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HIGH PURITY SILICA REFLECTIVE HEAT SHIELD DEVELOPMENT
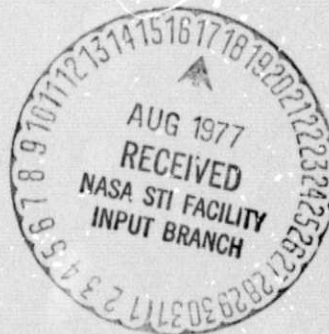
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16. Abstract

A hyperpure vitreous silica material is being developed for use as a reflective and ablative heat shield for planetary entry. Various purity grades and forms of raw materials were evaluated along with various processing methods. All are critically important to the success of this concept. Slip casting of high purity grain was selected as the best processing method, resulting in a highly reflective material in the wavelength bands of interest (the visible and ultraviolet regions).

The selected material was characterized with respect to optical, mechanical and physical properties using a limited number of specimens. The process has been scaled up to produce a one-half scale heat shield (18 in. dia.) (45.72 cm) for a Jupiter entry vehicle.

This work is now being extended to improve the structural safety factor of the heat shield by making the hyperpure silica material tougher through the addition of silica fibers.

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ABSTRACT

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The selected material was characterized with respect to optical, mechanical and physical properties using a limited number of specimens. The process has been scaled up to produce a one-half scale heat shield (18 in. dia.) (45.72 cm) for a Jupiter entry vehicle.

This work is now being extended to improve the structural safety factor of the heat shield by making the hyperpure silica material tougher through the addition of silica fibers.

INTRODUCTION

Probes entering the atmospheres of the outer planets such as Jupiter will require heat shielding capable of withstanding convective and radiative heating environments much more severe than current experience. The radiative heating arises from the bow shock wave accompanying the probe during entry. The high entry velocity of probes into the atmospheres of the massive outer planets leads to extremely high temperatures of the gases in the bow shock wave. The heating mode shifts from entirely convective to predominantly radiative as the entry velocity increases. These extremely high radiative heat loads lead to high heat shield mass fractions. As much as 30 to 50 percent of the probe weight is the heat shield for conventional ablative heat shield materials such as carbon-phenolic.

The predominance of radiative heating during entry suggests a different approach to heat shield design. A heat shield that reflects the radiation to prevent it from being absorbed would result in an appreciably lighter heat shield.

A program to develop a reflective heat shield as an alternate to the carbon-phenolic heat shield was initiated at Ames Research Center in 1971[1]. The current choice of material for the reflective heat shield is slip cast fused silica. The background and review of the multitude of requirements leading to this choice is too long to be included in the introduction and is included in a separate section. Suffice it to say at this point that the ceramic structure must be free of impurities to avoid absorption of thermal radiation, it must be thermal shock resistant, and it should accommodate strain sufficient to be compatible with light-weight supporting substructure during aerodynamic loading. Specifically, the scope of the current development effort described in this paper deals with the approach to materials development, evaluation of test specimens, and a description of the current effort to develop a tougher material, i.e., a material with a higher strain at failure.

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BACKGROUND

Radiation-dominated heat shield environments can be anticipated for entry
into the atmospheres of some of the outer planets. Even for a shallow entry
angle, preliminary calculations of the heat shield environment for Jupiter entry
indicate peak radiative heating rates on the order of 15 kW/sq cm. To contrast
this level of heating with previous experience, it should be pointed out that
the combined radiative and convective heating for the Apollo spacecraft upon
lunar return attains levels of 0.2 to 0.3 kW/sq cm. Typical heating rates for
entry into several planetary atmospheres are shown in Figure 1, and compared with
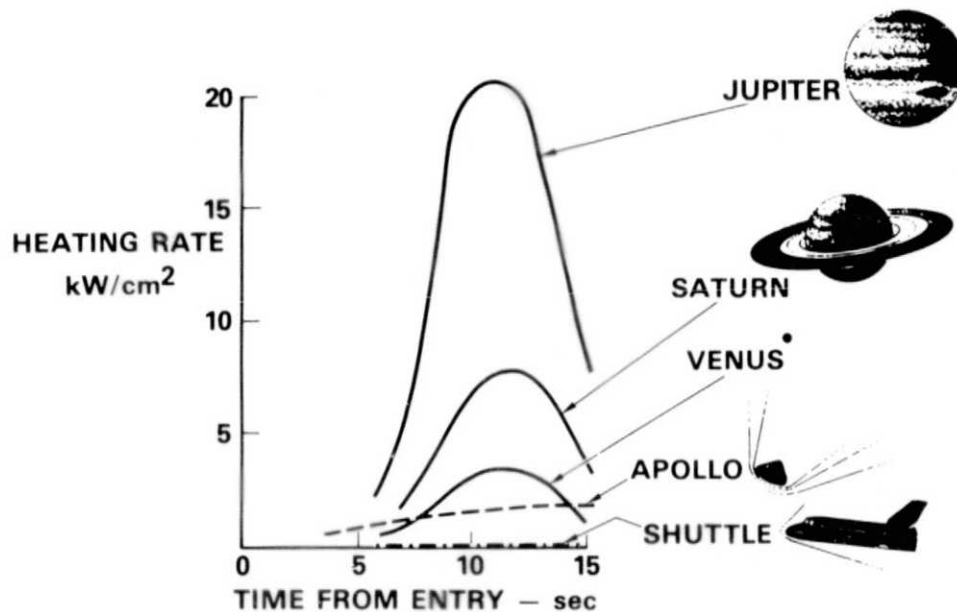earth entry heating rates.

