A STUDY OF FIBER MATERIALS FOR USE
IN TEMPERATURE RESISTANT FIBER
REINFORCED COMPOSITES

Report of Research For
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ABSTRACT

This study has been directed at characterizing the micro-properties of candidate ceramics and glasses for use in making fibers used in fiber reinforced material composites. Particular emphasis has been given into developing techniques to guide the optimization of fiber properties. The Scanning Electron Microscope (SEM) and X-ray Diffractometer (XRD) have been used to help collate the method of synthesis, crystal structure and surface morphology with physical performance parameters. As a result, progress has been made in characterizing such materials. This increased understanding makes the previous research worthy of further study.

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INTRODUCTION

This research work is funded in its entirety by NASA-Ames Research Center. The purpose is to examine and characterize new candidate fiber materials.

A candidate fiber material should withstand high temperature as well as exhibit significant strength. Ceramic and modified glass materials appear to offer this capability of forming a superior inorganic fiber. The data base for those materials are presently insufficient to provide adequate background for evaluating candidate materials and developing their optimum properties.

Instruments, such as the Scanning Electron Microscope (SEM) and X-ray Diffractometer (XRD), are used to characterize these new candidate fiber materials. As a result, small dimensional changes such as structural (phase), bonding, and surface characteristics can be monitored under various conditions. These instruments also provide data on the crystal interactions, crystal conformation and crystal alignment of candidate fiber materials.

This program is very innovative: in the selection of compositions and structures suitable for fiber materials; in the methods used for fiber synthesis; and in the method of analysis. This report, submitted to the NASA-Ames Research Center, is constructed from the year-long research on candidate fiber materials.

Research and instruction is being done at the facilities at NASA-Ames Research Center.

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REVIEW OF COMPLETED WORK DURING PROGRAM PERIOD

Completed work done during the contract year can be separated into two major areas.

The first major area involves instructing students from San Jose State University, Foothill and DeAnza Junior Colleges on the principles of material analysis, on the use of various types of instruments, on various ideas or directions to pursue in order to understand the characteristics of candidate fiber materials, and to help solve any problems which may develop in the course of their research.

The second major area involves research on candidate fiber materials. The scanning electron microscope and the x-ray diffractometer are used for the purpose of characterizing such candidate fiber materials. This research can be divided into three primary subjects.

FIBROUS INSULATION MATERIALS

Early in the 1970's a new low density rigidized insulation material was selected to thermally protect the aluminum structure of Space Shuttle Orbiters from the high temperatures normally encountered during atmospheric reentry. The material developed for the Shuttle, a fibrous high silica insulation, was called Reusable Surface Insulation (RSI). Research, into RSI and other types of low density fibrous insulation materials, was initiated to increase the basic understanding of these materials and to improve their properties. The knowledge obtained from this research was used to develop other alternate insulation materials.

The development of a new family of insulation materials, with a wide range of compositions and properties, was one of the results of this research. That family of materials was called Fibrous Refractory Composite Insulation (FRCI). FRCI is a composite of two ceramic fibers with no additional additives to bond the fibers together. One fiber is an 11μ diameter aluminoborosilicate fiber (Nextel 312 or AB312). It is a drawn fiber cut into 0.31 cm (1/8") lengths and has a nominal and empirical composition of 62% Al_2O_3 - 14% B_2O_3 - 24% SiO_2 and $3Al_2O_3$ - B_2O_3 - $2SiO_2$, respectively. The other fiber is the high-silica blown fiber (microquartz) used in producing silica RSI. It has a nominal composition of 99.7% SiO_2. In addition, silica has a diameter range of 1-3μ and variable fiber lengths. The properties of FRCI are determined by its fiber composition and density.* One composition (FRCI 20-12) was eventually adopted for use on future Space Shuttle Orbiters. The advantage of using FRCI, in general, lies in the fact that it possesses a higher strength, over silica RSI, at an equivalent density. It also provides a higher expansion coefficient substrate material that allows the application of a wide range of coatings without introducing a [illegible] tensile stress, and it has the potential of a higher [illegible] capability. These advantages can be maximized by knowing

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[illegible] 40-20 is a Fibrous Refractory Composite Insulation [illegible] Nextel 312 (AB312) and 60% silica. This silica bonds only [illegible]. It has a density of 20lb/ft^3. Many compositions and [illegible] exist.

the behavior of the two individual fibers in FRCI and their interactions. As a result properties such as strength, temperature capability and reentry life of these resultant materials can be improved. Research is currently being done to further understand this complex behavior of FRCI and to improve the existing properties of these insulation tiles.

Current research also involves monitoring processing modifications of FRCI tiles for possible use on advanced space vehicle. Morphological changes, as a function of time at constant temperature, are being studied with the SEM. This gives a pictorial representation of the various tiles as they change with time. Valuable information can be obtained, from this study, on how to improve FRCI tiles. Analysis with the XRD for structural (phase) changes gives additional information for the improvement of FRCI tiles.

The knowledge obtained from research on the RSI and FRCI systems has been applied to a new fibrous systems. Research is presently being done to develop a process by which to combine other higher temperature fibers together. The tieing together of these fibers will possibly produce a reusable insulation tile with improved properties and give a better understanding of fibrous systems.

