card file only extends through 1964 at present; however, the 1971 index was obtained during the course of this program. Since the index gives the eight strongest lines with relative intensities for each spectrum, identification is always possible using the index alone. Other data and references can, of course, only be obtained from the cards. The paragraphs below describe the results of the X-ray studies conducted on basic raw materials and the most promising material system candidates.

(1) Aluminum Trihydrate

The starting material in our manufacture of aluminum phosphate (Reynolds' RH730) is referred to by the manufacturer both as hydrated alumina $Al_2O_3 \cdot 3H_2O$ and aluminum hydroxide $Al(OH)_3$. The diffraction file gives different spectra for these two materials, although the differences are minor. Analysis of RH730 gave a spectrum most closely resembling that of $Al_2O_3 \cdot 3H_2O$. However, the same was true of a reagent grade sample (Baker and Adamson) identified on the bottle as $Al(OH)_3$. The attempt to distinguish between the two materials appeared futile.

More significant is the fact that the RH730 converts readily to alumina when heated, as shown by spectra obtained after one hour at 250°F, 600°F, 1100°F, and 1472°F. The treatment at 250°F did not bring about any change in the spectrum, but after the treatment at 600°F, the spectrum had disappeared, and only a broad maximum at about $\theta = 33.5^\circ$ was obtained, indicating an essentially amorphous structure. After the treatment at 1100°F, the maximum was somewhat narrower and more distinct, and established itself at $\theta = 33.6^\circ$, which corresponds to $d = 1.39$ Å. With the exposure to 1472°F, it continued to take on the appearance of a definite peak, and additional peaks, although braod, appeared, the largest one being located at $\theta = 18.8^\circ$, corresponding to 2.39 Å. The spectrum thus developing indicated a mixture of χ- and σ- alumina exactly as can be expected,[1] although, after 16 hours at 1472°F, χ-alumina appeared to be the only form present. Corroborating data was obtained through a TGA analysis to 1742°F on a sample of RH730. The total weight loss was 34%, which is just the water content in the molecule $Al_2O_3 \cdot 3H_2O$, as well as in the molecule $Al(OH)_3$. The loss continued up to a temperature of approximately 1560°F but the bulk of it (30%) occurred in the range between 482°F and 707°F. It was in this range that the original spectrum was first seen to have disappeared.

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[1] Stumpf, H.D., et al., "Thermal Transformation of Alumina and Alumina Hydrates," Ind. & Eng. Chem., Vol. 42, No. 7, July 1950

(2) Aluminum Phosphate ($AlPO_4$)

Following the exothermic reaction with phosphoric acid (100% stoichiometric ratio), essentially the same spectrum prevailed, except that the intensity had been reduced by approximately a factor of three. The absence of any new spectral lines showed that the aluminum phosphate formed was amorphous. The spectrum did not change significantly after heat treatment for one hour each at 150°F and 200°F. On the other hand, after subsequent treatment for one hour at 250°F, lines indicating the presence of crystalline $AlPO_4$ appeared. These lines did not indicate berlinite, the quartz form, as expected, but instead the cristobalite form. Since the cristobalite spectrum is poor in strong lines, and since this form was quite unexpected, it was felt that additional verification was needed. To this end, a portion of the sample was later heated for an additional two hours at 250°F, giving a total of three hours at this temperature. The lines observed earlier grew stronger, and additional lines in the spectrum appeared, thus establishing the presence of the cristobalite form beyond doubt. The formation of this variety was not exclusive, however. In fact, at the end of the three-hour period, the predominant spectrum was that of berlinite even though this spectrum had not been observed at all after the first hour.

After one hour at 350°F (sample had been at 250°F for one hour, not three), the most prominent spectrum was that of berlinite, and a weak spectrum showing some unreacted RH730 still remaining was obtained. In addition, a spectrum indicating the presence of the tridymite form was observed, which again was quite unexpected. No references have been found in the literature for the formation of either the cristobalite or the tridymite form of $AlPO_4$ at these low temperatures. Although the spectrum for the tridymite form was observed on several later occasions, this is the only time it was obtained from a sample not containing silica. This is significant because the differences between the spectra representing the tridymite form of SiO_2 on the one hand, and of $AlPO_4$ on the other, are so minor that a distinction cannot be made with absolute certainty.

After one hour at 600°F, a complete spectrum for berlinite was obtained. No other lines were detected. The exclusive presence of berlinite was also observed, after identical heat treatment, in samples with originally stoichiometric ratios, expressed in terms of the phosphoric acid, of 80%, 90%, and 110%. (In this report, the stoichiometric ratio is 100% unless otherwise noted.)

The literature indicates that high temperature conversions of berlinite to the tridymite and cristobalite forms can be expected,[2] and this was investigated. Berlinite samples kept at 1200°F for 3 hours and 18 hours remained berlinite; neither showed the slightest sign of any conversion. After another sample had been kept for 1 hour at 1500°F, the strongest peak in the spectrum for the cristobalite form could just barely be detected.

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[2] Beck, W.R., "Crystallographic Inversions of the Alumina Orthophosphate Polymorphs and Their Relation to Those of Silica," J. Am. Cer. Soc., Vol. 32 (1949)

A berlinite sample kept at 1600°F for 1 hour showed the spectra for both berlinite and the cristobalite form, the latter being more prominent. In addition, a weak but definite spectrum indicating the presence of $Al(PO_3)_3$ was noted. A sample which was heated to 1650°F and then immediately removed from the furnace showed no sign of conversion from berlinite. When a berlinite sample was kept at 1742°F for 1 hour, the berlinite spectrum completely disappeared and instead the spectrum for the cristobalite form was obtained. Again, a weak spectrum indicating the presence of $Al(PO_3)_3$ was observed. Subsequent treatment of this sample for 1 hour at 1500°F did not bring about any change in the spectrum. The results of these high temperature experiments were quite surprising since conversion to the tridymite form was expected.

(3) Additives

Characterization by X-ray diffraction of various additives has been carried out, and results are given in the following:

1. Spectra obtained on Min-U-Sil powder showed α-quartz exclusively without heat treatment, and also following two hours each at 350°F, 600°F, and 1650°F. Although the presence of an amorphous substance, such as vitreous silica, is possible, it is not probable in view of the fact that the spectrum was not affected by the various treatments.

2. Lithafrax 2121 and β-eucriptite gave identical spectra: in each case, eucryptite, $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ is the only crystalline material present.

3. The spectrum for Thermal Grain No. 3 showed spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, exclusively. Identical spectra were obtained from four samples which were heated and removed from the furnace, one at a time, when the temperature reached 1300°F, 1400°F, 1500°F, and 1600°F.

4. The analysis of Lithafrax 2122 was not quite as clean-cut. The spectrum resembled most closely the spectrum for a sample of petalite, $Li_2O \cdot Al_2O_3 \cdot 8SiO_2$, which had undergone some form of heat treatment (no details given on the card). The lines showed good agreement in their positions, but not always in their relative intensities. Five lines remain unidentified.

Silica Fiber Reinforced $AlPO_4$ - A laminate consisting of $AlPO_4$ and silica fiber cloth (Astroquartz*) was manufactured, and analyzed after postcure at 600°F. In addition to the berlinite spectrum, lines representing the tridymite form were quite prominent. It was pointed out earlier that the spectra for the tridymite form SiO_2 and $AlPO_4$ are virtually indistinguishable, and it is therefore conceivable that the presence of tridymite (SiO_2) is indicated. It was also seen earlier, however, that the as-received

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* J. P. Stevens Co.

fibers are fused silica, and conversion of fused silica into tridymite is certainly not expected at temperatures as low as 600°F. In all probability then, the fibers were still fused silica, while some of the $AlPO_4$ was in the tridymite form.

Silica Powder in $AlPO_4$ - A sample of $AlPO_4$ containing 25% silica powder was heated to 1650°F and then removed immediately from the furnace. Apparently no reaction occurred: the spectra for berlinite and α-quartz were both obtained. The similarity between the two spectra was striking: the total spectrum was made up of double peaks, one in each pair produced by the quartz and the other by the berlinite. A few weak lines indicating the presence of some of the tridymite form of the phosphate were also noted.

Petalite in $AlPO_4$ - A sample containing 25% petalite was analyzed after treatment for one hour at 600°F. The spectra for berlinite and heated petalite were obtained, and in addition, the three strongest lines in the spectrum indicating the presence of the tridymite form were quite prominent. Following an expansion run to 1200°F, the berlinite spectrum had become considerably stronger, the petalite spectrum had become slightly weaker, and the tridymite lines had disappeared altogether. A sample containing 50% petalite was analyzed after three expansion runs to 1600°F. The petalite spectrum was more pronounced, as expected, due to the higher concentration. Furthermore, conversion from berlinite to the cristobalite form was evidenced by a cristobalite spectrum which was actually stronger than the berlinite spectrum obtained. No lines indicating any presence of the tridymite form were detected.

Spodumene in $AlPO_4$ - Samples containing 25% spodumene were analyzed after treatment for one hour at 350°F and 600°F. In each case the spectra for berlinite and spodumene were obtained. After an expansion run to 1600°F, the spodumene spectrum was essentially unchanged, while the intensity of the berlinite spectrum was considerably reduced. Instead, fairly prominent spectra appeared representing the cristobalite form of $AlPO_4$, and in particular the tridymite form. A sample containing 50% spodumene was analyzed after three expansion runs to 1600°F. Except for the higher intensity of the spodumene spectrum reflecting the higher initial concentration of spodumene, the total spectrum was very similar to the preceding one.

β-Eucryptite in $AlPO_4$ - The investigation of β-eucryptite was initially impeded by the difficulty in sample fabrication caused by the very rapid exothermic reaction between this additive and the phosphoric acid. This applied equally to the so-called β-spodumene, which appears to be essentially the same material. In spite of this difficulty, a sample was produced from a mix containing 25% β-spodumene, and was analyzed following postcure at 600°F. A definite spectrum for berlinite was obtained, and a few lines indicating the presence of the tridymite form were seen. On the other hand, only the strongest line in the eucryptite spectrum was seen as a weak but definite line, while a second line may have been just barely detected. Thus, not more than a small amount of β-spodumene was still present in this sample.

Various solvents, such as isopropyl alcohol, DMAC, and acetone, added in attempts to slow down the exothermic reaction, all had the same effect: the X-ray analysis showed that these solvents inhibited the phosphoric acid reaction not only with the additive, but with the hydrated alumina as well. Consequently, samples of poor mechanical integrity were produced. Instead, samples containing 25% β-eucryptite in the mix were made successfully simply by adding water, although in order to produce good samples the amount of acid added had to be increased. X-ray analysis of these samples showed no trace of eucryptite after B-staging (250°F) or after cure (600°F). On the other hand, there was some indication that Li_3PO_4 may have been present after the cure.

In subsequent sample fabrication, the β-eucryptite was added after B-staging to avoid the reaction between the additive and the phosphoric acid. In every analysis of a sample made in this manner, a prominent eucryptite spectrum was obtained. Following postcure at 600°F of samples containing 25% and 50% β-eucryptite, the only other prominent spectrum obtained was that of the tridymite form. In the case of the sample containing the lower percentage of β-eucryptite, the strongest line in the berlinite spectrum showed up weakly. Analysis of a sample containing 15% β-eucryptite following one expansion run to 1600°F also produced the spectrum for the tridymite form and only the strongest line in the berlinite spectrum. Additional analysis was performed on samples obtained from a tile containing 50% β-eucryptite after different thermal treatments. After one hour at 1600°F, much of the tridymite form appeared to have changed into the cristobalite form, but no berlinite was seen. On the other hand, following three cycles to 1600°F in the thermal expansion apparatus, the most prominent form was berlinite, with the tridymite form showing up weakly, and the cristobalite form not at all. The eucryptite spectrum was still by far the strongest, while a few rather weak lines indicated that another lithium aluminum silicate, possibly petalite, may have been forming. Following 68 hours at 1600°F, all known crystalline forms of $AlPO_4$ had virtually disappeared. Only the strongest line in the berlinite spectrum may have been present as a weak line. The eucryptite spectrum was still strong, although its intensity had been reduced considerably. Several lines, including the strongest one obtained, have not been identified. They apparently represent one or several crystalline substances which have not yet been included in the powder diffraction file.

c. Preliminary Matrix Screening Studies

(1) Thermal Expansion Studies

Thermal expansion measurements were made on an apparatus which permits continuous measurement and recording of specimen expansion as well as permanent growth and shrinkage during programmed heating and cooling cycles. While a wide range of heating rates and temperatures are available up to 200°/min and 2000°F, current tests are conducted over a 6-hour cycle at a heating rate of 8°/min up to a maximum temperature of 1600°F.

The specimen for this measurement is a one inch long rectangular section cut from the molded tile. The apparatus has been calibrated so that a direct readout in percent elongation is obtained from the specimen. The thermal expansion curves obtained from those candidate matrix systems which showed promise are contained in the appendix to this report. A curve for the 100% $AlPO_4$ material is shown for comparison purposes.

The most promising, with respect to attenuation of the α - β berlinite inversion, are the additives spodumene and petalite. Of the three filler percentages, the 50% by weight addition is the most effective, providing a total elongation of slightly less than 0.5%.

Only one other system showed definite promise in attenuating the maximum elongation of the base $AlPO_4$ mixture. This was the β-eucryptite system. At the 50% by weight loading, the thermal expansion up to about 1200°F was essentially zero; however, between this temperature and 1600°F severe permanent shrinkage was evident. Although considerable effort was devoted to the elimination of this shrinkage, all attempts at alleviating what appeared to be a sintering reaction between the β-eucryptite and the $AlPO_4$ were unsuccessful. During multiple runs to determine the effect of repeated 1600°F cycling, it was noted that the shrinkage occurring in the β-eucryptite system became less and less with the number of cycles, eventually resulting in a system which has zero expansion.

The spodumene and petalite systems were shown to be very stable systems when multiple thermal expansion runs were performed up to 1600°F. The spodumene system on the second cycle shows a tendency to grow in length, indicating the formation of crystobalite. On the third cycle the indications are the same, however, it appears that the crystobalite phase is reversible because no additional overall growth was measured after cooling.

The petalite material shows a very slight tendency to shrink starting at approximately 1300°F. However, the net result is a permanent growth of approximately 0.2%. On the second and third cycles, the reverse is the case, with a permanent shrinkage of approximately 0.1% on the second cycle and 0.05% on the third cycle. However, the total elongation during the second and third run was identical, being 0.5% maximum.

The substitution additives of magnesium hydroxide, lithium hydroxide, and boric oxide showed little promise of alleviating the α - β inversion. A 10% magnesium hydroxide run did not produce any change in the total elongation of the base $AlPO_4$ matrix. The same was the case with the lithium hydroxide; however, at approximately 1440°F a catastrophic increase in its length was noted. It is not known what caused this spontaneous increase in length, but it was repeated several times, and in each case the specimen cracked during the test.

The system containing 10% boric oxide did effectively reduce the total elongation to approximately 0.9%. Additional work performed to add greater percentages of the boric oxide to the $AlPO_4$ matrix was unsuccessful due to the severe cracking which occurred in the molding. Cracking was so severe that the normal one inch long thermal expansion specimen could not be obtained.

A dehydrated aluminum trihydrate formulation was measured for thermal expansion and found to be identical to the 100% $AlPO_4$ system. In this case the aluminum trihydrate which had been treated at 752°F was measured. This was because the exposures up to 1472°F resulted in systems which were unstable in water.

The results of the thermal expansion study identify the negative thermal expansion additives as being the most effective in attenuating the total expansion of the $AlPO_4$, whereas the other reactive or heat treated materials were totally ineffective or could not be fabricated within the bounds of this effort.

(2) Thermal Aging Studies

Specimens from each of the matrix materials formulated were exposed for 68 hours at 1600°F. This test was conducted to determine the thermal stability of the materials with respect to weight and linear dimensional changes. The results of this study are presented in Table I. The unmodified $AlPO_4$ matrix was used as a control to evaluate the effect of the matrix modifications. In all cases, including the $AlPO_4$ matrix, there was a weight loss. The lowest weight losses were obtained with silica, spodumene, and petalite modified systems. All other formulations were equivalent or had greater weight losses than the $AlPO_4$ control material.

There were also significant changes in the dimensions of the specimens after the thermal exposure. The silica, spodumene, and petalite systems proved to be the most dimensionally stable systems. Except for the 50% spodumene material, all three materials showed a positive dimensional change (growth). All other materials, with the exception of the $AlPO_4$ and the system containing 10% boric oxide, showed a net shrinkage. Shrinkage was excessive for some systems (i.e., lithium metasilicate shrank >50% in volume), indicating many of the systems produce a sintering reaction at temperature.