FIGURE 1. ATMOSPHERIC ENTRY HEATING

The heating for the Jupiter entry presents a new heating regime where
radiative heating is significant, and where a different type of heat shield design
than that employed for the Apollo heat shield would be advantageous. The Apollo
heat shield is an efficient lightweight insulator that forms a carbonaceous char
when exposed to the hot gases during reentry. The radiation of energy from this
char, termed reradiation, is the principal means of energy dissipation for the
relatively efficient Apollo heat shield. An upper limit for the amount of radia-
tion from a carbonaceous char is about 1.8 kW/sq cm. (This amount estimated by
regarding the material as a black body and calculating the radiation for the

temperature of 4200°K, the temperature of carbon near its triple point.) The imposed heating for the Apollo is well below the radiation limit, whereas that for a Jupiter probe is well above this limit as shown in Figure 2. Consequently, reradiation from a carbonaceous heat shield for Jupiter entry is not necessarily the most efficient means of accommodating the energy imposed on the heat shield. Since the radiation limit for carbon is well below the level of the imposed heating during planetary entry, other mechanisms of energy accommodation must be considered. For environments like the Jupiter entry, Allen[2] indicated that the radiative heating should dictate the philosophy of heat shield design. He suggested a heat shield that would act like a mirror and reflect the gas cap radiation away from the space vehicle. Specifically, the scheme consisted of introducing small flakes of highly reflective metallic material into a base material of high transmissivity.
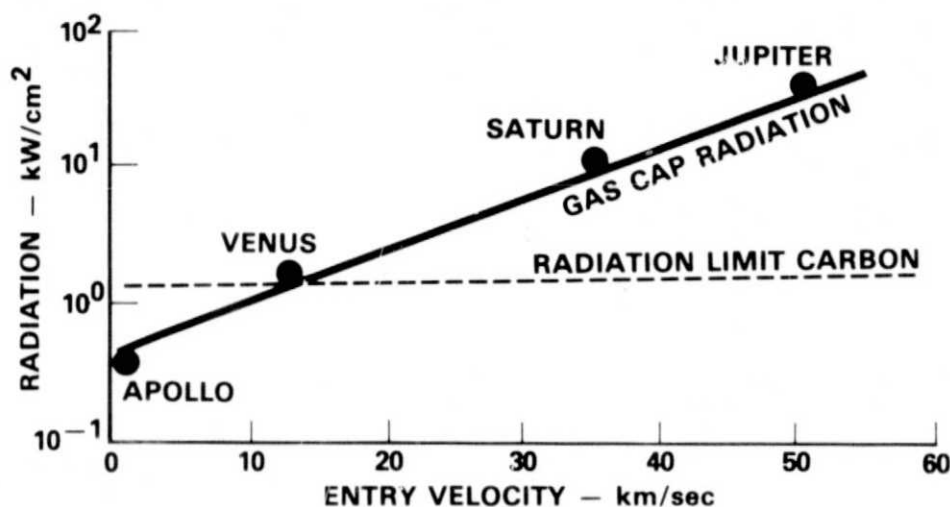

FIGURE 2. RADIATIVE ENVIRONMENTS FOR PLANETARY ENTRY

The concept described herein differs from that of Allen in that a dielectric material is used to reflect the radiant energy diffusely rather than a metallic material to specularly reflect it.

The process of reflectance in a dielectric body is best described by reviewing the familiar process of reflection in paints. An opaque white paint consists of a base liquid, "vehicle" or "binder," usually linseed oil which is quite colorless and transparent, and a pigment, which is suspended in the binder. For a white paint, the pigment particles are also colorless and transparent; oxides of zinc,

lead, and titanium are frequently used as pigments. The index of refraction of the pigment must be substantially different from that of the vehicle to meet the requirement of high reflectance which is achieved through internal refractions and reflections. Some light is reflected at the surface of the paint but the remainder penetrates and strikes a boundary between binder and pigment where a portion is reflected and a portion is refracted. The reflected part returns through the surface. The part refracted penetrates farther, a portion being reflected and refracted at each boundary surface where it crosses. Since reflection occurs for all wavelengths of the incident light, the paint reflects uniformly throughout the visible spectrum (i.e., it is white). The white color is not due to suspended white particles in the binder, but simply to a difference in index of refraction between pigment and binder, both of which are very transparent throughout the visible spectrum. Occurrences of this principle are quite common. This principle explains, for example, why tiny particles of salt, sugar, and snow, all of which are colorless and transparent, appear white. Air acts as the "vehicle" in these examples.

The key requirement of the reflecting heat shield for planetary entry probes is that reflection still must occur even though the front surface is melting or vaporizing. The convection heating is sufficiently intense to cause the surface to ablate during the entry. This concept was demonstrated in the laboratory utilizing Teflon in 1971.