COATINGS FOR FIBROUS INSULATION MATERIALS

RSI and FRCI tiles are low density rigidized ceramic fiber materials that require a high emmittance and water-impervious coating in order to properly function as a heat shield material on the Space Shuttle Orbiter. One coating material that meets these requirements while maintaining critical dimensional tolerances is the Reaction Cured Glass (RCG) coating. The RCG coating has been used on the surfaces of RSI tiles on past flights of the Space Shuttle Columbia. In addition to meeting these requirements, the RCG coating is beneficial and compatible with the tile substrate (RSI or FRCI). It is compatible because it has a low thermal expansion coefficient. A reduced residual tensile stress is thereby achieved at the interface between the ultra low thermal expansion coefficient silica RSI substrate and the RCG coating which prolongs the resultant heat shield material life time. It is beneficial because the RCG coating exhibits a chemical and morphological stability to temperatures of 1260°C and above for extended periods of time at atmospheric or reduced pressure.

It is known that the RCG coating works but the details of its complex structure with two immiscible undefined glasses present is not known. In order to understand the RCG coating further and then improve it, the magnitude of the phase separation between the two immiscible glasses within the coating and the composition of the glass phases must be known. However, this information is very difficult to obtain and is the main reason why the behavior of the RCG coating is not totally understood. Research is being done on the RCG coating to better understand its behavior and to increase its temperature capability.

The knowledge obtained from research on the RCG coating has been applied to similar coating systems. Current research is being done to improve the RCG coating by substituting one component in the composition for another. For example, Germania (GeO_2) is being used in place of boron oxide (B_2O_3) to increase viscosity. This will develop a new coating with an increased temperature capability. However, this substitution must be studied further to determine if any adverse effects (i.e., structural instability) outweigh the enhanced temperature capability. This study may then lead to the development of other coatings using related oxides or components. As a result coatings with improved properties may be attained as well as a better understanding of coating systems for fibrous insulation materials.

Current research on the RCG coating is being done by exposing it into different conditions in an Arc-Jet environment. An Arc-jet environment simulates the convectively heated environment which the Space Shuttle Orbiter must survive during reentry from space. This unique research is being done at NASA-Ames Research Center at Moffett Field. An Arc-jet environment consists of immersing a coating on a tile into an accelerated stream of highly ionized plasma (hot gases) under vacuum. [illegible] stream increases the temperature of the coating, to a [illegible] level, as it flows over it. The coating is then left at [illegible] for a specific length of time. The structural (phase) [illegible] characteristics of the coating, and the bonding of [illegible] tile substrate, can be monitored with the SEM and XRD as [illegible] this type of heat treatment.

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MISCELLANEOUS RESEARCH MATERIALS

In addition to doing research on the FRCI tiles and the RCG coating, research is also done on other types of materials. For example, a study is being done on selectively-heated fibers to determine their physical state and strength after different phases of treatment. Some test specimens include carbon fibers with Nickel (Ni) coatings, Nextel 312 or AB312 fibers: non-irradiated and irradiated with Nitrogen (N) atoms, polyimide foam, quartz fibers and SiC fibers. These specimens are tested for strength on a Instron testing machine. Structural (phase) changes, bonding and surface characteristics are analyzed with the SEM and XRD.

Research is also done on laser-irradiated materials to determine the state of their morphology after treatment. Test specimens include glassy carbon, silica wafers, and silicon. Analysis is done with the SEM to get a pictorial representation of the unique bonding and surface characteristics.

Consultation has also been done on the analysis of aluminum oxide (Al_2O_3) layers of the wind tunnel interior. The purpose was to determine the number of layers present in the sample. Consultation was also done on polychrome coatings over metal surfaces after chemical attack. The purpose was to determine if the chemical attack penetrated through the polychrome and into the metal surface. Although the majority of consulting work is done with the SEM, many materials are also analyzed on the XRD.

PHOTO DESCRIPTIONS

The following photos are some examples of the research materials analyzed during the contract year. In all cases valuable information was obtained and applied to the understanding of these materials.

Photos 1 through 5 show the insulation material FRCI 40-20 with the two fibers used in the processing of this tile. Silica (SiO_2) is the finer fiber while Nextel 312 or AB312 ($3\ Al_2O_3 - B_2O_3 - 2SiO_2$) is the larger fiber. The material has been heat treated where the bonding of the silica fibers to the Nextel 312 or AB312 fibers give strength to the tile.

Photos 6 through 10 show the RCG coating used on RSI and FRCI tiles. Photos 6 through 9 show the changes in the RCG coating after reentry from space. Photo 10 shows the original RCG coating unaffected (no heat treatment has been administered). Photos 11 through 13 show Nextel 312 fibers with rayon. An organic binder and lubricant are also present in this advanced insulation material. These fibers have been heat treated and their specific purpose is to replace silica. Hopefully, this will lead to a higher temperature capability for many future insulations.

Photo 14 is glassy carbon irradiated by a laser. The original surface was smooth but irradiation with the laser has modified it.

Photo #1: FRCI 40-20, Coated Au-C/Pd, Tilt 0°, 30x. Note: finer silica fibers (1-3μ DIA, variable length) and larger Nextel 312 or AB312 fibers (11μ DIA, 0.31cm (1/8" length).