Density changes for each of the materials were also measured before and after thermal aging. As expected, those systems having a dimensional increase had a slight density reduction after the exposure. Those systems showing a large shrinkage had a corresponding high increase in density.

Reviewing the results of the 1600°F thermal aging, two factors are apparent: First, the additives which are low or nonreactive with the phosphoric acid tend to be the most stable systems in terms of weight loss, dimensional stability, and density changes. Those additives which are reactive tend to exhibit less stability after thermal exposure.

TABLE I

PHYSICAL PROPERTIES FOR MATRICES BEFORE AND AFTER THERMAL AGING AT 1600°F FOR 68 HOURS

Matrix Formulation	Weight Loss (%)	Linear Dimensional Change (%)	Density, g/cc	
			Before	After
$AlPO_4$	3.3	+2.7	1.53	1.36
$AlPO_4$ + 25% Silica	0.75	+1.0	1.53	1.47
$AlPO_4$ + 25% Spodumene	0.77	+0.26	1.36	1.34
+ 35% "	0.68	+0.12	1.71	1.69
+ 50% "	0.57	-1.50	1.48	1.48
$AlPO_4$ + 25% Petalite	0.77	+0.12	1.49	1.47
+ 35% "	0.85	0.00	1.44	1.43
+ 50% "	1.45	+0.07	1.385	1.365
$AlPO_4$ + 25% β-Eucryptite	4.5	-5.8	1.54	1.78
+ 35% "	6.7	-5.0	1.41	1.55
+ 50% "	3.07	-0.57	1.41	1.39
$AlPO_4$ + 10% Lithium Aluminate	2.25	-5.1	1.23	1.41
+ 30% " "	4.34	-8.8	1.30	1.69
$AlPO_4$ + 10% Lithium Metasilicate	2.25	-4.2	1.45	1.62
+ 30% " "	6.15	-17.3	1.13	2.20
$AlPO_4$ + 20% MgO	4.76	-3.9	1.50	1.61
$AlPO_4$ + 20% $Mg(OH)_2$	5.22	-0.35	1.42	1.35
$AlPO_4$ + 10% H_3BO_3	4.1	+3.6	1.38	1.19

(3) Mechanical Properties

The mechanical property data was obtained on the five most promising systems listed below:

$AlPO_4$ (control)

$AlPO_4$ + SiO_2 (Min-U-Sil)

$AlPO_4$ + spodumene (Thermal Grain No. 3)

$AlPO_4$ + petalite (Lithafrax 2122)

$AlPO_4$ + β-eucryptite

Tables II and III present the flexure and compression results, respectively. In both flexure and compression it is shown that the additives do improve the mechanical integrity of the base $AlPO_4$ matrix. Of the four modified systems, the spodumene imparts the greatest improvement in both flexure and compression. This could possibly relate to the high density of the spodumene system; however, it should be understood that every attempt was made to fabricate specimens of optimum density. The recorded densities have been found to be representative of each system throughout the program. The silica and spodumene are denser systems and are easily compacted into test specimens, whereas the petalite and the β-eucryptite are more difficult to process and are not nearly so easily compacted.

The specimens noted failed by thermal shock when inserted into the preheated 1600°F test fixture. It is thought to be the result of microcracking during the 1600°F exposure temperature, as was the case for the other noted specimens. However, our observations at high magnification and rubbing tests with pigmented water did not show any surface cracks. Since cracking had been observed in some of the matrix systems during the 1600°F exposure, it is quite possible that a weakened structure is present in those specimens that thermal shocked. It is planned to do additional testing on new specimens.

(4) Electrical Properties

Figures 3 and 4 contain the results of the dielectric constant and loss tangent measurements performed at MIT from room temperature to +1600°F at 8.52 GHz. The data reported is that obtained on specimens of the homogeneous matrix after being exposed to 1600°F for 24 hours. The purpose of these tests was to determine the changes in dielectric constant and loss tangent properties caused by the additives when compared to the base $AlPO_4$ matrix. A 100% $AlPO_4$ sample was included for comparison. The data shows that sample E containing a 25% addition of silica produces the least change. The remaining three specimens - sample B containing 50% spodumene, sample C containing 50% petalite, and sample A containing 50% β-eucryptite - all show a significant increase in dielectric constant at room temperature and +1600°F. The spodumene sample has the highest initial dielectric constant.

TABLE II

FLEXURE STRENGTH AND MODULUS FOR MATRICES EXPOSED 24 HOURS AT 1600°F

Matrix Formulation	Flex Strength, psi		Modulus, psi x 10^6		Density, g/cc
	R.T.	1600°F	R.T.	1600°F	
$AlPO_4$	356 475 594	*	0.39 0.43 0.50	*	1.34
$AlPO_4$ + 25% Silica	1,800 1,924 1,710	*	2.36 2.29 2.46	*	1.59
$AlPO_4$ + 35% Petalite	917 1,040 1,065	1,010 ** **	0.67 0.59 0.60	1.28 *	1.47
" + 50% Petalite	889 726 810	1,010 893 **	0.57 0.53 0.56	0.73 0.63	1.36
$AlPO_4$ + 35% Spodumene	2,500 2,480 2,320	*	2.16 2.15 2.07	*	1.68
" + 50% Spodumene	2,410 2,310 2,250	4,200 3,200 2,900	1.92 1.78 1.64	2.41 2.23 2.36	1.59
$AlPO_4$ + 50% β-Eycryptite	1,290 1,280 1,310	830 709 765	0.95 0.92 0.97	0.57 0.51 0.46	1.46

* Specimens failed from thermal shock

** Cracked specimens

TABLE III

ROOM TEMPERATURE COMPRESSIVE STRENGTH OF MATRICES EXPOSED 24 HOURS AT 1600°F

Matrix Formulation	Ultimate Compressive Strength, psi
100% $AlPO_4$	4,880 4,990 5,360
$AlPO_4$ + 25% Silica	6,690 6,200 6,410
$AlPO_4$ + 35% Petalite	8,730 9,340 7,000
+ 50% Petalite	4,090 5,211 5,320
$AlPO_4$ + 35% Spodumene	18,200 16,600 18,700
+ 50% Spodumene	12,400 11,500 10,000
$AlPO_4$ + 50% β-Eucryptite	8,140 8,300

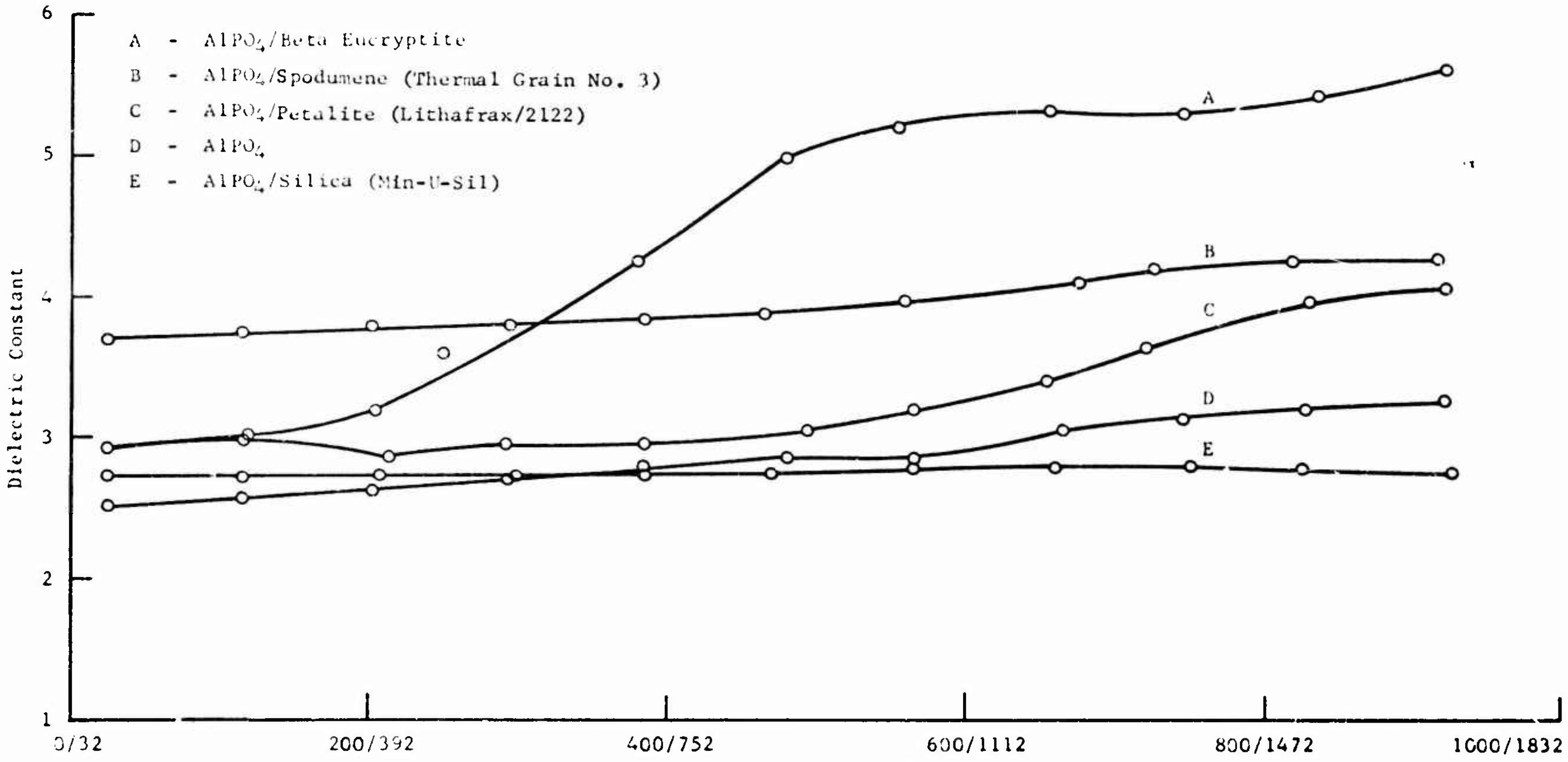


FIGURE 3. DIELECTRIC CONSTANT VS. TEMPERATURE FOR CERAMIC MATRICES (8.52 Gz)

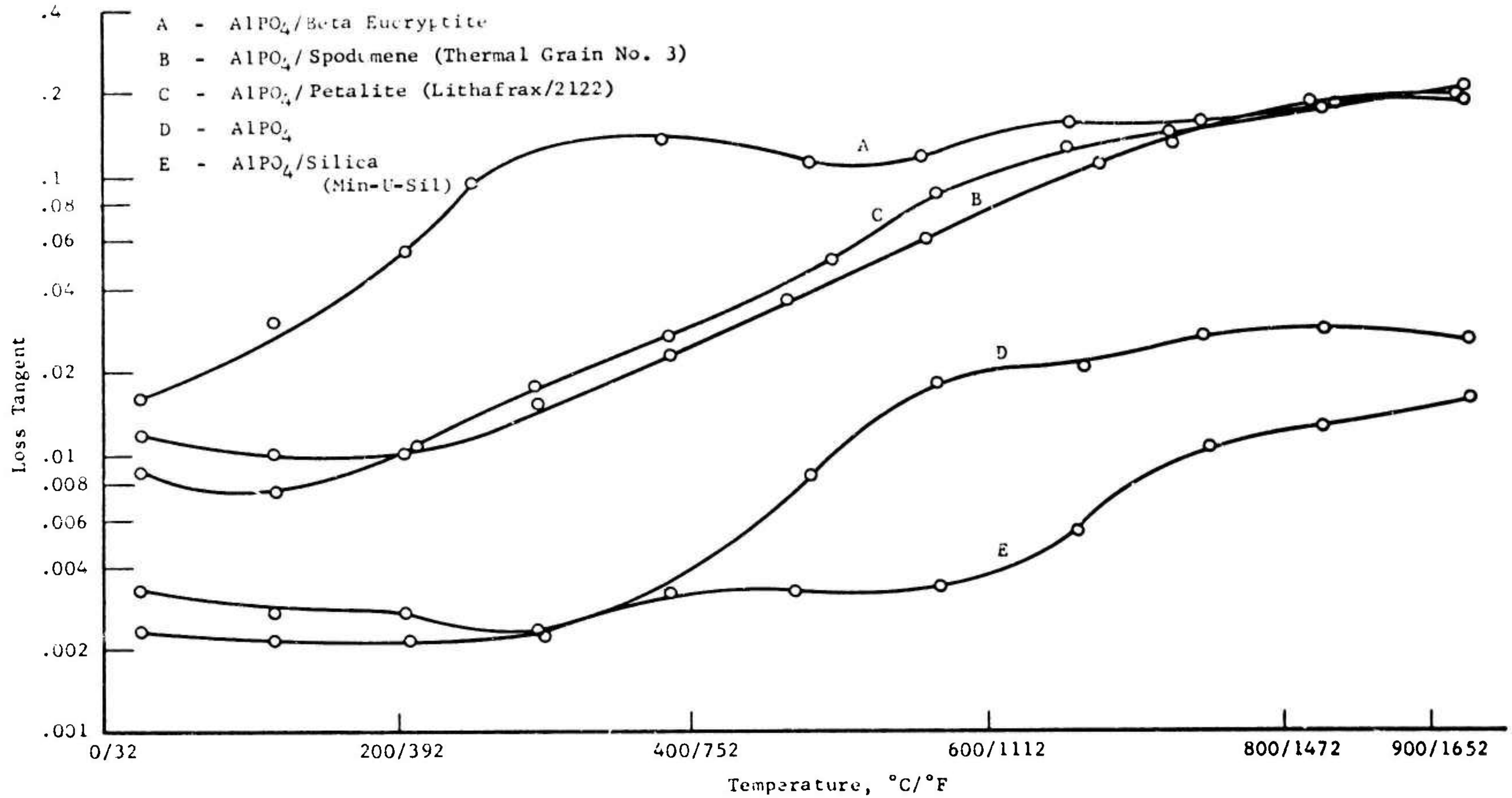


FIGURE 4. LOSS TANGENT VS. TEMPERATURE FOR CERAMIC MATRICES (8.52 Gz)

It also has the lowest coefficient of dielectric constant with temperature, whereas the β-eucryptite has the highest, and the petalite sample is intermediate.

The increase in loss tangent from room temperature to +1600°F was significant for all five samples, however, the silica additive system and the 100% $AlPO_4$ system still maintained a desirable low level. The spodumene, petalite, and the β-eucryptite samples produced comparatively large values at the high temperature.

From this first set of dielectric data it can be concluded that the dielectric constant changes caused by the addition of the various additives are considered to be acceptable for the intended RAM application. These values will be further enhanced with the incorporation of quartz reinforcement which should lower the dielectric constant to even more acceptable levels. It is anticipated at this time that, with the exception of the β-eucryptite system, a dielectric constant not greater than 3.2 can be achieved for all other systems. These same general hypotheses cannot be made regarding the loss tangent. Loss tangent values cannot be predicted from a pure rule-of-mixtures calculation, but rather will require dielectric measurement. It is planned during the next reporting period to prepare specimens in the form of composites containing the quartz reinforcement to be tested for dielectric constant and loss tangent vs. temperature at 8.52 GHz.

(5) Microstructure

A series of scanning electron microscope (SEM) studies were performed on five ceramic matrix systems listed below and silica fiber reinforced composites based on these matrices. The following matrices were examined:

1. Unmodified $AlPO_4$
2. $AlPO_4$/25% silica additive (Min-U-Sil)
3. $AlPO_4$/50% spodumene additive (Thermal Grain No. 3)
4. $AlPO_4$/50% β-eucryptite additive
5. $AlPO_4$/50% petalite additive (Lithafrax 2122)

Processing conditions for preparation of the matrix specimens are described in the Matrix Study section of this report. Physical and mechanical properties and the effect of thermal aging at 1600°F for the matrix materials are shown in Tables I, II, and III. Processing conditions for the silica fiber reinforced composites are contained in the Composite Fabrication section of this report.

In addition to SEM examination of the matrices and fiber reinforced composites, the silica reinforcing fibers were examined for possible degradation after elevated temperature exposure.

All matrices and composites were examined after the initial 2 hours at 600°F cure condition and after exposure at 1600°F for 68 hours. The maximum operating temperature for the composite is 1600°F, and 68 hours at this temperature is considered typical of service life at the maximum temperature since normal operating temperatures will be a few hundred degrees lower.