The ability of Teflon to reflect light can best be explained by considering its composition. Teflon is a partially crystalline material in which the amorphous and crystalline zones are uniformly distributed, and the degree of crystallinity varies between 50 and 70 percent depending on the manufacturing process. The difference in index of refraction of the adjacent amorphous and crystalline zones evidently enables reflections and refractions to occur at the boundaries of these zones. This explains the white appearance of Teflon under normal conditions.

The following tests were conducted to determine if Teflon would remain white while undergoing ablation. Surface recession rates were obtained in convective heating alone, radiative heating alone, and combined convective and radiative heating on ablation models. The ablation tests were performed in the Ames Advanced

Entry Heating Simulator. This facility is capable of subjecting test samples to an intense independent radiative flux such that a simultaneous convective free jet can be superimposed over the model. The test models were sequentially inserted one at a time into the heating environment for different lengths of time. Four models were usually tested. The thickness of the ablation specimens was measured at the stagnation point after the test and compared to the prerun measurement to determine the surface recession. For each model the surface recession measurement was plotted against time. The slope of these linear curves gave the surface recession velocity. White Teflon was compared to black Teflon (35 percent graphite pigmented) under nearly identical heating environments. While the recession rate for both white and black Teflon under convective-only conditions was nearly the same (Figure 3), the recession rates of combined heating were considerably different. White Teflon displays the characteristic feature of reflectance with no change in surface recession, whereas the black Teflon recedes at nearly five times the convective-only rate. Obviously, absorption of the incident radiation seriously degrades the performance of the black Teflon. Also shown on this figure is the recession of white Teflon under radiation-only testing in which very little recession occurs because the majority of the radiation is being backscattered out of the material.
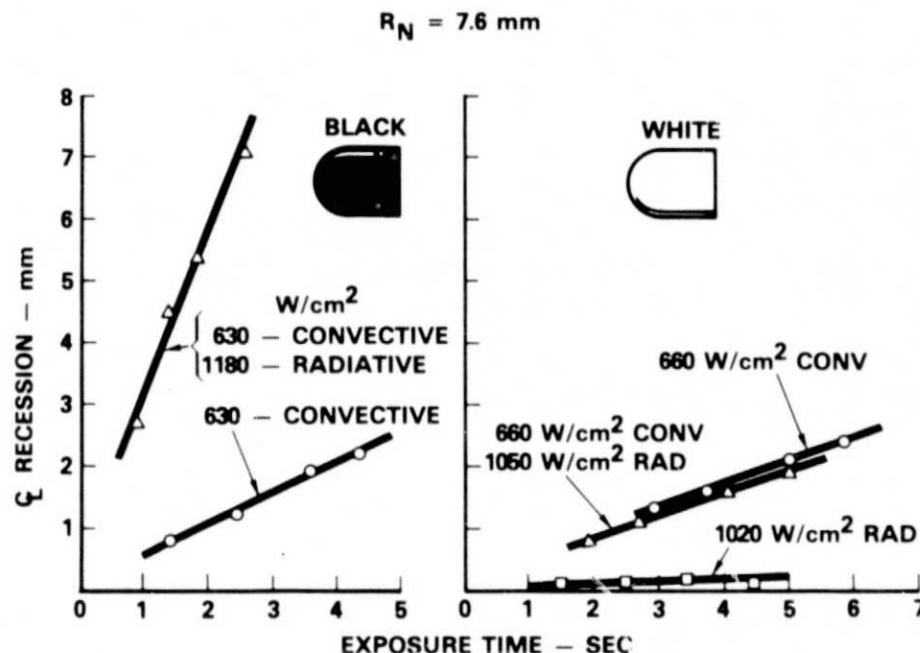
R_N = 7.6 mm

FIGURE 3. COMPARISON OF BLACK AND WHITE TEFLON UNDER CONVECTIVE
AND RADIATIVE HEATING CONDITIONS

The low heat of vaporization of Teflon rules it out as a heat shield material for outer planet entry. This shortcoming of Teflon, along with other considerations, led to the selection of consolidated particles of amorrhous silica with its high heat of vaporization as the material for an outer planetary probe heat shield. In this application the void space around the particles act as the "vehicle" or matrix providing the required differing index of refraction. The thermal shock resistance property of silica makes it stand out above all other possible refractory materials that would also possess the required dielectric reflectance property. Substantial development effort devoted to silica was motivated by a desire to obtain the reflectance and low absorption qualities of Teflon.

To be effective as a reflective heat shield, the spectral characteristics of the incident energy and the spectral absorption of the heat shield material must be considered. For most outer planet atmospheres at typical entry angles and velocities, the radiant energy consists of a continuum source in the wavelength region of about 1.0 μm down to about 0.2 μm (near IR - visible - near UV), upon which is superimposed emission bands at various wavelengths (see Figure 4). As