Photo #2: FRCI 40-20, coated Au-C/Pd, Tilt 0°, 50x. Same areas as photo #1.

Photo #3: FRCI 40-20, coated Au-C/Pd, Tilt 5°, 1000x. Area within rectangular box of photo #2. Note: silica fibers bonding to AB312 fiber.

Photo #4: FRCI 40-20, coated Au-C/Pd, Tilt 5°, 3000x. Higher magnification of photo #3. Silica fiber on top and on right side of AB312 fiber.

Photo #5: FRCI 40-20, coated Au-C/Pd, Tilt 5°, 5000x. Higher magnification of photo #4. Silica fiber on top and on right side of AB312 fiber.

Photo #6: RCG Coating ST #1, coated Au, Tilt 0°, 50x.

Photo #7: RCG Coating ST #1, coated Au, Tilt 0°, 500x. Higher magnification of photo #6.

Photo #8: RCG Coating ST #4, Coated Au, Tilt 0°, 50x.

Photo #9: RCG Coating ST #4, Coated Au, Tilt 0°, 500x. Higher magnification of photo #8.

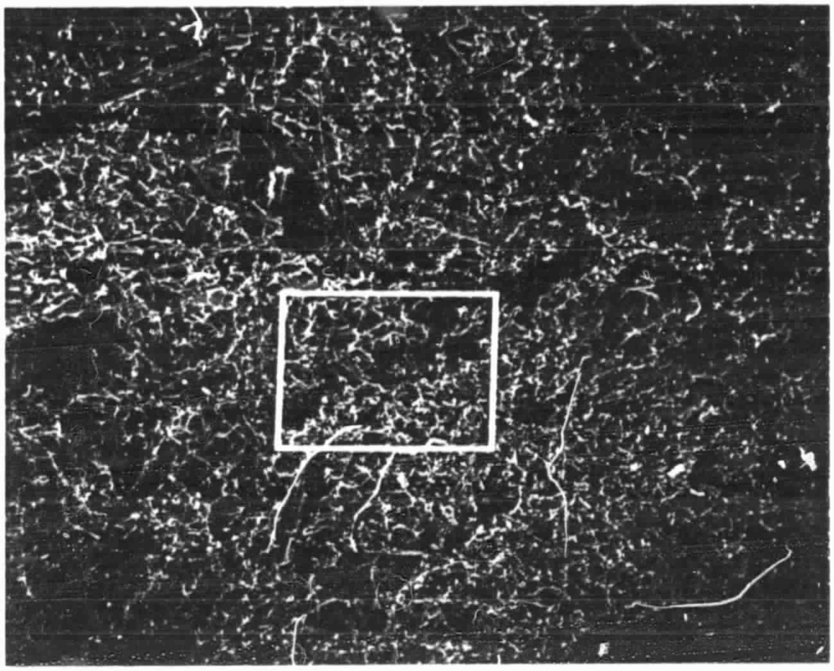
Photo #10: RCG Coating, Coated Au, Tilt 0°, 500x.

Photo #11: MST-HD Sample #1. Heat treated for 4 hrs @ 500°F. Coated Au, Tilt 0°, 30x. (Average Fiber Diameter = 0.032", variable length).

Photo #12: MST-HD Sample #1, Coated Au, Tilt 0°, 300x. Higher magnification of photo #11.

Photo #13: MST-HD Sample #1, Coated An, Tilt 0°, 1000x. Higher magnification of photo #11.

Photo #14: Laser Irradiated Glassy Carbon, Uncoated, Tilt 0°, 30x. Writing lower right hand corner, from left to right: 0020 - photo number, 25k - accelerating voltage in SEM, 10 x 5 NM (10 x 10^5 NM) - which is the length of above horizontal white bar.



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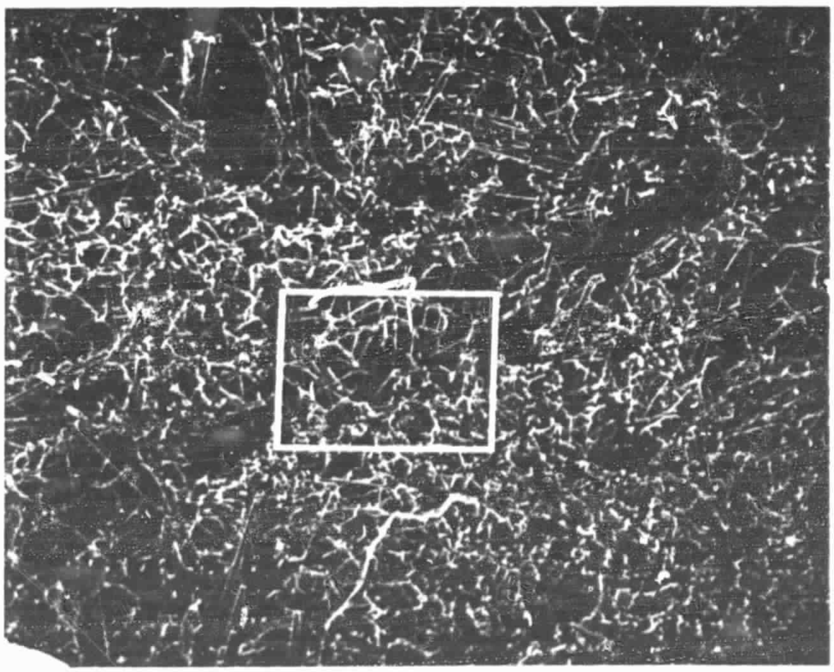