Figure 5 shows the $AlPO_4$/spodumene ceramic matrix after the initial 600°F cure and after the 1600°F heat soak at magnification of 1060X. Figure 6 shows the same matrix at a magnification of 10,600X after the 600°F and 1600°F exposures. It is apparent in the case of this matrix, as well as all of the other candidate matrices, that a sintering action is taking place during the long-term 1600°F exposure.

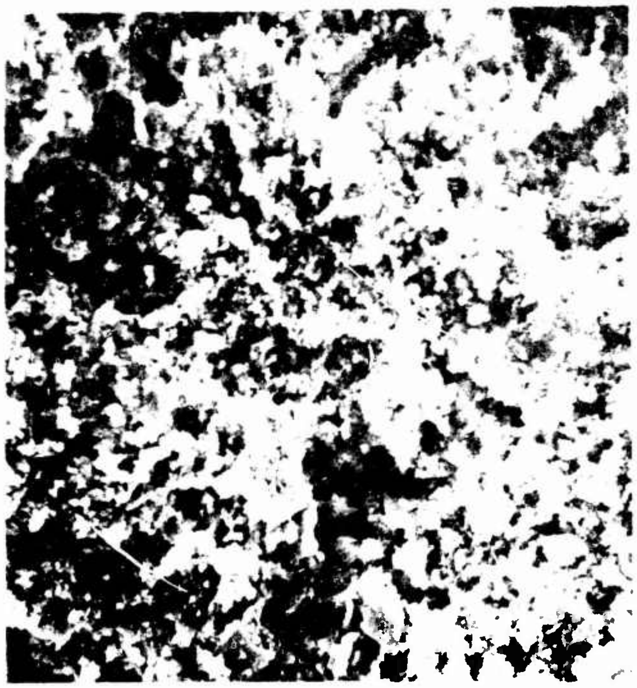
Figure 7 shows a silica fiber reinforced laminate based on the $AlPO_4$/ spodumene ceramic matrix after 600°F cure and after 1600°F heat soak. Again, the sintering and densification of the ceramic matrix is apparent. This matrix, as well as the others, appears to give little bonding or reaction with the reinforcing fibers. In the case of the 600°F specimen, particles clinging to the fibers are probably bonded by the silicone resin size which is cured during the matrix curing step.

Figure 8 shows the $AlPO_4$/50% petalite matrix after 600°F and 1600°F exposures and a magnification of 1100X. Figure 9 shows this same matrix and exposure condition at a magnification of 11,000X. Again, the sintering action is apparent.

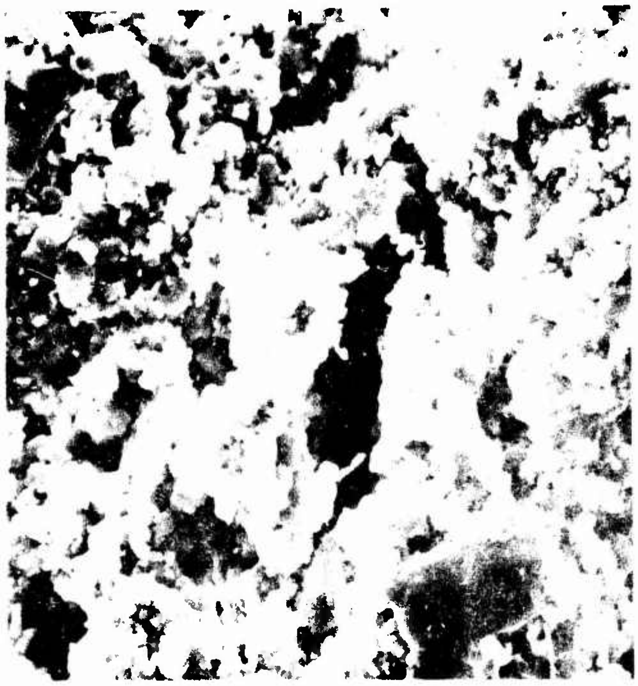
Figure 10 shows silica fiber reinforced composites based on this matrix system after the 600°F and 1600°F exposures. The dense, nonporous material separating certain individual fibers after 600°F exposure is attributed to the silicone resin size. After exposure at 1600°F for 68 hours the matrix has densified and shows substantially reduced porosity.

Figure 11 shows the $AlPO_4$/50% β-eucryptite ceramic matrix after 600°F and 1600°F exposures at 1100X magnification. The sintering of this matrix material is very apparent even at the lower magnification. Figure 12 shows the same matrix after identical thermal exposure conditions at a magnification of 11,000X. The sintering of the particles and the resulting change from jagged edge particles to smooth, rounded particles which are knitted together demonstrates the high reactivity of the β-eucryptite additive.

Figure 13 shows a rather surprising phenomenon in that the unmodified $AlPO_4$ matrix undergoes a sintering action during the 68-hour heat soak at 1600°F. This is surprising in that investigations at Whittaker R&D, as well as by various other workers, has shown the melting point of ortho-aluminum phosphate to be in excess of 3000°F. The ability to achieve sintering at this lower temperature could well be an advantage if it allows processing refractory materials into shapes at a substantially lower firing temperature than their maximum use temperature. Figure 14 further illustrates the change of the sharp irregular particles to a rounded, smooth shape.



(a) After 600°F Exposure (1060X)



(b) After 1600°F Exposures (1060X)

Figure 5. $AlPO_4$/50% Spodumene Ceramic Matrix

(a) After 600°F Exposure (10,600X)

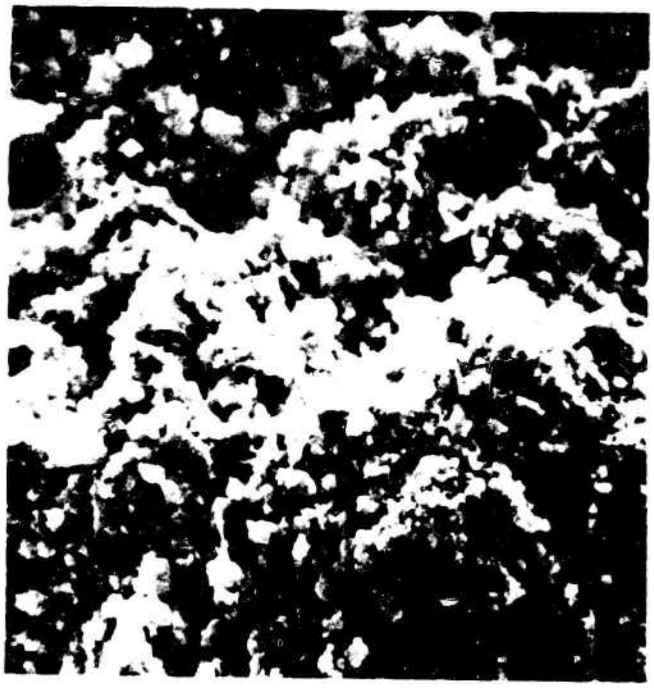
(b) After 1600°F Exposure (10,600X)

[illegible]

(a) After 600°F Exposure (1100X)

(b) After 1600°F Exposure (1100X)

Figure 7. Broken Surface of Silica Fiber Reinforced Composite with $AlPO_4$/50% Spodumene Ceramic Matrix



(a) After 600°F Exposure (1100X)

[illegible]

(a) After 600°F Exposure (11,000X)

(b) After [illegible] Exposure (11,000X)

Figure 4. [illegible]

(a) After 600°F Exposure (1100X)

(b) After 1600°F Exposure (1100X)

Figure 10. Broken Surface of Silica Fiber Reinforced Composite with $AlPO_4$/50% Petalite Ceramic Matrix

(a) After 600 F Exposure (1100X)

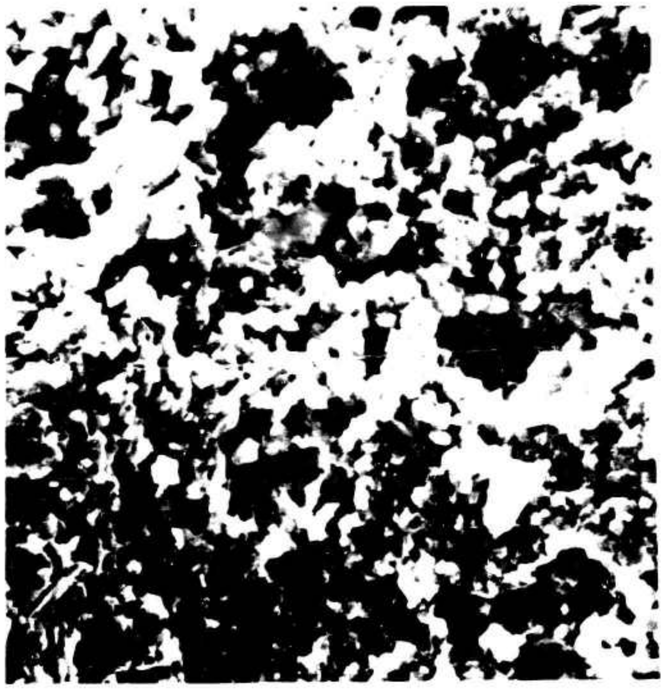
(b) After 1600°F Exposure (1100X)

Figure 11. $AlPO_4$/50% β-Eucryptite Ceramic Matrix

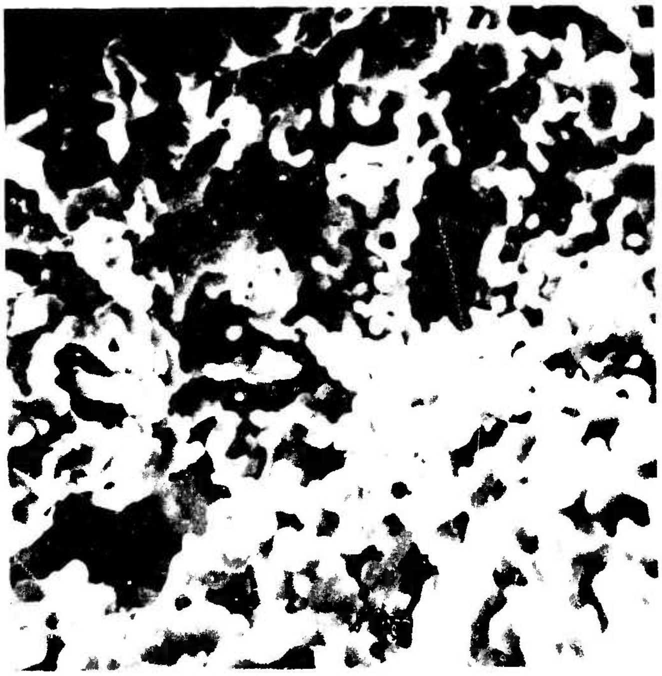
(a) After 600°F Exposure (11,000X)

(b) After 1600°F Exposure (11,000X)

[illegible]



(a) After 600 F Exposure (1100X)



(b) After 1600 F Exposure (1100X)

Figure 14. Unmodified Alumina Phosphate Matrix

(a) After 600°F Exposure (11,000X)

(b) After 1600°F Exposure (11,000X)

Figure 14. Unmodified Aluminum Phosphate Matrix

Figure 15 shows silica fiber reinforced composites based on the unmodified $AlPO_4$ and again the long-term 1600°F exposure appears to result in a densified, low porosity matrix. As in the case for the other matrices, reaction with or adhesion to the silica fibers is not apparent.

Figure 16 shows the $AlPO_4$/25% silica ceramic matrix. As with all the matrix materials, sintering is apparent. However, in this case the porosity appears to be significantly less than with the other matrices, with the sintered particles having a very dense and glassy-like appearance. Unlike the other matrices, the particles tend to retain sharp and jagged edges after the long-term 1600°F exposure.

Figure 17 shows a silica fiber reinforced composite based on this matrix and illustrates the dense nonporous matrix that is formed at 1600°F between the reinforcing fibers. Because of the unusual and potentially promising nature of this particular matrix, additional photomicrographs (Figures 18 and 19) were taken. The $AlPO_4$/25% silica system at this point in the program exhibits a combination of desirable properties which makes it a primary candidate matrix. Future investigations based on variations of the amount of silica additive from the present 25% are planned.

Due to concern over possible degradation of the silica fiber properties at 1600°F, a study involving a series of SEM observations was conducted. Figure 20 shows an uncoated silica fiber drawn at Whittaker R&D.

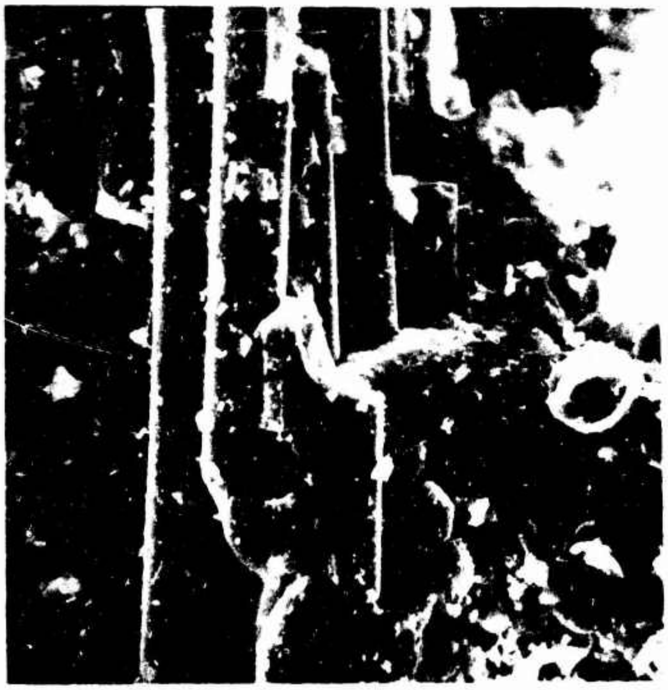
Figure 21 is a commercial silica fiber supplied by J. P. Stevens Company under the trade name of Astroquartz. The Astroquartz fiber is supplied with an aminosilane finish which is apparent in this figure.

Figure 22 shows the aminosilane finished Astroquartz fiber after exposure to 1600°F. The material in the center of the fiber in a longitudinal direction is believed to be residue from the aminosilane size. A bundle (yarn) of individual fibers was exposed to the 1600°F temperature. The size apparently flowed at some elevated temperature and accumulated in the contact area between the adjacent fibers. This same pattern of residue on fibers is apparent in many of the composite photomicrographs.

Due to the acidic nature of the chemically reacted ceramic matrix and the water (steam) generated during the curing process, a problem of degradation of the silica fiber exists. The most satisfactory solution to this problem to date has been the use of a silicone resin size to coat the fiber. Figure 23 shows silica fiber coated with the Dow Corning DC805 silicone resin.

Figure 24 shows a fiber coated with the resin size following exposure to 1200°F. Some residue of the resin still is apparent on the fiber after this exposure condition. Figure 25 shows the silica fiber after further exposure of 1600°F. At this temperature the size as well as the original finish appear to have been completely removed. A small nodule on the fiber is apparent in the lower left-hand corner of Figure 26. This area was examined further at a magnification of [illegible] and apparently is an [illegible] size [illegible] the silica fiber itself.