NOMINAL JUPITER ATMOSPHERE
NO BLOWING
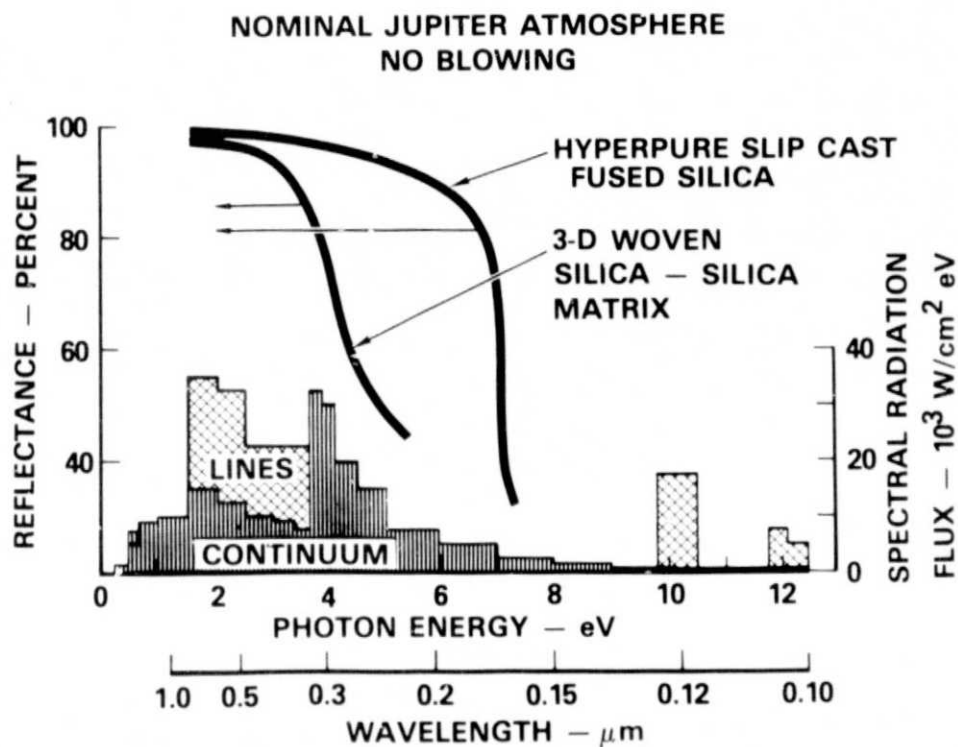
FIGURE 4. REFLECTANCE OF CANDIDATE REFLECTIVE MATERIALS
NOMINAL JUPITER ATMOSPHERE NO BLOWING

the emission bands are associated with the quantum changes in the energy levels of rotation and interatomic variation of the atmospheric gas molecules, the specific emission bands will be a function of the composition of the planetary atmosphere. For the outer planets the emission bands (and they contribute a very significant fraction of the total radiant energy) are in the visible and ultra-violet regions. Therefore, the reflective heat shield material must have a high intrinsic transmissivity in this wavelength region to be an effective backscattering reflector.

Silica, in addition to its high temperature capabilities and high heat of ablation, is highly transparent from about 2 μm down to about 0.18 μm where an absorption edge occurs. However, the presence of impurities in the silica can greatly increase the absorption in the UV region and reduce the effectiveness of the backscattering. Consequently, a major interest in this program was to use the purest of raw materials, and the avoidance of any contamination throughout the processing. For an example of purity effects, Figure 4 shows the reflectance of pure slip cast material (24 ppm total metallic impurities) compared to a less pure 3-D woven silica composite with a colloidal silica binder (above 4000 ppm total metallic impurities).

A small clean area was dedicated exclusively to the processing of silica for this program since it was known that purity would be very important. A recently expanded and improved clean area, also dedicated to the processing of silica, is shown in Figure 5.
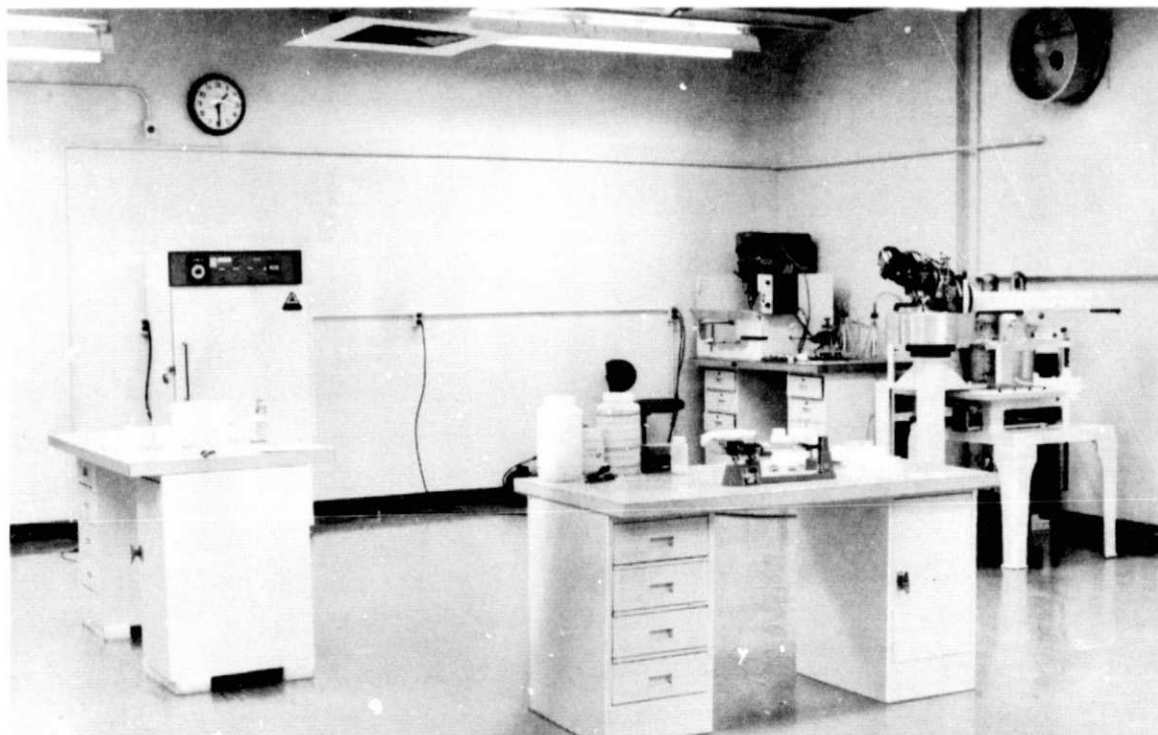