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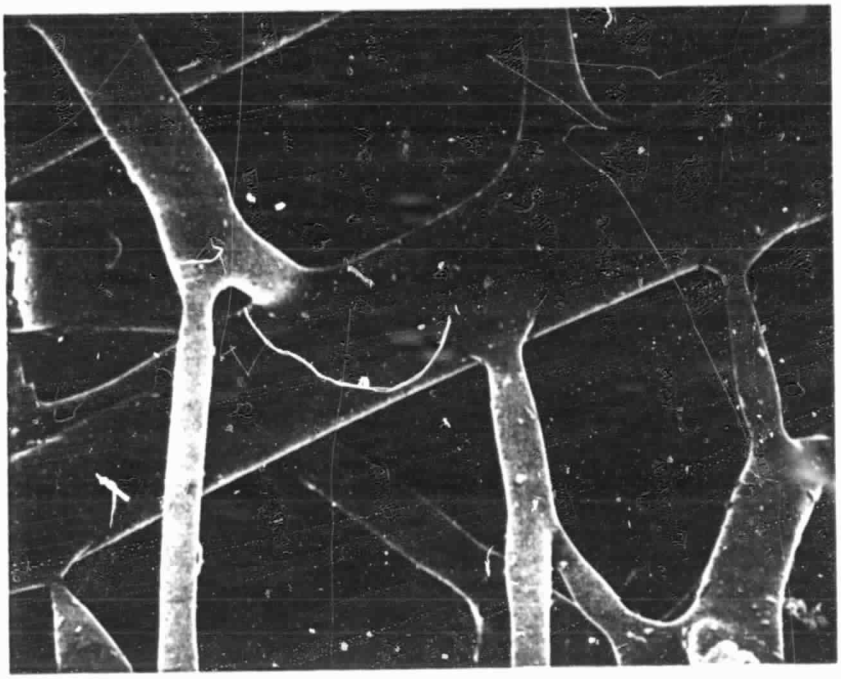

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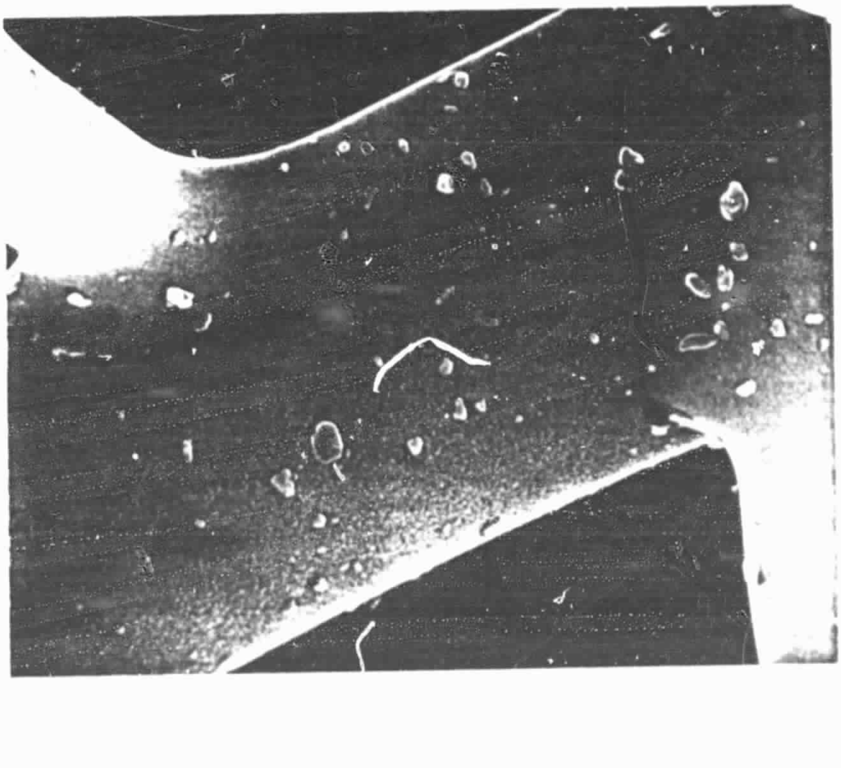