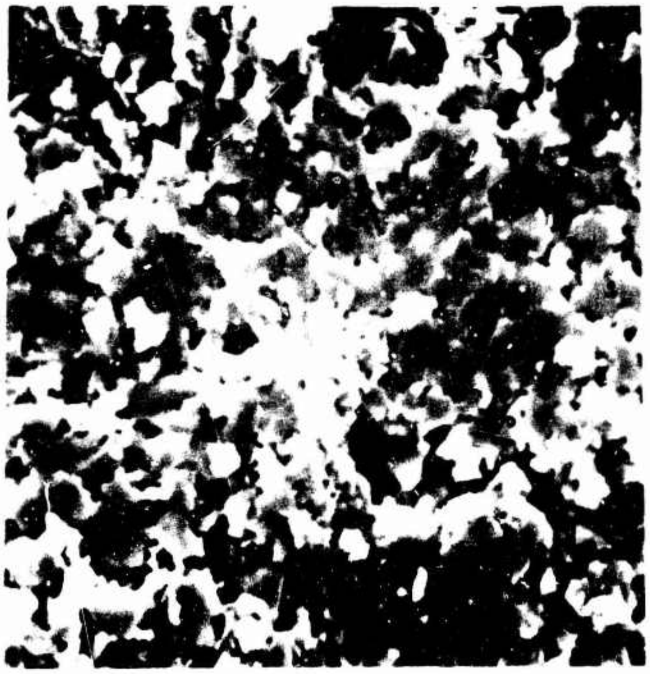
(a) After 600°F Exposure (1100X)



(b) After 1600°F Exposure (1100X)

Figure 15. Broken Surface of Silica Fiber Reinforced Composite Based on Unmodified Aluminum Phosphate Ceramic Matrix

(a) After 600°F Exposure (1100X)



(b) After 1600°F Exposure (1100X)

Figure 16. Aluminum Phosphate/25% Silica Ceramic Matrix

(a) After 600°F Exposure (11,000X)

(b) After 1600°F Exposure (11,000X)

Figure 17. Aluminum Phosphate/25% Silica Ceramic Matrix

(a) After 600°F Exposure (2000X)

(b) After 1600°F Exposure (1800X)

Figure [illegible]

(a) After 600°F Exposure (935X)

(b) After 1600°F Exposure (1870X)

Figure 19. Broken Surface of a Silica Fiber Reinforced Composite Based on $AlPO_4$/25% Silica Ceramic Matrix

Figure 20. Uncoated Silica Fiber after 1600°F Exposure (4670X)

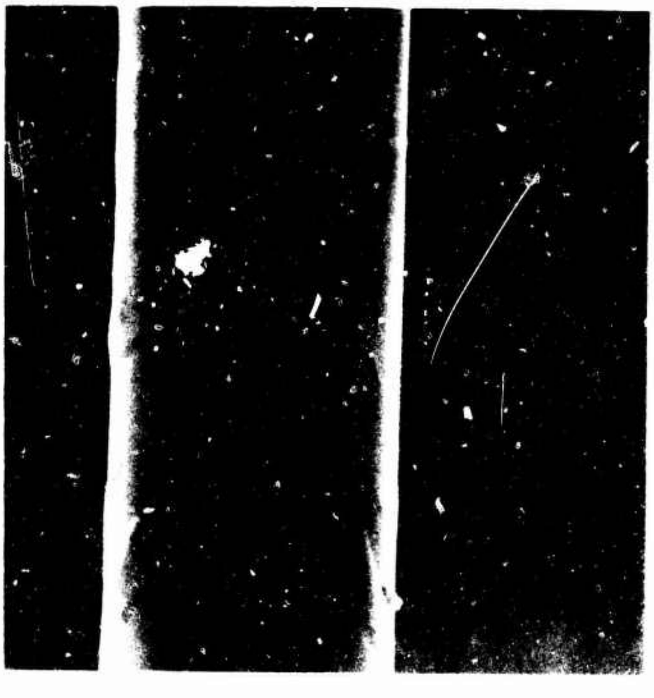


Figure 21. Silica Fiber (Astroquartz) as Supplied with an Amm. [illegible] as Finish (4670X)

Figure 22. Silica Fiber (Astroquartz) as Supplied with an Amino Silane Finish after Exposure to 1600°F (4670X)

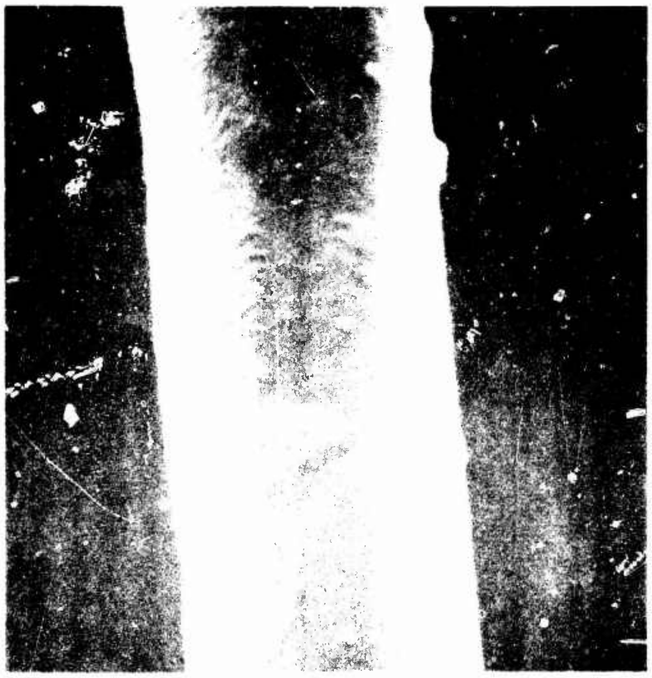


Figure 23. Silica Fiber (Astroquartz) with an Amino Silane Finish Followed by Coating with a DC805 Silicone Resin Size (4670X)

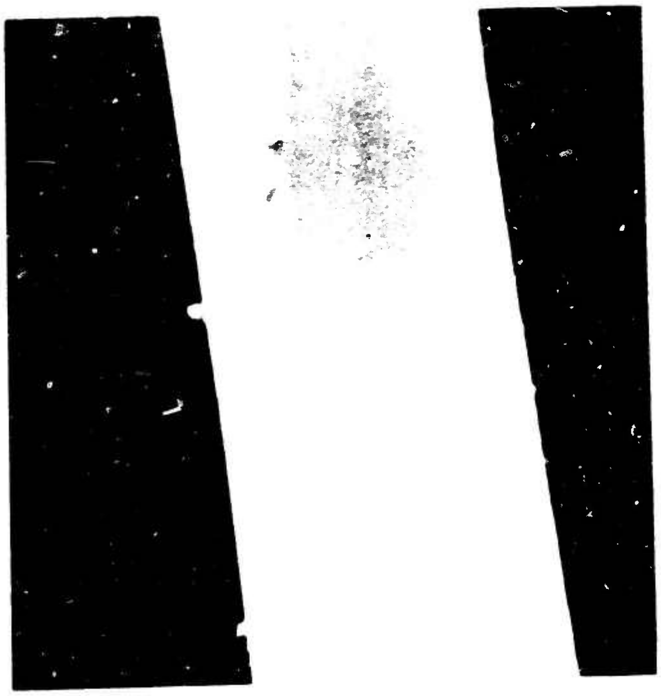


Figure 24. Silica Fiber (Astroquartz) with an Amino Silane Finish Followed by Coating with a DC805 Silicone Resin Size after Exposure to 1200°F (4670X)

Figure 25. Silica Fiber (Astroquartz) with an Amino Silane Finish Followed by Coating with a DC805 Silicone Resin Size after Exposure to 1600°F (4670X)

Figure 26. Silica Fiber (Astroquartz) with an Amino Silane Finish Followed by Coating with a DC805 Silicone Resin Size after Exposure to 1600°F (20,000X)

2. COMPOSITE LAMINATE FABRICATION STUDIES

The purpose of this task was to establish processes for producing high-quality composite laminates. Of primary concern was the complete impregnation of the woven fabric reinforcement with the liquid uncured matrix system, conditioning of the prepreg so as to be suitable for handling and layup, and the development of cure schedules. This was required for each of the different matrix systems listed below:

- $AlPO_4$
- $AlPO_4$ + 25% Silica
- $AlPO_4$ + 50% Silica
- $AlPO_4$ + 35% Spodumene
- $AlPO_4$ + 50% Spodumene
- $AlPO_4$ + 35% Petalite
- $AlPO_4$ + 50% Petalite

The initial work in the process development task utilized standard, inexpensive 181-style E-glass fabric. A laminate matrix content target of 40% was established for all matrix systems. The different matrix systems were modified by diluting with water to obtain the proper consistency for impregnating the fabric. During the earlier tasks in which unreinforced matrix tiles were pressed, a viscous matrix system was used with subsequent drying cycles to produce a thermoplastic powder consistency. The consistency of the matrix for impregnating the reinforcement must be fluid enough to impregnate the discrete fiber bundles but viscous enough to maintain the 40% by weight loading. An increasing amount of water was required for the more heavily filled systems. Impregnation was accomplished by manual squeegee methods.

In the initial impregnated state the prepreg material contains excessive water which contributes to higher void volumes in the cured composite. Treatment at 150°F for five minutes removed water, advanced the reaction, and gave a drapable and tacky material. Each of the seven matrix systems produced a very high-quality prepreg material after drying. It was easily handled and enhanced the layup procedures by maintaining its shape and being adherent to adjacent plies.

The initial laminate fabrication involved 10-ply, 4" x 4" specimens. The uncured layup was placed on a Mylar-covered aluminum caul plate for curing. A layer of porous, Teflon-coated glass fabric was laid on the top surface of the layup followed by a number of dry glass bleeder plies to remove air, water, and excess matrix from the laminate during the elevated temperature cure cycle. The entire layup was then vacuum bagged with a Mylar film sealed to the aluminum caul plate. This assembly was placed in an autoclave and vacuum attachments made.

The cure schedule which produced the highest composite density and structural integrity for all of the matrix systems is given below:

- Insert bagged layup into room temperature autoclave.
- Apply full vacuum pressure (28 inches of mercury - minimum).
- Apply 100 psi autoclave pressure.
- Heat to 350°F at a rate of 3 to 5°/minute.
- Maintain temperature, vacuum, pressure for two hours.
- Cool under pressure and vacuum to below 150°F before removing.
- Postcure in an air circulating oven from 350° to 600°F at a rate of 10°F/minute maximum and hold at 600°F for one hour.
- Cool to room temperature before removing from oven.

The above process was investigated for each of the candidate matrix systems. It proved to be the simplest and most reproducible process for obtaining high quality composites.

The fabrication process developed was now used to prepare silica fiber* reinforced composites. The same high quality composite which was obtained with the E-glass was achieved using the silica reinforcement. The only difference noted was a greater per-ply thickness when using the silica reinforcement. The earlier E-glass laminates had yielded a per-ply thickness in the cured composite of between 0.0095" and 0.010" for the low filler matrix system. Ply thickness averaged 0.011" and 0.012" per ply for the matrix systems containing 50% by weight additive.

3. COMPOSITE CHARACTERIZATION STUDY

a. Thermal Aging

The initial set of silica reinforced laminates prepared under the fabrication process study were to be used to evaluate long term thermal stability at different temperatures. During early testing a problem was encountered with degradation of the composite's room temperature strength after exposure at 1600°F. This was identified as a problem of degradation of the reinforcement since the matrix realized an increase in strength after 1600°F exposure. It was initially believed that degradation might be due to exposure of the reinforcement to phosphoric acid from the uncured matrix. This problem had been encountered earlier with E-glass reinforcement and results in a very poor quality laminate Because of the elevated temperature degradation of the composites, optimization of the fabrication process was delayed until an investigation could be made into the problem.

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* J. P. Stevens Co., Astroquartz®, Fabric Style 581

Test results on silica reinforced laminates before high temperature exposure revealed that the room temperature strengths had not been affected and eliminated the possibility that the phosphoric acid had degraded the reinforcement. It was also revealed that there was no significant difference between the matrix systems. Laminates based on all matrix systems showed a similar type of degradation. A study program was initiated to investigate the cause of the problem and to establish a solution. Initially, silica fabric as received from the supplier was exposed in air to 1600°F. Prior to exposure the fabric was very strong and pliable. After exposure at 1600°F and even at temperatures as low as 1100°F, the silica fabric became very brittle and weak and failed from being folded.

Silica fibers were examined before and after thermal exposure using a scanning electron microscope (Figures 20 through 26). No conclusions could be formed from this investigation. The surface finish on the silica fabric is gamma aminopropyltriethoxysilane. Previous work at WRD, which involved the drawing of silica filaments, established that a surface finish increased the room temperature fiber strength. However, when heated above 1000°F silane finishes had a tremendous detrimental effect on the filament strength. Attempts were made to remove the finish by heat cleaning and by water boil. The most successful method for removing the fabric finish was a two-hour water boil. The integrity of the fabric after the boiling procedure was somewhat less than the original as-received condition, but the sample which had been heat cleaned at approximately 900°F was more deteriorated. Samples of the fabric which had been water boiled and heat cleaned along with as-received material were exposed to 1100 and 1600°F. There was little difference between the heat cleaned sample and the original sample. However, the sample which had been boiled clean was obviously much less degraded.

In order to determine the effect of fabric finish on the strength of the ceramic composites, three series of laminates were prepared for flexural testing before and after a thermal exposure. Laminates were prepared from each matrix material. The first series was prepared from quartz fabric which had been heat cleaned for one hour at 900°F. The second series was prepared using quartz fabric which had been cleaned by boiling in distilled water. The third series was prepared from quartz fabric which had been water boil cleaned and then treated with a DC805 silicone resin size. Mechanical properties were measured on the three series of laminates in both the unaged and aged condition at room temperature, 1100°F, and 1600°F (Table IV).

It is obvious from the test results that the water boil cleaning of the reinforcement followed by application of a silicone resin size provides the highest strength values for each matrix system in the unaged condition. With the exception of the $AlPO_4$/50% silica matrix system, it also provides the highest strength for the 1600°F aged systems. The water boil cleaning and DC805 silicone resin size was selected as the surface treatment for the silica fabric for the remainder of the program.

Table IV

MECHANICAL PROPERTIES FOR COMPOSITES, BEFORE AND AFTER THERMAL AGING, USING DIFFERENT TREATMENTS FOR THE ASTROQUARTZ REINFORCEMENT

Matrix/ Test Temp.	Treatment #1				Treatment #2				Treatment #3			
	Flex., psi		Modulus, psi x 10^6		Flex., psi		Modulus, psi x 10^6		Flex., psi		Modulus, psi x 10^6	
	Un-aged	Aged* 1600°F	Un-aged	Aged 1600°F	Un-aged	Aged 1600°F	Un-aged	Aged 1600°F	Un-aged	Aged 1600°F	Un-aged	Aged 1600°F
100% $AlPO_4$												
RT	5140	-	2.31	-	6860	2690	2.18	2.14	21000	3250	3.94	2.58
1100°F	9120	3260	2.53	1.76	7120	3380	1.01	1.32	17160	5020	3.05	3.42
1600°F	9220	4800	1.97	2.39	4840	5370	0.79	1.74	9130	6720	2.73	3.39
$AlPO_4$ + 25% SiO_2												
RT	7560	2010	3.07	1.60	6930	1770	2.9	1.46	17120	2590	2.82	1.61
1100°F	8470	3840	2.35	1.94	10520	2140	1.01	0.94	13180	4120	2.28	2.40
1600°F	9660	5580	1.61	1.84	4080	3650	0.66	1.32	8040	4900	2.57	2.82
$AlPO_4$ + 50% SiO_2												
RT	7340	1940	2.46	1.38	4310	840	2.21	0.48	20000	1850	2.64	1.66
1100°F	9800	3000	1.65	1.58	6020	1450	0.78	1.08	16740	3200	1.85	2.45
1600°F	4620	4360	0.63	1.43	2180	2230	0.50	1.12	7310	3030	2.44	2.78
$AlPO_4$ + 35% Spodumene												
RT	5680	752	1.77	0.43	6190	1400	1.88	1.18	16560	2240	2.73	2.06
1100°F	8340	1390	1.86	1.34	11090	3470	2.38	1.83	16520	2140	2.79	2.30
1600°F	5940	2360	1.01	1.57	8120	3360	1.90	2.66	6320	3820	2.30	2.89
$AlPO_4$ + 50% Spodumene												
RT	4000	-	2.19	-	5880	910	2.35	0.46	20940	2100	3.14	2.01
1100°F	5900	-	1.55	-	8520	1550	1.59	1.40	22360	4290	1.71	4.19
1600°F	4980	2390	1.31	1.66	4750	2260	1.14	2.09	5680	5560	2.79	3.51
$AlPO_4$ + 35% Petalite												
RT	4580	1340	2.46	1.04	3710	910	2.50	0.63	18200	1770	2.72	1.41
1100°F	10940	2870	2.54	2.50	8150	2370	2.00	2.17	19200	3340	1.57	3.02
1600°F	8960	3060	1.71	2.77	7160	-	1.64	-	8350	3820	2.18	3.66
$AlPO_4$ + 50% Petalite												
RT	5550	1070	2.50	0.66	2470	990	2.15	0.56	18000	1570	2.74	1.87
1100°F	9370	2100	1.38	2.45	7890	2140	1.49	1.85	16000	3520	2.11	3.00
1600°F	3170	2110	0.44	1.65	5680	1750	0.74	2.19	6750	3920	2.00	3.11

Notes:
1. Treatment #1 - Heat clean at 900°F for 1 hour.
2. Treatment #2 - Water boil clean for 1 hour.
3. Treatment #3 - Water boil clean for 1 hour + DC8.5 size.
4. Aging time at 1600°F - 5 hours.

Panels were prepared from each matrix system and specimens cut for aging at 1100°F and 1600°F for durations of 1 hour, 10 hours, 50 hours, 100 hours and 200 hours. The samples were evaluated for the following properties or characteristics after each exposure duration:

- Density
- Porosity
- Microstructure
- Weight Loss
- Dimensional Change
- Thermal Expansion
- Thermal Shock Resistance

Figures 27 through 30 show the weight loss and density changes for the different periods of time for composites based on each candidate matrix system. Most of the weight loss occurs in the first hour and can probably be attributed to the silicone resin size and dehydration of unreacted aluminum hydroxide. Dimensional changes were insignificant and therefore not plotted. After 1100°F exposure no dimensional change occurred. After 1600°F there was approximately a 1% growth in laminate thickness which occurs at the initial one-hour cycle and does not exceed this value after the 200 hours exposure.