FIGURE 5. DEDICATED CLEAN ROOM FOR HYPERPURE SLIP CAST FUSED SILICA

A survey was conducted of all available high purity forms of silica and small quantities of the various types available were obtained. We obtained cloth, yarn, wool, powders, grains, and even precursor materials such as silicone resin, from which silica was made by burning it in air.

Laminated Cloth and Yarn Composites

Laminated silica cloth, Astroquartz and Refrasil were reinforced with Astroquartz yarn "nails" and bonded with colloidal silica. These samples were fabricated by installing the layers of silica cloth between plywood platens having a hole pattern through which Astroquartz yarn "nails" were manually installed on 3/8 inch centers, (.95 cm) through the thickness. These parts were then vacuum impregnated with Syton colloidal silica binder. Density could be controlled from 70 to 102 lbs/ft^3 (1120 to 1632 Kg/m^3) by this vacuum impregnation process.

In another approach to producing a silica cloth laminate, we used the highly reflective powder produced by the air pyrolysis of Dow Corning 184 silicone resin as a binder. This particulate material had reflectance values of no lower than 95% of any wavelength between 0.22 and 1.5 μm. The method of utilizing this binder in 2-D laminates was to pyrolyze the resin "in place." However, the pyrolyzed part had poor interlaminar strength, and this binder provided little or no improvement in the reflectance of the Refrasil cloth.

The 2-D laminating approach to fabrication of silica-silica heat shield material was deemphasized primarily due to poor reflectance of the candidate raw materials.

Felted Fibrous Materials

The felting of fibrous structures was considered as a candidate method of fabricating a reflective heat shield. This fabrication technique involved the felting of fibers with colloidal silica or ethyl silicate binder. The felted structure then would be pressed to a given density, fired, and reimpregnated and refired a number of times to achieve a suitable density. This processing method was abandoned because the available colloidal silicas were determined to contain sufficient impurities to preclude their use as a binder material. Also, the use of ehtyl silicate as a binder would involve using an acid hydrolyzing agent which would present processing as well as contamination problems. The felting, pressing, reimpregnating procedure was also deemed unattractive because of the numerous processing steps involved resulting in more chances for foreign contamination to be introduced.

Molded Fibrous Materials

Two approaches were taken in an attempt to fabricate molded fibrous silica structures having a particulate silica binder. The first approach was to densify a low density flexible fibrous silica matt by molding it under pressure and then reimpregnating it with a colloidal silica binder. The second approach involved the use of the particulate silica pyrolysis product of silicone resin as a binder for high purity silica fibers.

The first approach was started before the time that colloidal silica binders were virtually ruled out as a binder candidate because of their high impurity level. This first approach involved the use of low density ($\sim$3.5 lb/ft^3) (56 Kg/m^3) Microquartz felt which was impregnated with colloidal silica binder and molded under pressure before or during the microwave curing of the binder. The molded parts were then reimpregnated a number of times with colloidal silica in order to increase their density.

Four samples were prepared by this method. The results of the densification process are as follows: after one impregnation the bulk densities varied from 25 to 45 lb/ft^3 (400 to 720 Kg/m^3), depending on molding pressure which varied between 0.17 and 27.8 psi; (1.17 and 191.68 KPa) after 9 impregnations all four specimens had densities between 80 and 90 lb/ft^3 (1280 and 1440 Kg/m^3). These specimens were evaluated for density, shrinkage in two directions, and strength after firing from 800 to 2300°F (700 to 1533°K). Density increased from 83 to 117 lb/ft^3 (1328 to 1872 Kg/m^3) as the firing temperature increased. Shrinkage was highly anisotropic as would be expected due to the orientation of the fibers, the highest being through the thickness (8% at 2300°F) (1533°K). The highest flexural strength obtained was 4830 psi (33.7 MPa) after firing at 2100°F (1422°K) for 3 hours. The 2300°F (1533°K) firing resulted in a lower strength, indicating the start of devitrification.

The second basic approach toward fabricating molded fibrous structures having a particulate silica binder was adapted in an effort to take advantage of the very high reflectance observed for the silica powder resulting from air pyrolysis of Dow Corning 184 silicone resin. The ultimate goal was to use this as a binder for the very high purity silica fibers.