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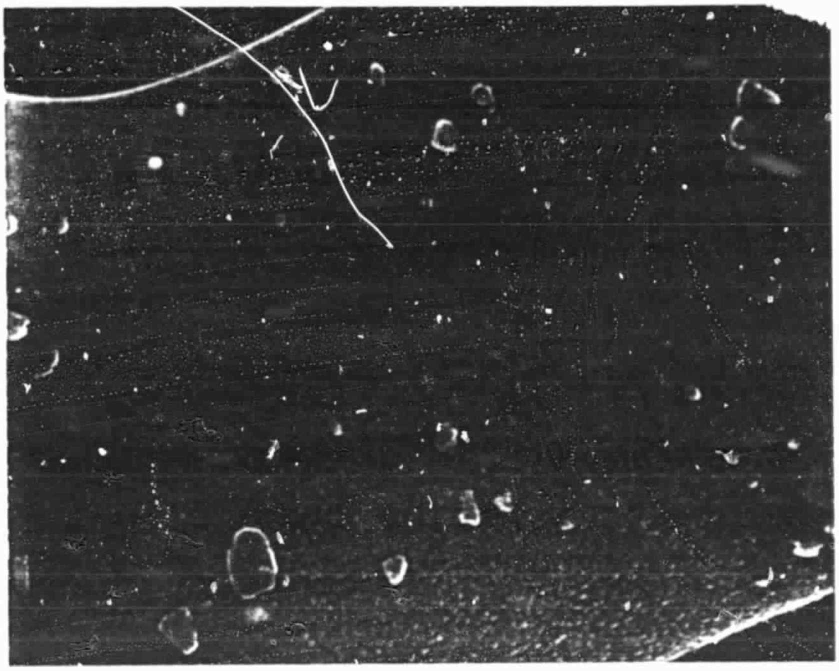

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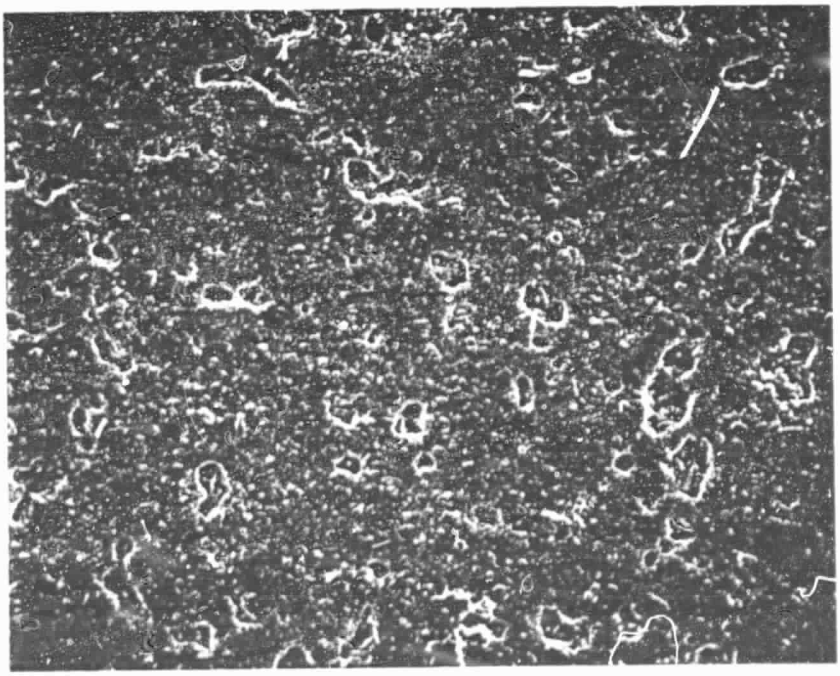

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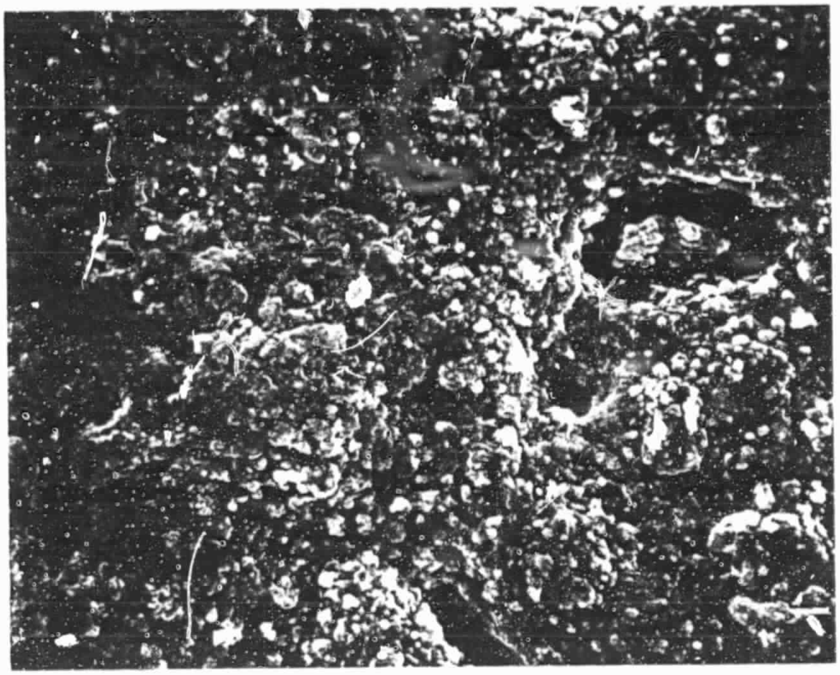