Porosity and microstructure were observed visually using an optical microscope (96X). In general, the porosity appeared unchanged due to thermal exposure. However, some microcracking of the matrix-rich areas in the laminates was apparent. This microcracking probably contributes to the lower mechanical properties obtained after exposures at 1100°F and 1600°F. Thermal expansion was measured perpendicular to the laminate plane. These values are shown in Table V.

Specimens from each matrix system were subjected to thermal shock after each of the thermal aging exposures. This was performed by rapidly heating the specimens on a ceramic foam block to 1600°F using quartz lamp heaters. The time required for stabilizing the specimen at 1600°F was approximately three minutes. The time duration at 1600°F was two minutes, after which the heaters were removed and the specimens cooled using a low valocity fan blower. The specimens were examined for delamination, permanent thickness changes, etc. The specimens, after thermal shock exposure, revealed no visual changes in physical integrity.

b. Electrical Properties

The electrical property measurement required fabrication of specimens of a cylindrical shape 1" in diameter by 1" in length. Specimens were prepared from each of the seven candidate matrix systems and submitted to Massachusetts Institute of Technology for testing of dielectric constant and loss tangent at X-band frequency from room temperature through 1600°F.

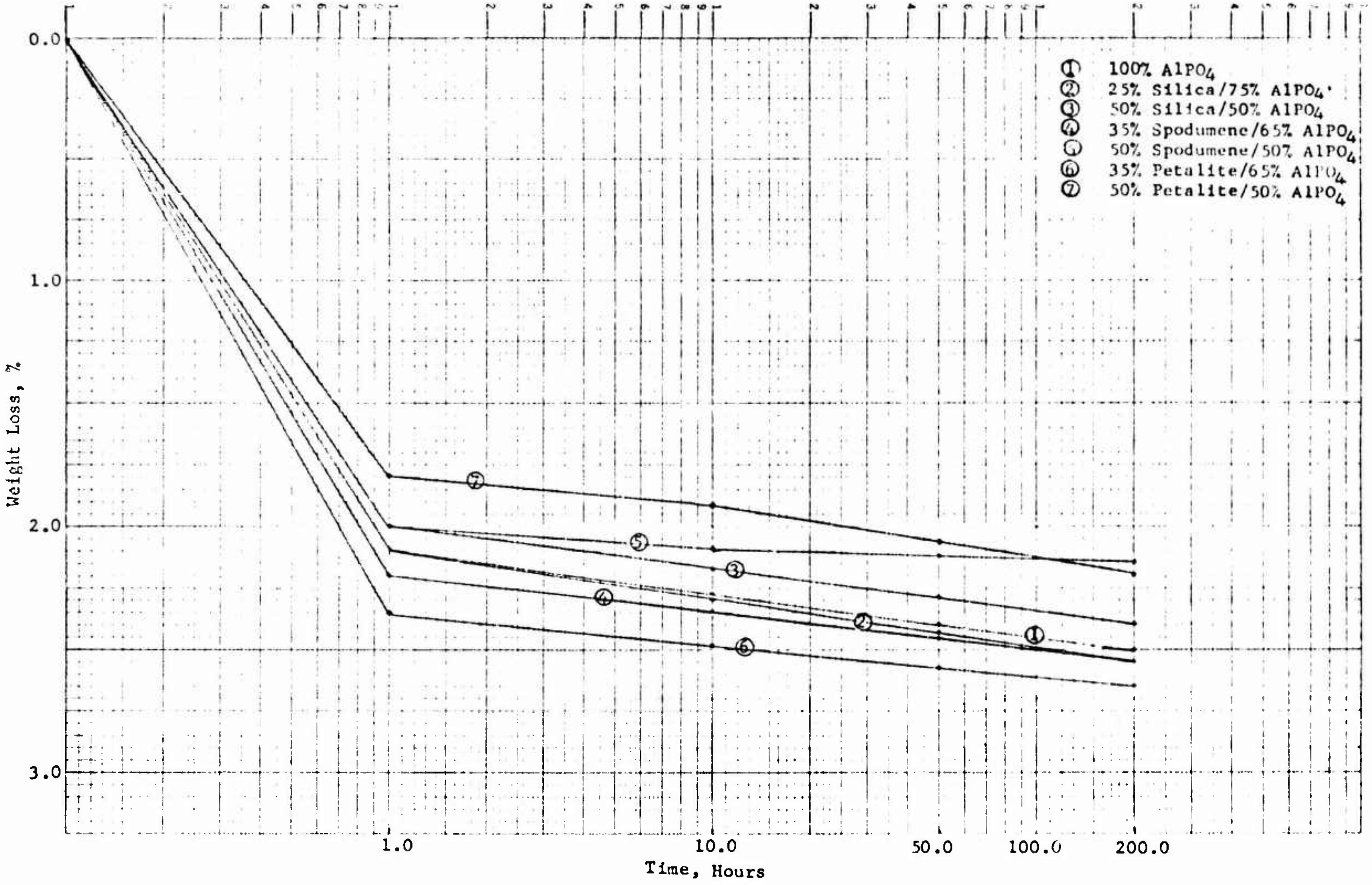

Figure 27. Weight Loss of Composites after 1100°F Exposure

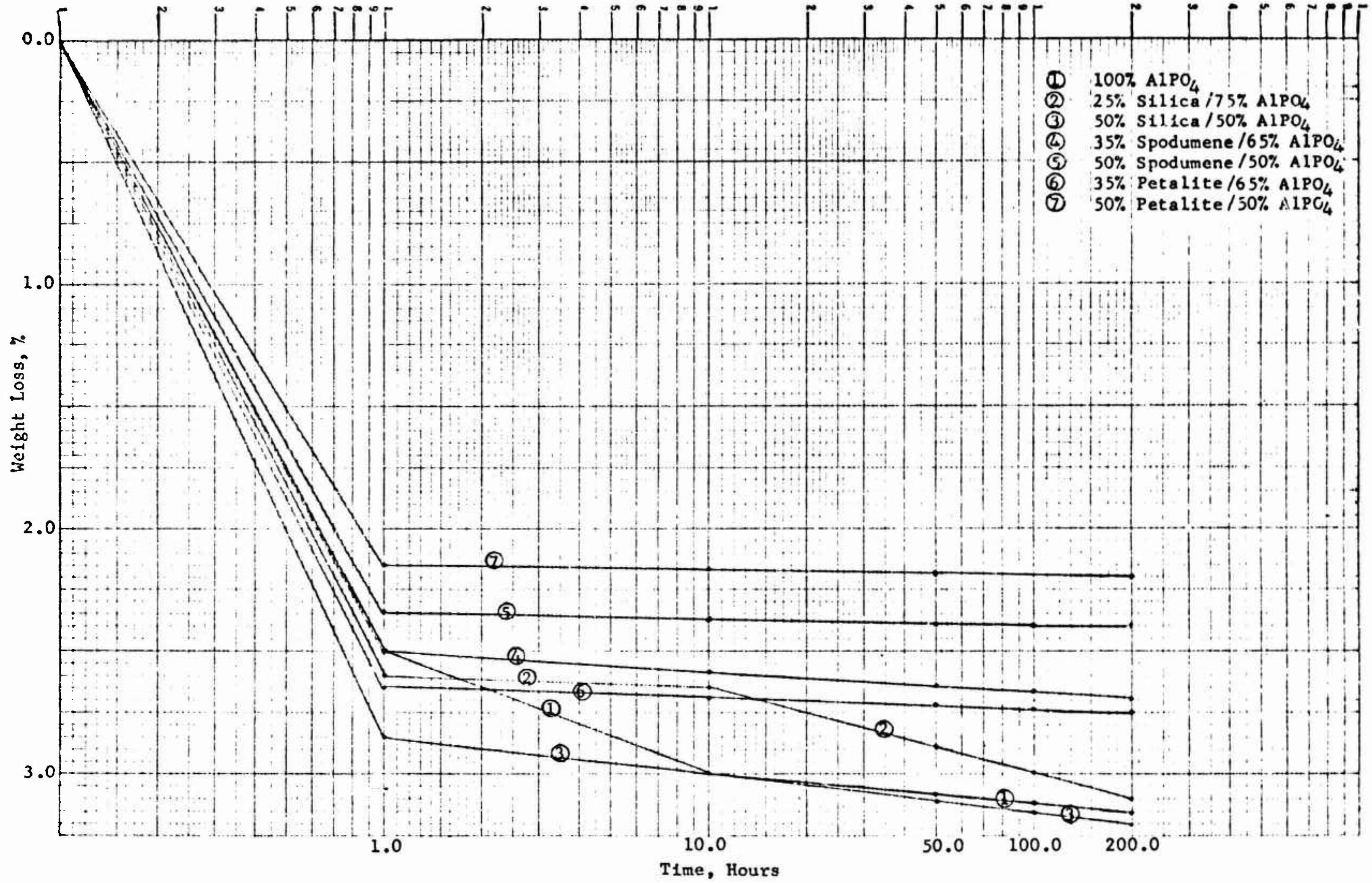

Figure 28. Weight Loss of Composites after 1600°F Exposure

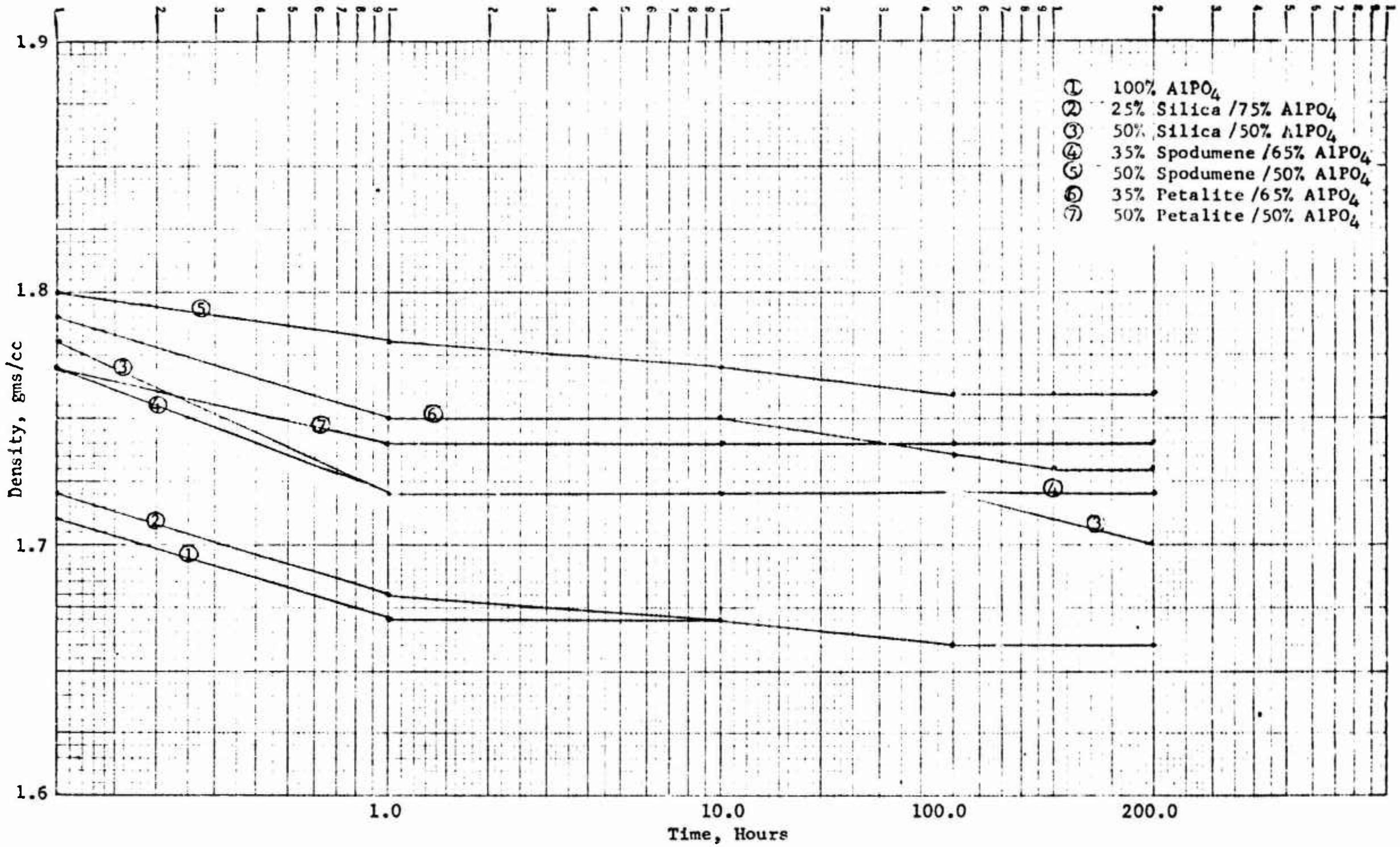

Figure 29. Density Change of Composites after 1100°F Exposure

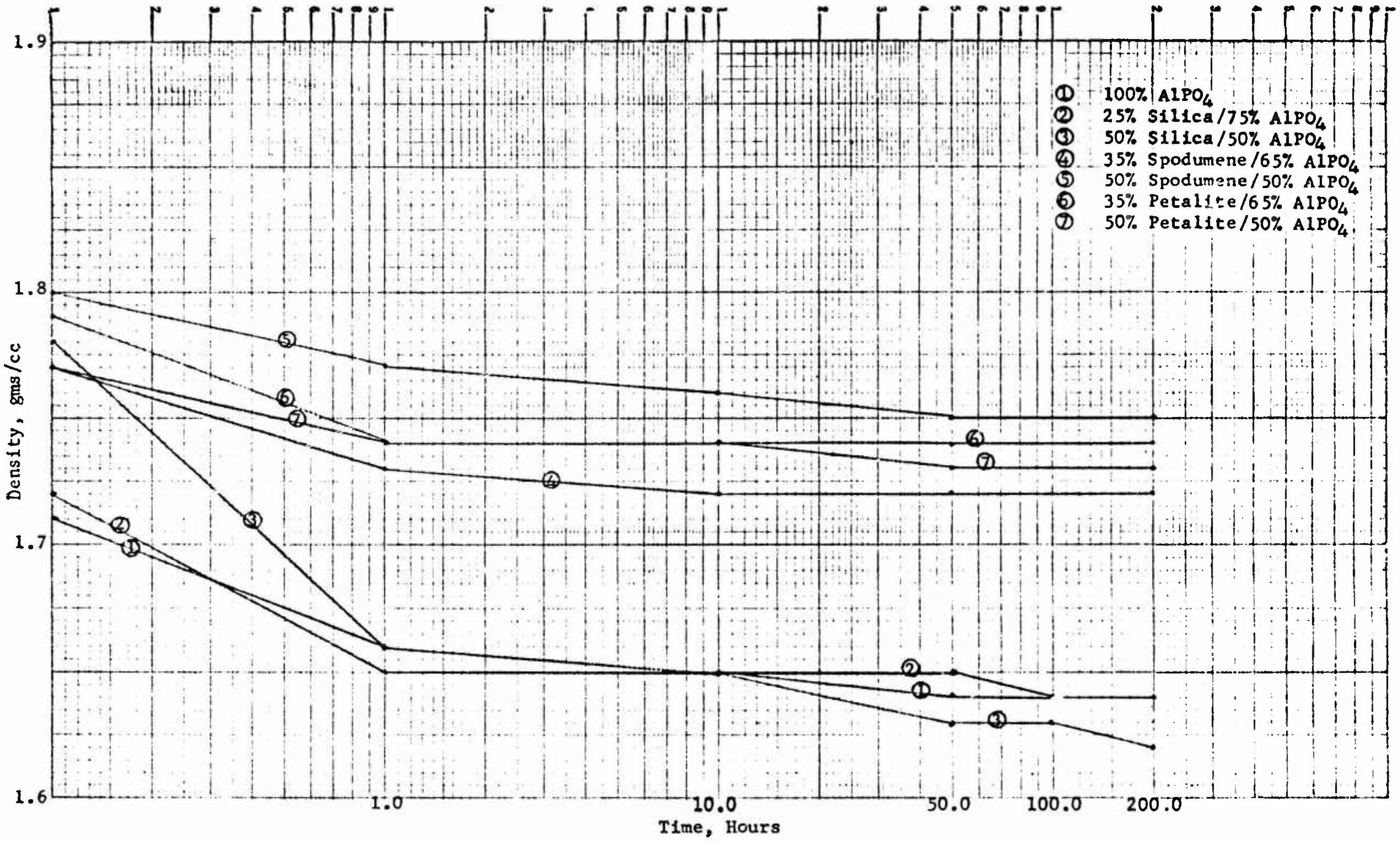

Figure 30. Density Change for Composites After 1600°F Exposure

TABLE V

THERMAL EXPANSION OF SILICA FABRIC REINFORCED COMPOSITES*

Matrix System	Expansion, Percent**
100% $AlPO_4$	2.50%
$AlPO_4$ + 25% Silica	2.40%
$AlPO_4$ + 50% Silica	2.20%
$AlPO_4$ + 35% Spodumene	.98%
$AlPO_4$ + 50% Spodumene	.70%
$AlPO_4$ + 35% Petalite	1.20%
$AlPO_4$ + 50% Petalite	.93%

* Laminate thickness direction

** RT - 1600°F after 5 Hours Exposure at 1600°F

Figures 31 and 32 show the results obtained on these specimens. In all cases the ply orientation for the specimens was perpendicular to the length. Listed below are the densities obtained for the composite specimens:

Matrix	Density, Grams/cm^3
100% $AlPO_4$	1.558
$AlPO_4$ + B_2O_3	1.632
$AlPO_4$ + 25% Silica	1.753
$AlPO_4$ + 50% Silica	1.611
$AlPO_4$ + 35% Spodumene	1.729
$AlPO_4$ + 50% Spodumene	1.772
$AlPO_4$ + 35% Petalite	1.713

Prior to measurement of density and electrical properties, the specimens were aged for 100 hours at 1600°F.