Several preliminary molded fibrous samples of this type were prepared using Microquartz and +99% pure Astroquartz fibers. The fibers were mixed with the catalyzed liquid resin, after which the resin was cured by heating the sample to $\sim$190°F (361°K) for 2 hours or more under pressure. After molding/curing, the samples were pyrolyzed to convert the silicone resin to particulate silica binder. The typical pyrolysis schedule was to place a slight pressure in the thickness direction during pyrolysis by means of a simple dead weight to prevent expansion cracking as the resin was converted to silica.

A major problem with the silicone bonded, molded fiber approach was contamination which appeared as a discoloration. This contaminant was assumed to be entrapped carbon from the decomposition of DC-184 silicone binder. Unsuccessful attempts were made to solve this problem, including reducing the pyrolysis heating rate for sample MF-10 to 20°F/hour (266°K/hour) and prolonging the air heating of pyrolyzed parts in an effort to oxidize residual carbon and organic compounds The discoloration could not be removed.

Another problem associated with this approach was that the as-pyrolyzed parts had a rather low density (40 to 50% of theoretical). Although this fabricated density could probably be increased, it was concluded that parts fabricated by this method would need to be reimpregnated with additional binder material of some sort in order to obtain sufficient mechanical strength. The requirement of several reimpregnations would present additional contamination and processing problems.

In view of the above considerations, this approach was deemphasized in order to concentrate on more attractive fabrication techniques.

Dry Pressing

The dry pressing approach to the fabrication of a silica heat shield involves the use of primarily very high purity silica powders and very small amounts of water and a temporary organic binder and lubricant. Basically, powders of appropriate particle sizes are combined with the binder, dry pressed to a desired shape, and then sintered at high temperature.

Ultra high purity (under 10 ppm total metal impurities) or "hyperpure" silica powder is not available in powder form. Therefore, methods were developed for preparing and qualifying hyperpure silica grains. The starting material used for this preparation was transparent high purity silica rods purchased from two different suppliers, Dynasil Corp. of America, and Amersil Inc. The hyperpure powder prepared from the material from either vendor, appeared to be identical.

The as-received rods were in various lengths of 4 inches (10.16 cm) or more and in various diameters up to 3/4 inches (1.9 cm). The as-received rods were cut to smaller lengths and each individual piece was subjected to a cleaning process and was carefully examined. Crushing and ball milling processes were used to

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reduce the silica material to hyperpure powder without introducing contamination. The product from ball milling of hyperpure silica powder was separated into coarse grain for use in the next mill batch and finer grain for dry pressing.

The procedure developed for the dry pressing and sintering of hyperpure silica grains was as follows:

The silica powders were mixed with an aqueous solution of polyvinyl alcohol (PVA) by ball milling. The PVA was the temporary binder which burns out during sintering. The consistency of the slurry formed was adjusted by adding PVA solution. When the slurry reached the proper consistency (thickly flowing) it was poured in a thin layer on absorbent paper which was held in a plaster mold. The slurry was dried to a cake of the proper water content and then granulated. The granules were sealed in a polypropylene bottle and stored (usually overnight) to allow the moisture content to equalize throughout the material. The material was then pressed to the desired shape using conventional molds and a hydraulic press, completely dried, and fired. The firing cycle was started at room temperature, increased to peak temperature and held at peak temperature 5 hours at which time the sample was removed from the furnace and allowed to cool rapidly.

Polyvinyl alcohol (PVA) was used exclusively as the binder for preparing material for dry pressing until a burnout test was conducted on the PVA alone showing that it has a residue of 0.67% after 5 hours at 2000°F (1366°K) in air. If this residue is presumed to consist entirely of oxides of metal impurities, an introduction of 67 PPM impurities into a fired dry pressed part would result from the use of 1% PVA binder. Therefore, an effort was made to find a less contaminating binder.

A sample pressed without binder had no green strength, showing that some binder was necessary. Burnout tests were performed on several candidate materials, the two most promising of which (from the standpoint of low residue) were sugar and hydroxypropylcellulose, a product used in the food industry having the trade name of Klucel. Samples made using these materials as binders had little or no green strength. A sample made using 3% sugar as binder exhibited barely acceptable green strength and poor fired strength.

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PVA was thus established as the best binder available at that time. A study was run varying the amount of binder used and a minimum of 0.5% PVA, based on total solids, was required. This amount of binder will introduce approximately 35 PPM impurities, including oxygen, into the fired sample.

The silica used for dry pressing high purity vitreous silica bodies included the hyperpure silica powders prepared by ball milling and the very fine (0.2 to 0.3μm) silica powder produced by the air pyrolysis of Dow Corning 184 silicone resin.

The approach taken toward the study of dry pressed bodies was to mix 2 or 3 different particle size distributions of powders, (sedimentation technique per ASTM D422-63) followed by pressing and sintering, while studying the processing data and the optical properties of the samples resulting from each combination of particle size distributions. A mixture of 2 or more particle size distributions produces a higher density part than a single particle size distribution due to more efficient packing of particles.