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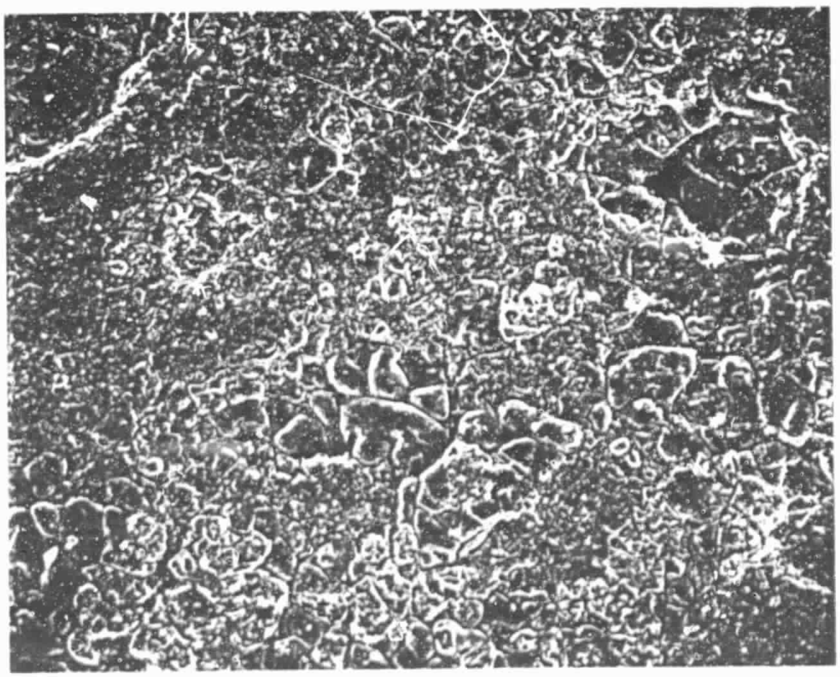

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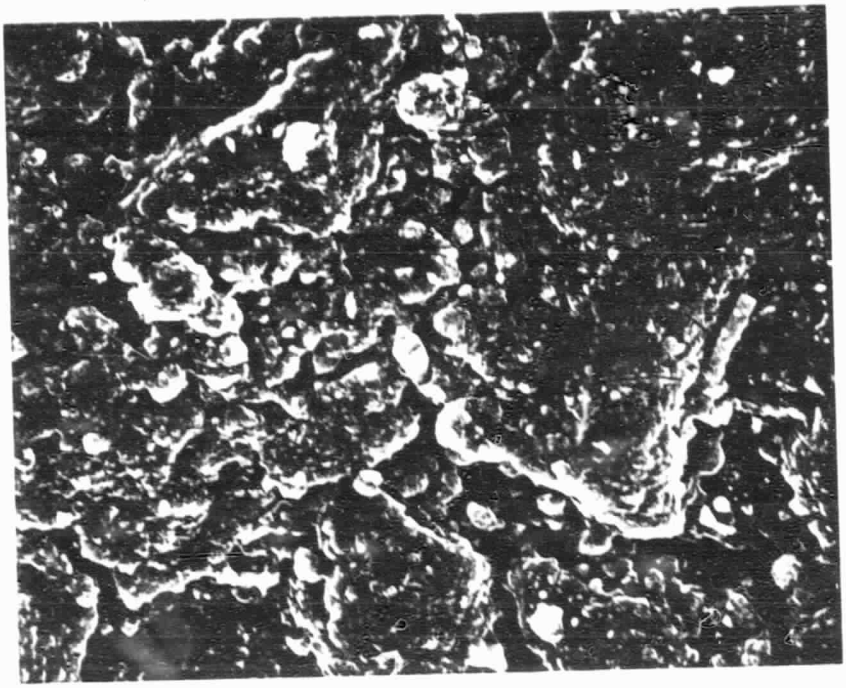

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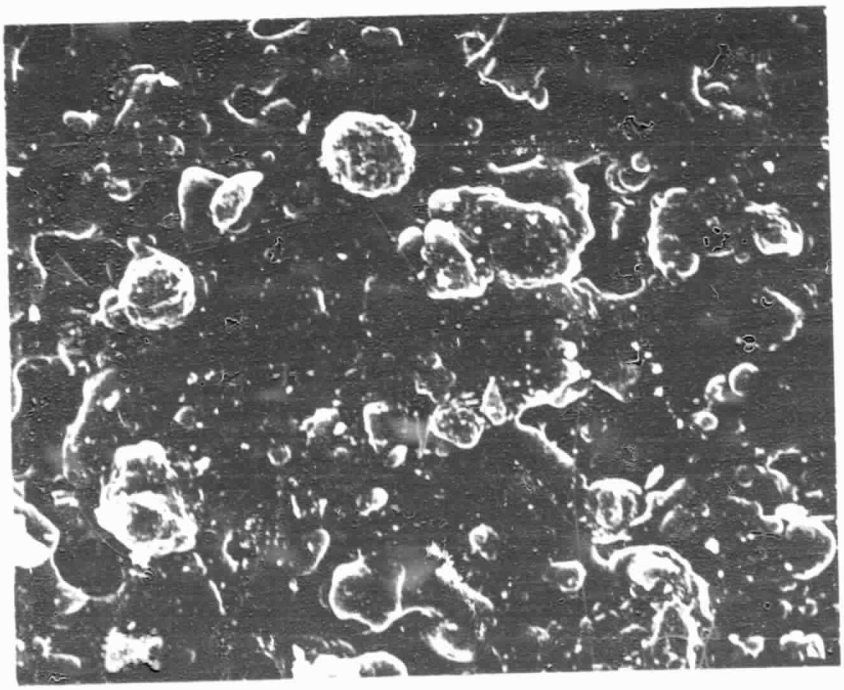