Table VI shows the actual measured dielectric constant and loss tangent values for each of the composites at temperatures through 1600°F. The composites based on 100% aluminum phosphate and aluminum phosphate with silica additives possess the lowest and most stable dielectric constant and loss tengent properties. The systems containing spodumene and petalite have slightly higher but stable dielectric constant properties, however, they become rather lossy at higher temperatures.

c. Mechanical Properties

Flexural strength and modulus were measured on specimens of the seven composite materials which had been thermal cycled to 1100°F and 1600°F for 5, 10, 25, and 50 cycles each. The thermal cycle conditions consisted of heating from room temperature to 1100°F in approximately three minutes, holding at 1100°F for ten minutes, increasing the temperature to 1600°F over a period of one minute, holding at 1600°F for five minutes and rapidly cooling to room temperature. Heating was performed with a bank of quartz lamp heaters placed approximately 1" away from the specimen surface. After the exposure at 1600°F, the heaters were quickly removed and air was blown onto the specimens for rapid cool down to below 300°F. This thermal cycling condition is typical of what the material will experience in actual application. Table VII lists the flexural properties for each composite material after thermal cycling measured at room temperature, 1100°F and 1600°F. Property degradation occurs during the first five cycles after which increased numbers of thermal cycles does not further degrade the mechanical properties.

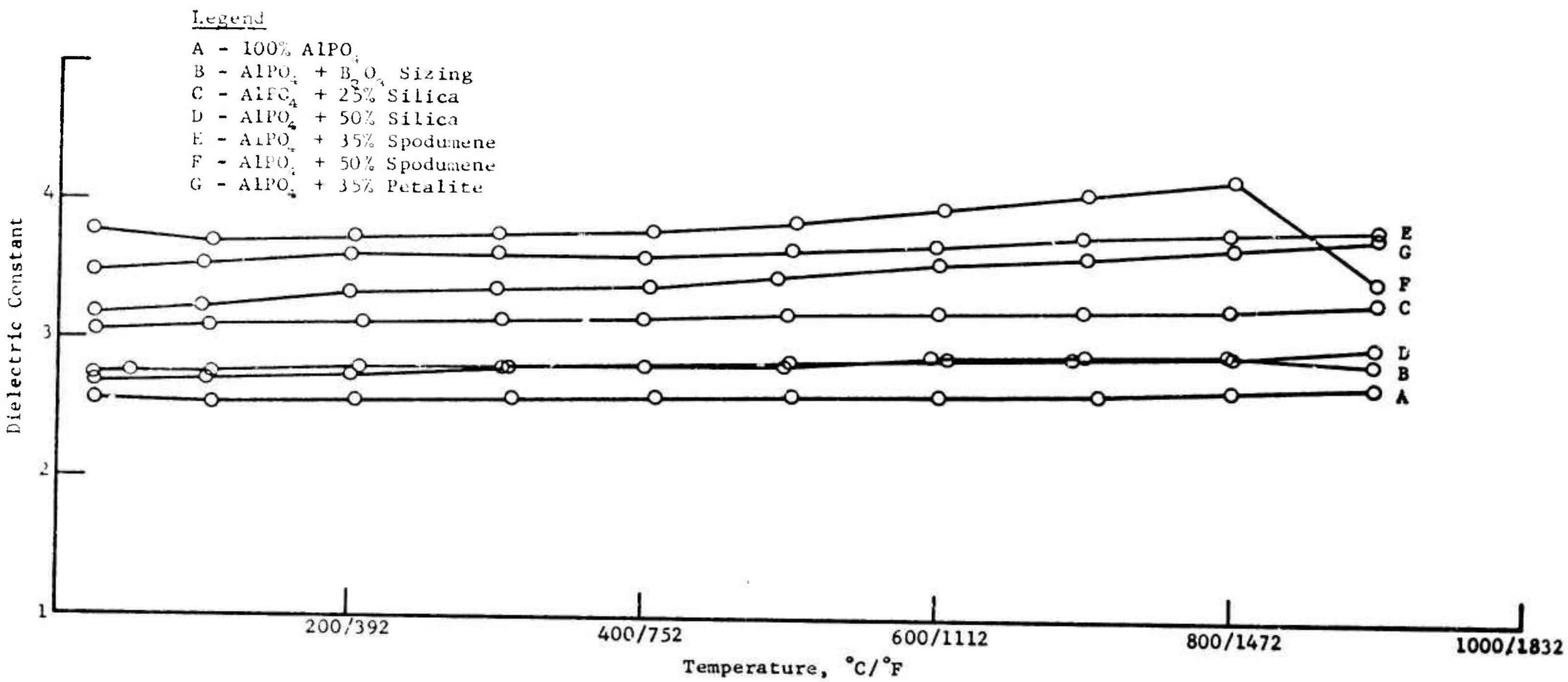

Figure 31. Dielectric Constant vs Temperature for Silica Fabric Reinforced Ceramic Matrices (8.52 GHz)

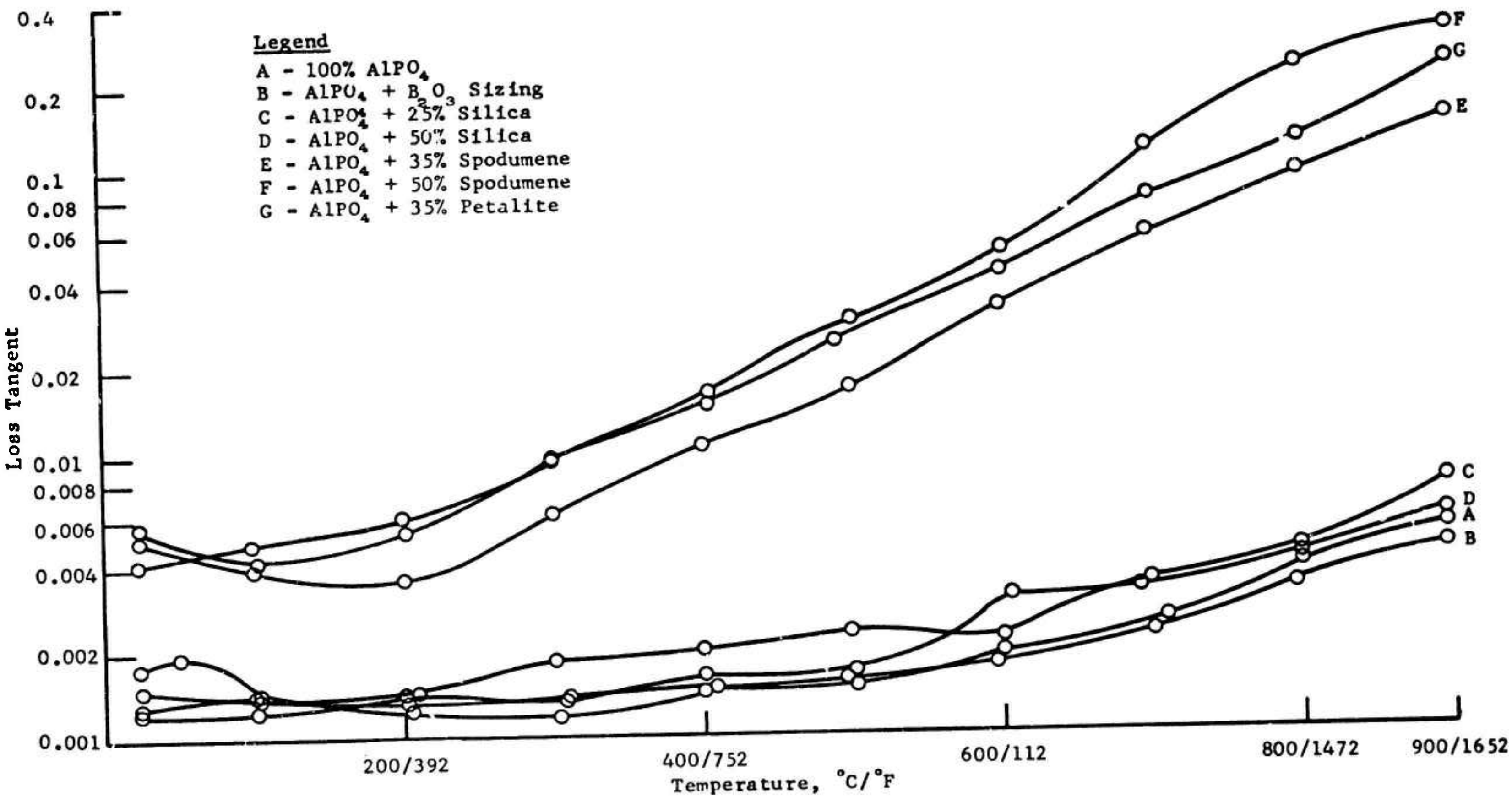

Figure 32. Loss Tangent vs Temperature for Silica Fabric Reinforced Ceramic Matrices (8.52 GHz)

TABLE VI

DIELECTRIC CONSTANT AND LOSS TANGENT VS. TEMPERATURE FOR SILICA FABRIC REINFORCED CERAMIC COMPOSITES (8.52 GHz)

AlPO$_4$/Matrix			AlPO$_4$/B$_2$O$_3$ Matrix			AlPO$_4$/25% Silica Matrix			AlPO$_4$/50% Silica Matrix		
T°C	K	tan δ	T°C	K	tan δ	T°C	K	tan δ	T°C	K	tan δ
25*	2.785	.00152	25*	2.875	.00189	25*	3.058	.00172	25*	2.870	.00131
	2.767	.00164		2.929	.00218		3.060	.00159		2.845	.00133
25**	2.780	.00146	25**	2.869	.00161	25**	3.028	.00131	25**	2.863	.00129
	2.767	.00147		2.924	.00175		3.033	.00128		2.839	.00122
104	2.77	.00136	50	2.88	.00192	102	3.05	.00140	102	2.87	.00121
202	2.78	.00131	103	2.88	.00138	208	3.06	.00143	200	2.88	.00140
310	2.79	.00139	204	2.90	.00124	301	3.07	.00186	307	2.90	.00137
407	2.80	.00147	302	2.90	.00118	399	3.08	.00201	399	2.91	.00161
501	2.81	.00146	400	2.91	.00143	497	3.10	.00228	499	2.93	.00164
600	2.82	.00190	495	2.92	.00154	600	3.11	.00216	605	2.94	.00307
709	2.82	.00248	595	2.95	.00172	698	3.12	.00339	691	2.95	.00333
800	2.84	.00384	699	2.96	.00221	797	3.13	.00439	800	2.97	.00408
896	2.85	.00524	796	2.97	.00326	897	3.16	.00760	897	2.99	.00575
25	2.77	.00126	896	2.94	.00443	93	3.06	.00197	28	2.87	.00144
			25	2.88	.00159	25	3.04	.00169			

AlPO$_4$/35 % Spodumene Matrix			AlPO$_4$/50% Spodumene Matrix			AlPO/$_4$ Petalite Matrix		
T°C	K	tan δ	T°C	K	tan δ	T°C	K	tan δ
25*	3.244	.00521	25*	3.372	.00605	25*	3.075	.00416
	3.242	.00590		3.394	.00588		3.095	.00405
25**	3.246	.0049	25**	3.388	.0057	25**	3.089	.00409
100	3.27	.0039	104	3.35	.0042	99	3.12	.0048
200	3.30	.0036	201	3.37	.0054	199	3.17	.0060
299	3.31	.0061	300	3.38	.0095	300	3.18	.0096
400	3.30	.0104	404	3.39	.0161	403	3.19	.0146
499	3.33	.0168	501	3.43	.0289	490	3.23	.0241
597	3.35	.0318	601	3.48	.0498	600	3.28	.0419
697	3.38	.0565	699	3.54	.113	699	3.31	.077
798	3.40	.0933	799	3.59	.220	800	3.34	.120
899	3.42	.141	897	3.22	.297	896	3.40	.228
25	3.31	.0047	25	3.37	.0054	25	3.16	.00425

* as received

** after oven drying

TABLE VII

EFFECT OF THERMAL CYCLING ON FLEXURAL PROPERTIES OF CERAMIC COMPOSITES

Number Cycles	R.T.		1100°F		1600°F	
	Flex. Strength, psi	Flex. Modulus, psi x 10^6	Flex. Strength, psi	Flex. Modulus, psi x 10^6	Flex. Strength, psi	Flex. Modulus, psi x 10^6
			$AlPO_4$			
0	21,000	3.94	17,160	3.05	9,130	2.73
5	3,225	1.53	5,380	2.37	7,390	2.44
10	3,050	1.57	4,290	2.36	5,700	2.88
25	2,730	1.44	4,510	2.42	6,480	2.79
50	2,850	1.76	5,210	2.19	6,560	2.81
			$AlPO_4$ + 25% Silica			
0	17,120	2.82	13,180	2.28	8,040	2.57
5	3,560	1.61	6,130	2.33	7,230	3.26
10	3,520	1.72	5,610	2.23	6,690	2.67
25	3,010	1.37	5,100	1.99	5,790	2.77
50	3,280	1.54	4,870	1.97	6,180	2.71
			$AlPO_4$ + 50% Silica			
0	20,000	2.64	16,740	1.85	7,310	2.44
5	639	0.19	1,180	0.22	1,560	-
10	558	0.13	871	0.24	1,600	0.56
25	563	0.16	927	0.17	1,760	0.64
50	511	0.13	1,120	0.17	1,630	0.47
			$AlPO_4$ + 35% Spodumene			
0	16,560	2.73	16,520	2.79	6,320	2.30
5	2,788	2.07	4,590	2.59	4,630	2.85
10	2,560	1.81	4,640	2.88	5,560	3.10
25	1,940	1.60	4,470	2.38	4,730	2.96
50	2,400	1.63	4,420	2.82	5,440	2.84
			$AlPO_4$ + 50% Spodumene			
0	20,940	3.14	22,360	1.71	5,680	2.79
5	2,380	1.85	4,170	2.64	5,590	3.04
10	1,500	1.53	3,430	2.39	4,750	2.86
25	2,190	1.85	3,930	2.46	3,970	2.61
50	1,800	1.86	4,300	2.65	4,170	2.60
			$AlPO_4$ + 35% Petalite			
0	18,200	2.72	19,200	1.57	8,350	2.18
5	1,960	1.56	4.230	2.97	6,000	3.12
10	1,590	2.25	3,800	2.79	5,860	3.11
25	1.920	1.63	4,170	3.04	5,580	3.03
50	1,860	1.55	4,380	2.87	4,910	3.30
			$AlPO_4$ + 50% Petalite			
0	18,000	2.74	16,000	2.11	6,750	2.00
5	1,920	1.72	4,510	2.88	5,030	3.19
10	2,140	1.88	3.970	3.21	5,320	3.31
25	2,580	1.93	4,270	3.09	4,940	2.92
50	1,735	1.41	4,040	2.74	3,850	2.75

d. Reproducibility Studies

Reproducibility studies were conducted on the seven composite materials. The reinforcement used for this study was inexpensive E-glass fabric. It was shown during the earlier portion of the program that the processing of composite laminates is not affected by the type of reinforcement. Two sets of laminates were prepared and evaluated to determine the reproducibility for each matrix system. The laminates were prepared in an identical manner over a three-day period. The criteria used to evaluate the reproducibility of each system were density, panel thickness, and thickness per ply of fabric. In addition, the relative ease of fabrication for each system was determined. Table VIII lists the data that was obtained during the reproducibility study. The quality of each laminate is usually indicated by its density or specific gravity. It had been determined earlier that a specific gravity on the order of 1.70 for the 100% aluminum phosphate matrix, 1.75 for the matrices with 25% and 35% additives, and 1.8 for the 50% additive system is indicate of a high laminate quality. All the laminates fabricated exceeded these minimum densities, indicating that good compaction and low porosity was obtained. The ease with which each of the systems was fabricated is indicated by a relative ranking of A, B, or C. This ranking is indicative of the time and degree of difficulty for the preparation of the matrix material and the impregnation of the reinforcement. The actual layup and laminating processes are identical for each system. Those systems which have low percentages of additive are the easiest to process. The most difficulty is incurred with the incorporation of the 50% additive for the spodumene and petalite systems. These two additives are not wet as readily as the silica additive and require a more lengthy and careful blending process. The reproducibility of each matrix system with regard to laminate quality is essentially identical.