The most promising dry pressed bodies were fabricated using a bimodal and a trimodal distribution. The bimodal consisted of 70% hyperpure powder of 7 μm average diameter and 30% hyperpure powder of 4 μm average diameter, and the trimodal system consisted of 50% hyperpure powder of 7 μm average diameter, 25% hyperpure powder of 4 μm average diameter, and 25% DC184 powder of 0.2 to 0.3 μm average diameter. The binder for these bodies was polyvinyl alcohol. Using a molding pressure of 8000 psi (55.16 MPa), the bimodal system of powders resulted in a pressed "green" density of 90 lb/ft^3 (1440 Kg/m^3), while the trimodal system con- taining the very fine grains pressed to a green density of 80 lb/ft^3 (1280 Kg/m^3).

The highest reflectance values resulted from lower density material in the case of both the bimodal and trimodal distributions. Desirable densities can be achieved by firing the bimodal material at 2050°F (1394°K) or lower. The lower shrinkage of the materials without the very fine grains is an advantage from the standpoint of processing and scale-up to full size heat shields. The optical properties of the bimodal and trimodal distributions appear to be very similar when both are fired at their optimum temperature for maximum reflectance.

Dry pressing is considered to be a viable approach to fabricating a high purity silica reflective heat shield. It has been calculated that to fabricate a full size 36 inch (91 cm) diameter heat shield, a molding force of 4,000 tons (3630 metric tons) would be required. This is based on a molding pressure of 8,000 psi (55.16 MPa). Presses of this size and much larger are available.

The scope of the work on dry pressing was limited in order to concentrate on slip casting, which is now considered to be the most promising approach to silica heat shield fabrication.

Slip Casting

Of the various fabrication methods evaluated in this program, slip casting is the most practical and produces the most reflective silica heat shield. The slip casting effort performed in this program was in two major areas:

o Casting development of hyperpure silica, and,

o Slip casting of miniature heat shields.

Both of these areas are described in this section.

The purest fused silica casting slips, commercially available, are too impure (3000 to 4000 parts per million metallic impurities) for use in making a reflective heat shield. Therefore, a method was developed for preparing hyperpure fused silica slip from the same material, Dynasil, which was discussed previously, as the raw material for hyperpure powder for dry pressing. The material was received in the form of rods four inches long or longer which were cut into short lengths of one inch or less. Each individual piece of silica was then cleaned and examined visually. The silica was then reduced to a coarse grit by crushing. The coarse grit was next combined with high purity water and processed into hyperpure casting slip by ball milling.

The hyperpure slip was characterized for solids content, viscosity, pH, and particle size distribution. All of these properties are interrelated, with the viscosity, pH and particle size distribution for slip of a given solids content being dependent on the milling time. We have determined that a casting slip of roughly 80% solids was optimum. The desired pH of typical casting slip was from

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3.5 to 4.0, with the pH decreasing with increasing milling time. The viscosity of slip suitable for casting was roughly 110 centipoises, (.11 Pa-S), as measured with a Brookfield Viscometer, and the slip was typically thixotropic.

The most important characteristic of the casting slip was the particle size distribution of the solids. The particle size distribution (ASTM D422-63) of a typical hyperpure casting slip is shown in Figure 6. The particle size distribution of a commercial silica casting slip is comparable to our distribution over the range of sizes measureable by this method. Other work indicates that the hyperpure material contains less fine grains below 2 μm in diameter.
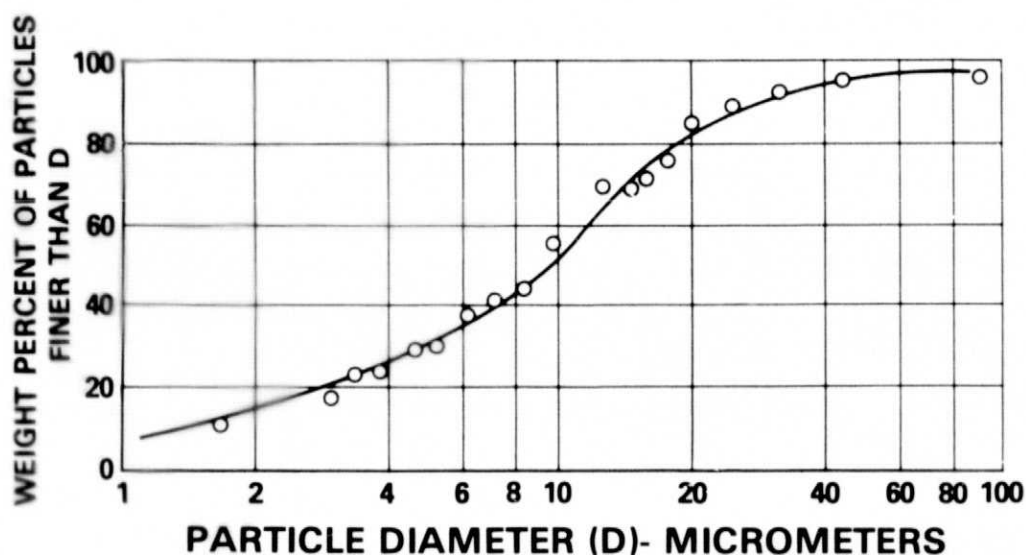

FIGURE 6. PARTICLE SIZE DISTRIBUTION OF A TYPICAL HYPERPURE
SILICA SLIP

Slip cast specimens were cast in plaster of paris molds according to standard ceramic processing methods. It was determined that vibration of the mold during casting has the desirable effect of increasing the green density of the cast parts. The vibration employed was 60 H_z with an amplitude of 0.010 inch (25.4 mm) which resulted in an increase in the green density of rougly 3.0% over parts cast without vibration.