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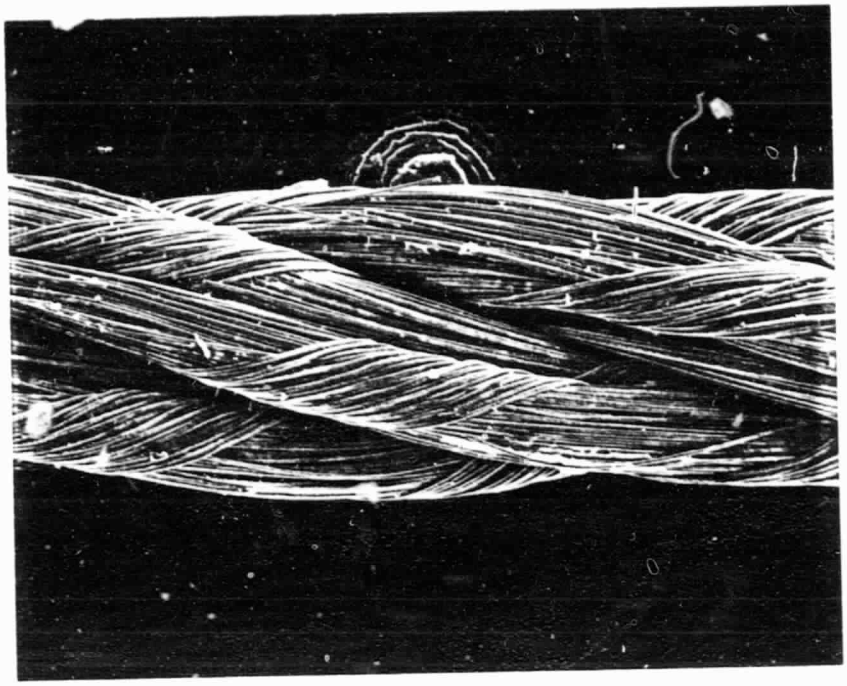

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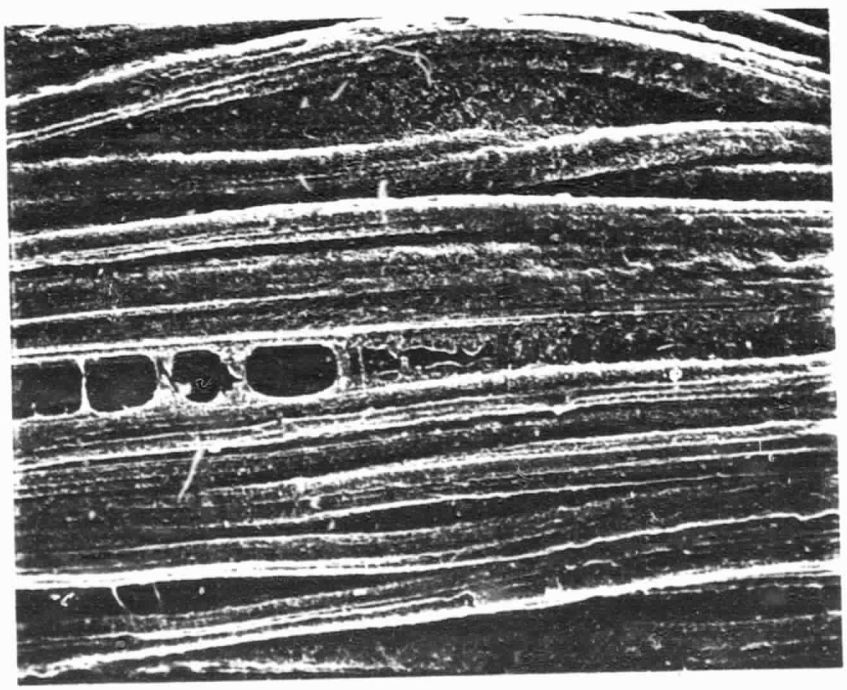