e. Composite System Selection

Prior to conducting the process optimization, the number of materials was reduced to the five most promising. The criteria for the selection are listed below:

- Electrical Properties
- Weight Loss After Thermal Aging
- Dimensional Change After Thermal Aging
- Density Change After Thermal Aging
- Mechanical Properties
- Processibility
- Reproducibility

Table IX lists the seven composite materials which were evaluated and their ranking on a 1 to 7 basis for the different criteria. The lowest numerical rating indicates the superior material. The following is a summary of each criteria:

TABLE VIII

RESULTS OF LAMINATE REPRODUCIBILITY STUDY

Matrix System	Density, g/cc		Per Ply Thickness, inches		Fabricability*
	1st Set	2nd Set	1st Set	2nd Set	
100% $AlPO_4$	1.79	1.81	0.0108	0.0104	A
25% Silica	1.89	1.93	0.0107	0.0102	A
50% Silica	1.91	1.90	0.0115	0.0118	B
35% Spodumene	1.85	1.88	0.0119	0.0117	A
50% Spodumene	1.85	1.86	0.0133	0.0120	C
35% Petalite	1.87	1.87	0.0112	0.0109	A
50% Petalite	1.86	1.86	0.0125	0.0121	C

* A = Excellent
B = Good
C = Fair

Table IX

CERAMIC COMPOSITES - SUMMARY RATING
(Based on a Ranking of 1 to 7)

Matrix	Thermal Expansion	Electrical Properties	Weight Loss*	Dimensional Change*	Density Change*	Mechanical Properties*	Mechanical Properties**	Processability	Reproducibility
$AlPO_4$ + 25% SiO_2	6	–	5	****	6	3	2	2	2
$AlPO_4$ + 50% SiO_2	5	–	7	"	5	7	7	5	5
$AlPO_4$ 35% Petalite	3	1	4	"	2	5	3	4	4
$AlPO_4$ + 50% Petalite	2	***	1	"	3	4	6	7	7
$AlPO_4$ + 35% Spodumene	4	2	3	"	4	6	4	3	3
$AlPO_4$ + 50% Spodumene	1	7	2	"	1	2	5	6	6
$AlPO_4$	7	–	6	"	6	1	1	1	1

* After aging at 1600°F.

** After thermal cycling

*** Could not fabricate

**** No significant difference, ~1%

Electrical Properties - It was earlier anticipated that low dielectric constant and loss tangent properties would be the most desirable for this particular RAM application. However, analysis of RAM configurations conducted by the Air Force Avionics Laboratory indicate that high dielectric constant and loss tangent properties are more advantageous. There is also the possibility of RAM designs which use materials having different dielectric constants. Some of the composite materials such as the $AlPO_4$ and $AlPO_4$ with silica additives were grouped so closely in properties that a realistic ranking could not be made. Therefore, only the two best and the one worst composite material are indicated. The $AlPO_4$ + 50% spodumene was rated the poorest material due to the large change in dielectric constant between the last two elevated temperature points. However, there is some reason to question the accuracy of this curve since earlier dielectric constant measurements on the matrix alone did not show such a phenomena. The materials rated best from an electrical standpoint are those based on the $AlPO_4$/35% petalite and $AlPO_4$/35% spodumene matrices. Both the dielectric constant and loss tangent properties of these materials are very similar over the temperature range measured.

Thermal Expansion - The low thermal expansion materials are more compatible with the C-A ribbons and allow stability of the RAM performance over a temperature range.

Weight Loss After Thermal Aging - All materials were considered satisfactory from a weight loss standpoint.

Dimensional Change After Thermal Aging - No significant dimensional change incurred for any of the seven candidate systems during exposures up to 1600°F.

Density Change After Thermal Aging - The matrix systems modified with spodumene and petalite additives show the least density change.

Mechanical Properties - Flexural properties were determined on both thermally aged and thermally cycled composites. For the thermal cycling the unmodified or lower additive matrices tend to give higher elevated temperature strength than do the matrices with the high additive contents. While not as apparent for the thermal aging, this same trend seems to hold true.

Processibility and Reproducibility - Equivalent ratings were made for processibility and reproducibility with the higher ratings going to the matrices having the lower additive contents.

The five materials selected to be carried into the optimization phase are listed below:

- 100% $AlPO_4$
- $AlPO_4$ + 25% Silica
- $AlPO_4$ + 35% Spodumene
- $AlPO_4$ + 50% Spodumene
- $AlPO_4$ + 35% Petalite

4. PROCESS OPTIMIZATION STUDIES AND PANEL EVALUATION

The process optimization task dealt with establishing a reliable process for the reproducible fabrication of large, flat panels. Once a reliable optimized process had been established for each of the five remaining candidate material systems, 12" x 12" flat panels were to be fabricated for acoustical vibration testing and free space dielectric testing. Preliminary work was also directed toward the fabrication of sandwich core or spacer materials.

a. Process Optimization

The process optimization task was initially conducted using standard E-glass 181-style glass fabric. The starting point for the optimization study was the process developed earlier for smaller laminates. This process worked equally as well with the larger 12" x 12" panels as it did with the earlier smaller panels. Modifications to the process such as more rapid heat up rates, additional drying of the prepreg material, and the use of multiple vacuum vents did not change the quality of the cured laminate. This study demonstrated that there is considerable flexibility in the process parameters. A reproducibility study was conducted which verified the adequacy of the process to produce high quality cured composites on a repetitive basis. Based on this study, it was decided to maintain the previously established laminating and curing process for the fabrication of the large test panels.

b. Acoustical Vibration Testing

A 10" x 10" x ~0.150" panel was prepared from each of the five candidate matrix systems and 1581-style Astroquartz fabric. The panels were aged at 1600°F for 100 hours before later being submitted to Wyle Laboratories in Huntsville, Ala. for acoustical vibration testing. Properties for these as well as the dielectric panels are given in Table X.

The acoustical vibration tests consisted of exposing the ceramic panels to 1600°F combined with a parallel incidence noise impingement of 165 db and with a frequency sweep from 200 through 700 Hz at a rate of one octave/minute. The panels were positioned in the acoustical chamber as shown in Figure 33. Mounting consisted of clamping two of the test panels to a fixed steel fixture by a bolted steel "picture frame". Directly behind the panels is a bank of quartz lamp heaters used to heat the panels from the backside to a temperature of 1600°F. The test panel edges were covered with a layer of asbestos fabric as shown in Figure 34. The asbestos was used to insulate the panel from the steel mounting fixture and to even out the clamping pressure around the square steel mounting bracket. On the opposite side of the chamber a plexiglass window allows the panels to be viewed during the tests. All panels were observed during the tests to determine the mode and time of failure.

Four individual test runs were performed under the above conditions with the exception of one test which was performed at approximately 350°F.

Figure 33. Panel Mounting as Viewed Through Monitor Window

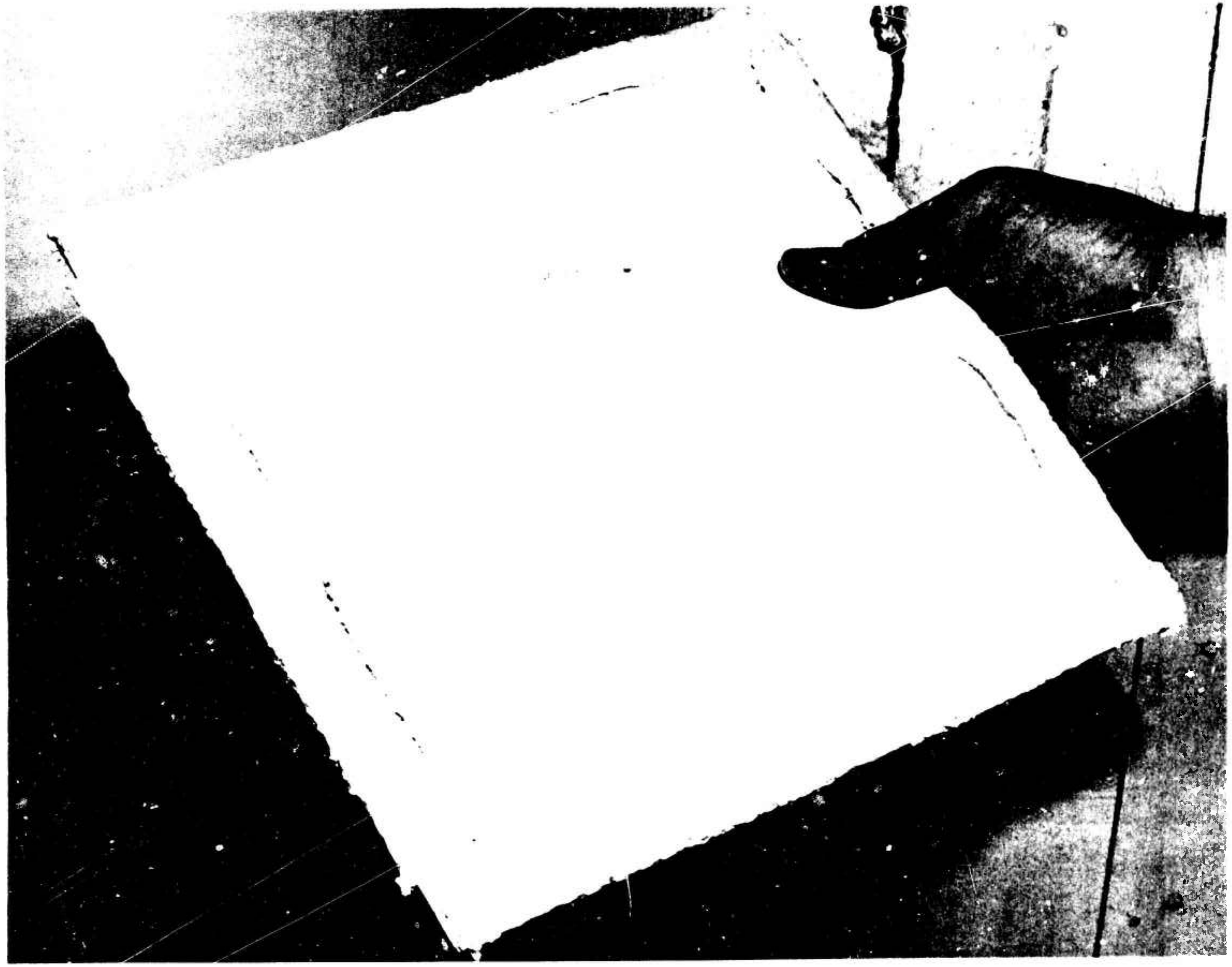

Figure 34. Panel with Asbestos Fabric Around Edges for Mounting

TABLE X

PROPERTIES FOR ACOUSTICAL VIBRATION AND DIELECTRIC TEST PANELS AFTER 100 HOURS @ 1600°F

Matrix Material	No. Plies Reinforcement*	Laminate Average Thickness (in.)	Reinforcement Content, % by Weight	Density, gm/cc
$AlPO_4$	11 30	0.141 0.407	57.0 55.0	1.61 1.57
$AlPO_4$/25% Silica	11 30	0.156 0.405	56.0 57.0	1.47 1.56
$AlPO_4$/35% Spodumene	11 30	0.154 0.395	51.5 55.0	1.63 1.64
$AlPO_4$/35% Petalite	11 30	0.165 0.405	49.0 52.0	1.60 1.68
$AlPO_4$/50% Spodumene	11 30	0.148 0.385	50.0 52.0	1.75 1.76

* 1581-Style Astroquartz Fabric

A discussion of each of the test runs follows:

Test No. 1 - The first test was performed on a panel containing 100% $AlPO_4$ (No. 66) and a panel containing $AlPO_4$ + 35% spodumene (No. 62). The panels were heated to 1600°F, at which time the acoustical noise was initiated. During the heat up, the panels were observed through the window. The 100% $AlPO_4$ panel developed a slight crack during heat up. Simultaneous with the noise input the crack propagated and opened up. Approximately 20 seconds later, at a frequency of approximately 250 Hz, a rectangular section of the panel came loose. The 35% spodumene panel cracked horizontally after approximately 20 seconds into the run. No further damage was incurred up to 700 Hz. Figure 35 is a photograph of the two panels at the conclusion of Test No. 1. The crack which extends horizontally in the middle of the panel is not visible. A better view of this crack is shown in Figure 39.

Test No. 2 - The second test involved $AlPO_4$ + 35% petalite (No. 60) and $AlPO_4$ + 50% spodumene (No. 65) panels. Under essentially the same conditions as test No. 1, both panels cracked at approximately 20 seconds into the run. Or again, at a frequency between 200 and 250 Hz. The upper panel, containing 35% petalite, cracked both horizontally and vertically. Figure 36 shows the panels still installed at the end of the test. A better view of the cracks are shown in Figure 39.

Test No. 3 - Test No. 3 consisted of a retest of the cracked 50% spodumene panel and the initial test of the 25% silica panel (No. 59). Again, the test conditions were essentially the same as those performed in the previous test. As in the former tests, at approximately 20 seconds into the run the 25% silica panel cracked vertically. On the 50% spodumene panel, a horizontal crack occurred during the low frequency portion of the run. These panels are shown in Figures 37 and 38.

Test No. 4 - Test No. 4 consisted of a rerun of the panels from the third test after they cooled to approximately 350°F. No further damage was incurred by either panel.

Following are pertinent points of the acoustical vibration testing:

- With the exception of the 100% $AlPO_4$ panel, no failures were observed during the heat up from room temperature to 1600°F.
- All panels cracked approximately through the center within 20 seconds after the acoustical noise had begun. This corresponds to a frequency of approximately 200 to 250 Hz and the frequency where the highest panel deflections occur.
- In all cases, after the cracking was seen to occur the test was continued through 700 Hz. No further damage occurred after the initial cracking, except for the 100% $AlPO_4$ panel from which a section of the panel broke out.

Figure 35. Panels Based on 100% $AlPO_4$ and $AlPO_4$/35% Spodumene After High Temperature Acoustical Vibration Tests

Figure [illegible]. Panels Based on AlPO$_4$/[illegible] Vermiculite and AlPO$_4$/[illegible] Specimens After High Temperature Acoustical Vibration Tests

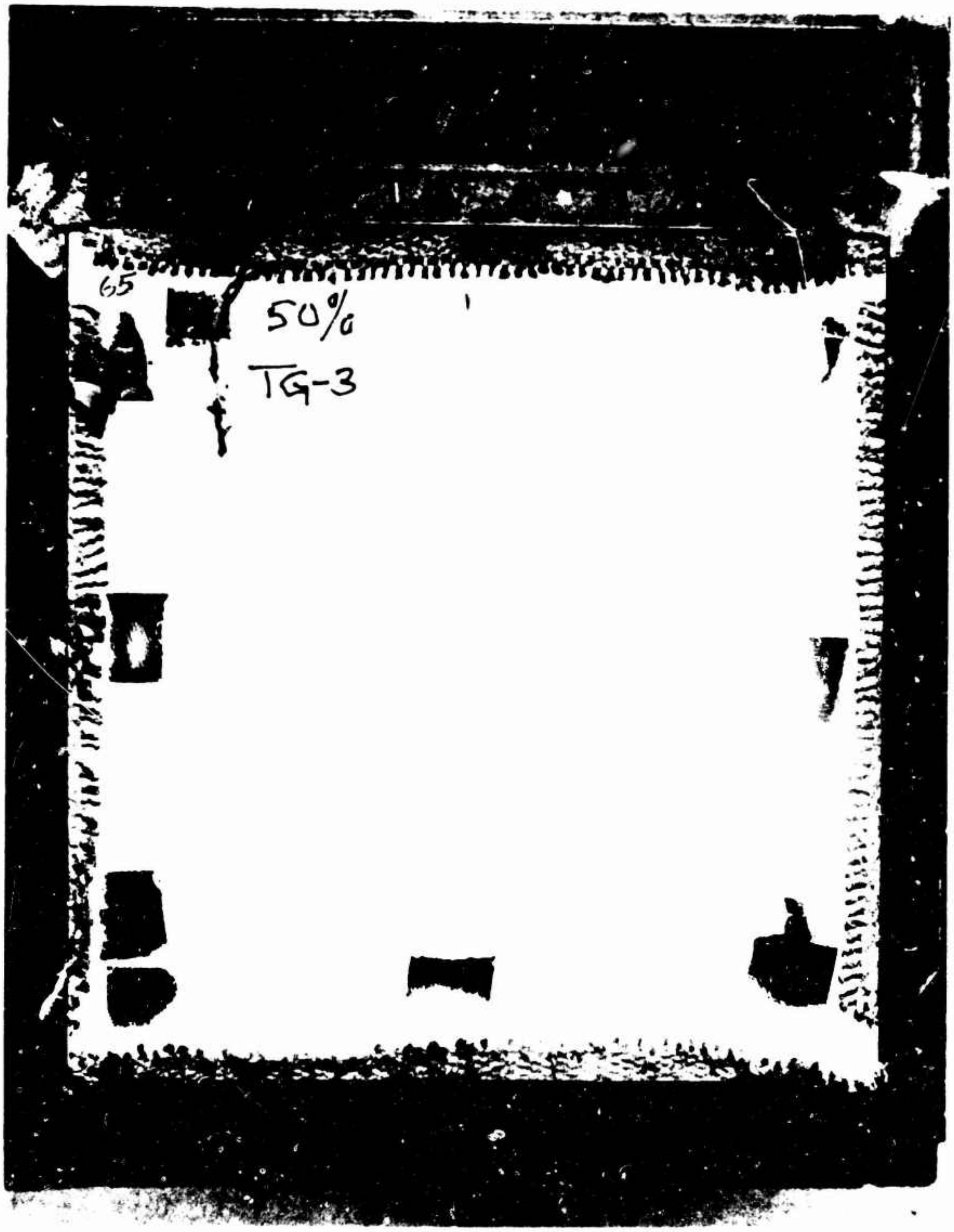

Figure 37. $AlPO_4$/50% Spodumene Panel After Second High Temperature Acoustical Vibration Test

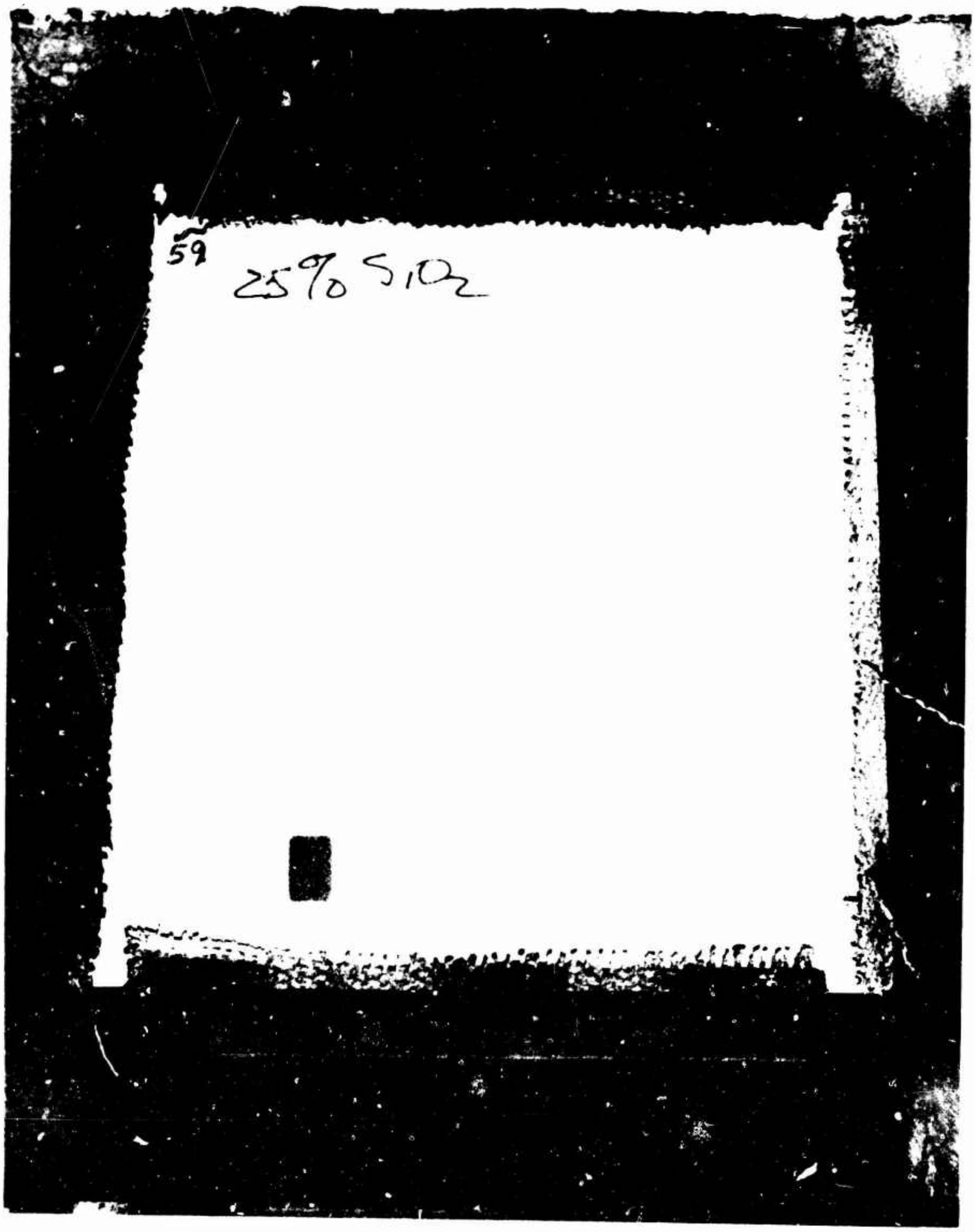

Figure 38. $AlPO_4$/25% Silica Panel After High Temperature Acoustical Vibration Test

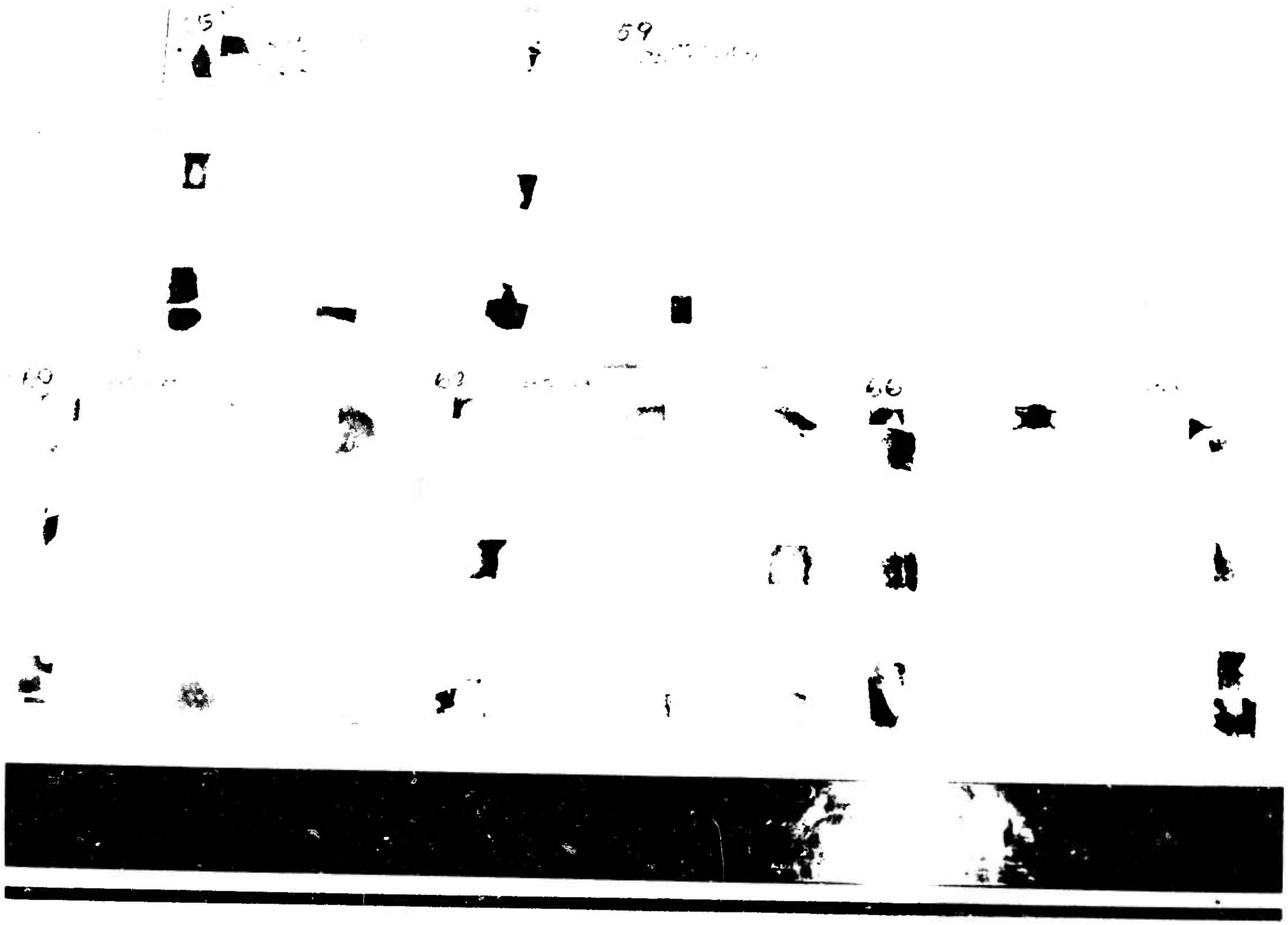

Figure 39. Ceramic Composite Test Panels After High Temperature Acoustical Vibration Testing

- The initial cracks were formed parallel to the weaker warp direction of the silica fabric reinforcement.

- Considering the mode of failure and the fact that on repeated runs there was little or no further damage, it appears that the cracking is probably due in part to the method of mounting the specimen. During the heat up, the steel frame expands much greater than the test panel, applying a stress to the panel. The stress is not sufficient to crack the panel (except in the case of the 100% $AlPO_4$ panel), but in combination with the acoustical loading results in stresses sufficient to crack the panel. After the panel cracks, the stress is alleviated and no further damage occurs. Two of the panels were exposed to additional acoustical tests with little or no further damage. It is obvious from these tests that the design for the actual RAM panel configuration must give strong consideration to a method of attachment which alleviates the stress problem due to thermal expansion mismatches.

- The panels probably would not have incurred cracking had the unsupported span of material been reduced. In the actual RAM configuration this type of support will be provided.

- No catastrophic failure was experienced as would have been the case with a brittle monolithic ceramic material. With proper design of the structure and attachment the material can be expected to perform satisfactorily in a high temperature/acoustical vibration environment.

c. Free Space Dielectric Testing

Test panels for free space dielectric constant and loss tangent measurements were fabricated and delivered to Arthur D. Little Laboratories in Cambridge, Mass. Testing will be performed at three frequencies between 2 and 18 GHz.

d. Development of a Core Spacer

Initial work was conducted toward development of a lightweight spacer core from the ceramic composite materials. This core material will be used in the sandwich RAM.

The design chosen for these initial studies was an egg crate core configuration having square cells spaced on 0.300" centers.

Laminates were prepared in a thickness of 0.050" and cut into 1/2" wide strips. Slots halfway through the 1/2" width were made at 0.300" increments and the strips intersected at 90± separations to form a square cell spacer material (Figures 40 and 41).

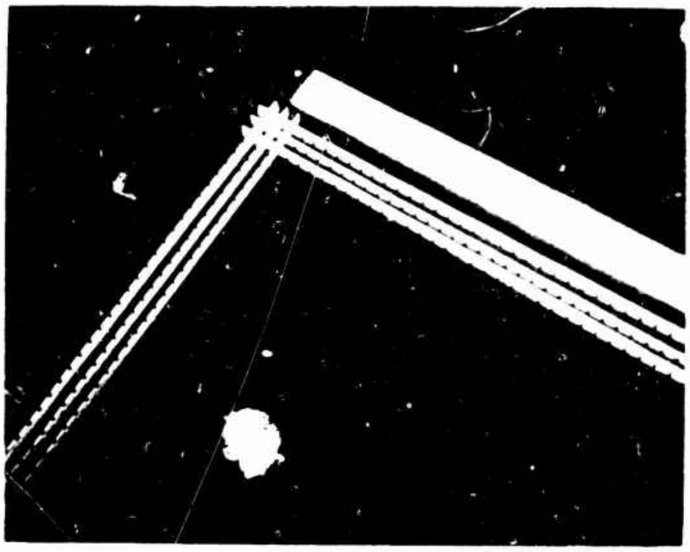

Figure 40. Sandwich Core Material Assemblies from Slotted Strips of Ceramic Composite

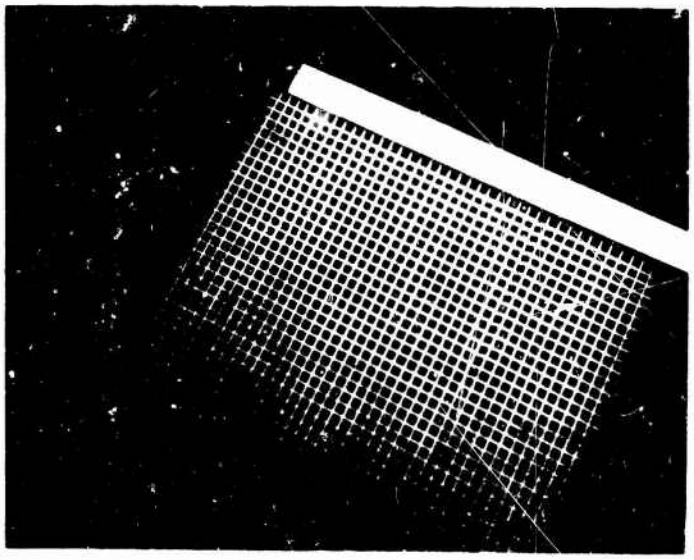

Figure 41. Assembled 'Egg Crate' Sandwich Core Material

SECTION IV

CONCLUSIONS

1. Ceramic matrix development efforts have eliminated the crystalline inversions of aluminum phosphate over the temperature range of interest (ambient to 1600°F). Lithium-aluminum-silicate additives were found to be the most effective method for achieving this of the approaches investigated. The ceramic matrices developed have sufficiently low thermal expansion (0.5 to 0%) over the temperature range of interest to be compatible with silica fiber reinforcement and the silica C-A ribbons.

2. Thermal cycling and/or aging of the silica fiber reinforced ceramic composite results in a decrease in room temperature properties but has a much smaller effect at elevated temperature where the RAM is intended to operate.

3. The dielectric constant for all of the materials developed is very stable over the room temperature to 1600°F range. Loss tangent for the spodumene and petalite modified matrix materials increases considerably at elevated temperatures. The other composite materials exhibit low elevated temperature loss tangent properties.

4. The fabrication process for the ceramic composite materials is relatively simple and highly reproducible for all five of the candidate materials.

5. To achieve optimum temperature resistance and strength in the composite it is necessary to remove the silane surface treatment from the silica fabric. A water boiling method was found to be the most effective. A silicone resin size applied to the cleaned silica fabric reinforcement provides protection from the uncured acidic matrix and results in higher mechanical properties in the composite both before and after thermal aging.

6. Acoustical vibration testing of fiber reinforced ceramic composites at 1600°F resulted in cracking of the panels but no catastrophic, brittle failure. These tests indicated that with proper design of the RAM sandwich panel/metal substructure and with adequate mounting techniques the material will perform satisfactorily in a high thermal/acoustical vibration environment.

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