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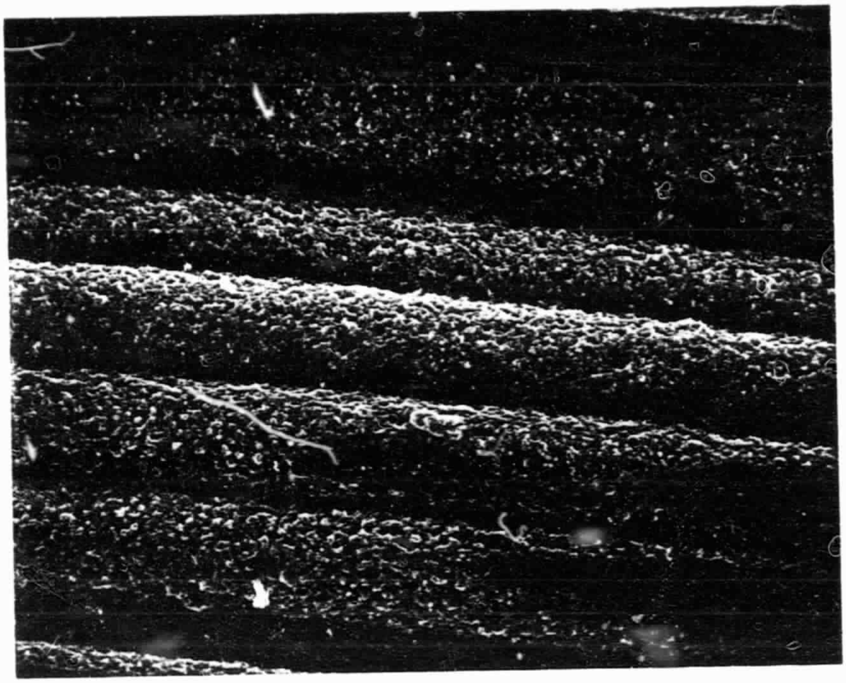

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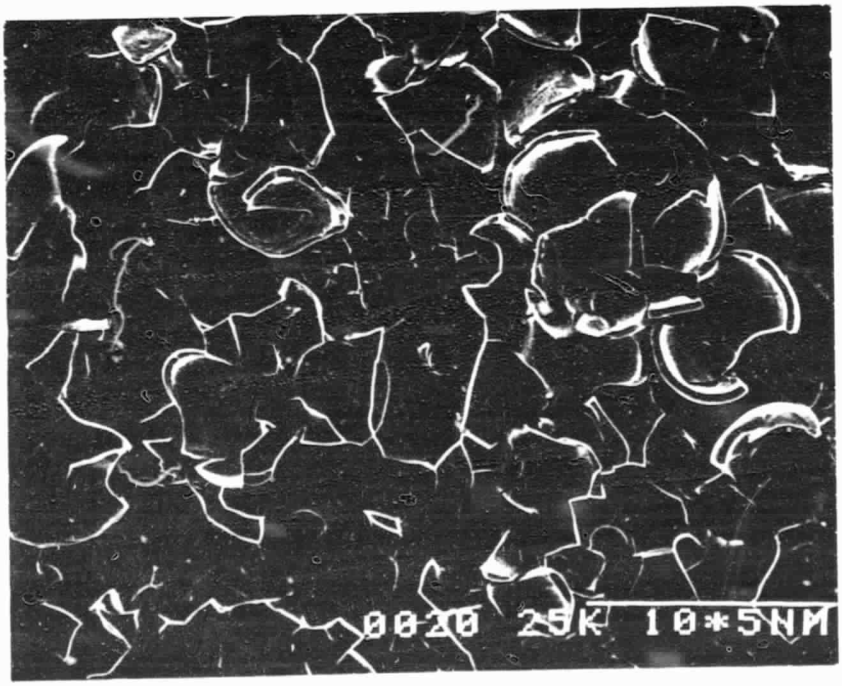

PHOTO #14

PROCEDURE FOR SEM OPERATION

The procedure taken in order to observe a sample under the SEM is as follows:

(1) Sample is machined or cut to an appropriate size.

(2) Sample is cleaned. This can be done with an air gun and vacuum or can be done using ethanol in an ultrasonic cleaner. The type of material will determine which process is used. This step is very important as it is desired to only remove collected material on the surface of the sample and not change any of the samples original features.

(3) Sample is mounted to SEM stub using silver paste and placed in sample holder.

(4) Sample is then coated with a metallic substance if it is non conductive. At NASA-Ames Research Center, the glass shop (N-212) will coat samples with a gold-palladium/carbon (Au-Pd/C) coating. Building N-230, Materials Science Branch, also has a Gold (Au) Sputter Coater which can be used. This step is important since an improper coating will create problems. An undercoated non-conductive sample will allow the phenomenom of charging to occur. Charging is a buildup of excess electrons possessing a current on the surface of the sample. When the current on the surface equals the current from the electron beam then an illuminating effect occurs known as charging. At this stage little or nothing can be seen on the CRT screen in the SEM. The sample will have to be recoated. An overcoated sample may hide some of the structural features and give a bad representation of the sample.

(5) Once the sample is properly coated the SEM can then be used to observe the morphology.

PROCEDURE FOR XRD OPERATION

The procedure taken in order to analyze a sample with the XRD is as follows:

(1) Sample is cut to appropriate size, then crushed to powder or machined to give planar surface.

(2) Crushed sample is packed into holder until a planar surface is obtained. Sample with planar surface is place into XRD "as is".

(3) Planar surface is aligned with diffractometer axis on sample holder in XRD.

(4) Sample is then analyzed with Copper (Cu) k_{α} radiation (x-rays).

SUMMARY

Research and development on various candidate fiber materials is a continuing process. All data from previous research are being evaluated and used to further understand the behavior and characteristics of these candidate materials. Successful research has been done on obtaining a better understanding of Fibrous Insulation Materials, Coatings for Fibrous Insulation Materials and other miscellaneous research materials. The progress in these areas is substantial but much research still remains to gain a total understanding of their behavior. This increase in knowledge makes the previous research worthy of further study.