After removing the hyperpure parts from the mold, specimens were dried very slowly to prevent cracks due to drying shrinkage. Parts were humidity dryed in a closed container, followed by air drying and then oven drying at 220°F (378°K).

The completely dried hyperpure slip cast specimens were fired by inserting them directly into a furnace, preheated to the desired firing temperature. The soak time at peak temperature used for firing all of the hyperpure slip cast samples prepared for this program was five hours.

SLIP CASTING MINIATURE HEAT SHIELDS

To obtain casting experience on a shape which is representative of a reflective heat shield, a series of subscale heat shields was made using commercial high purity silica slip. These samples were approximately 6 inches (15.24 cm) in diameter x 1 inch thick (2.54 cm) having a radius of curvature of 7 inches (17.78 cm).

The casting mold was fabricated from plaster of paris in four pieces using a polished wood master mold. The mold had a four inch (10.16 cm) deep riser so that excess slip could be held in position assuring a complete casting as the slip volume shrink during casting.

A total of five miniature heat shield shapes were fabricated. The first shield cracked in the mold because it was mistakenly allowed to dry overnight in the mold. The shield cracked radially because it was not permitted to shrink by the plaster male displacement portion of the mold.

The second miniature heat shield was removed from the mold soon after casting. It was dried overnight at room temperature, followed by drying in an air-circulating oven. The shield was then quench fired at 2100°F (1422°K). After firing it was observed to have severe shrinkage cracks.

The third heat shield was cast and dried in a manner similar to shield 2. After the drying cycle was completed, this shield was observed to have severe shrinkage cracks. The cracking problem was, therefore, concluded to be associated with drying shrinkage.

Therefore, when heat shield sample 4 was cast, steps were taken to insure uniform drying, which resulted in no shrinkage cracks. The shield was removed from the mold within 30 minutes of casting and placed in a plastic container with a sealed lid for a period of three days. The drying chamber lid was then unsealed, but the sample was maintained in the loosely covered container for a period of seven days, during which time it dried very slowly and uniformly. The sample was then removed from the container and allowed to dry at room temperature for one day. This was followed by an air-circulating oven dry for 4 hours at 120°F, (322°K)

200°F (366°K) and 350°F (450°K). The weight loss of the sample was monitored throughout the drying cycle. On a larger sample, measurements could be taken during the drying cycle to determine the point at which no further drying shrinkage takes place.

The above drying cycle resulted in no drying shrinkage cracks of heat shield 4, as confirmed by radiographic inspection. The radiography did, however, reveal several small gas voids. These voids were in the range of 0.010 to 0.040 inches (.0254 to .102 cm) in diameter and all were determined to be near the interior curved surface of the shield. The voids were removed by carefully sanding this surface with coarse silicon carbide abrasive paper. The excess riser was removed with a diamond blade band saw. All of the surfaces were then cleaned and the sharp edges were rounded with fine silicon carbide paper.

Shield 4 was quench fired at 2100°F (1422°K). After firing, the sample was observed to have cracks which were visible on the interior curved surface. Since it is virtually impossible to thermal shock slip cast fused silica in a furnace firing, we concluded that the cracks resulted from differential firing shrinkage.

Accordingly, a fifth 6 inch diameter heat shield was cast, dried, and prepared for firing in a manner similar to that described above for shield 4. Radiographic inspection revealed the shield to be crack free before firing. The shield was fired by installing it in a cold furnace and heating slowly to 2100°F (1422°K). Upon completion of firing, the shield had no visible cracks.

With the processing technique established using commercial purity slip, a sixth miniature heat shield was prepared using the hyperpure silica slip. The casting drying and firing techniques were identical to the fifth heat shield, and it was successfully completed with no evidence of cracks.

CASTING HALF SCALE HEAT SHIELDS

A similar development effort was conducted to develop necessary processes for making a half-scale heat shield, approximately 18 in. (45.72 cm) diameter.

Two changes were made in the process as part of the scale-up effort. The first was the change of the male displacement mandrel from porous plaster to a nonporous material. This was done so that water extraction would be accomplished all from one side so that no internal nonuniformity would be present, as would be the case when water extraction is from two sides.

The other significant change in the process was the addition of minus 40 mesh silica grains to the casting slip. This so called aggregate slip was selected for use over the standard slip because drying and firing shrinkage are reduced and the casting rate is greatly increased. Our major concern regarding aggregate casting was whether the large grains would degrade the reflectance. Accordingly, a series of specimens was made with various screen sizes and concentrations of grains. The optimum concentration of minus 40 mesh grain for our use was found to be 15 percent.

The completed 1/2 scale heat shield is shown in Figure 7. This shield is 17.5 inches (44.5 cm) in diameter, 6.1 inches (15 cm) high, and approximately one inch (2.54 cm) thick.

FIGURE 7. OUTER PLANETS ENTRY PROBE

1/2 Scale Hyperpure Silica Heat Shield
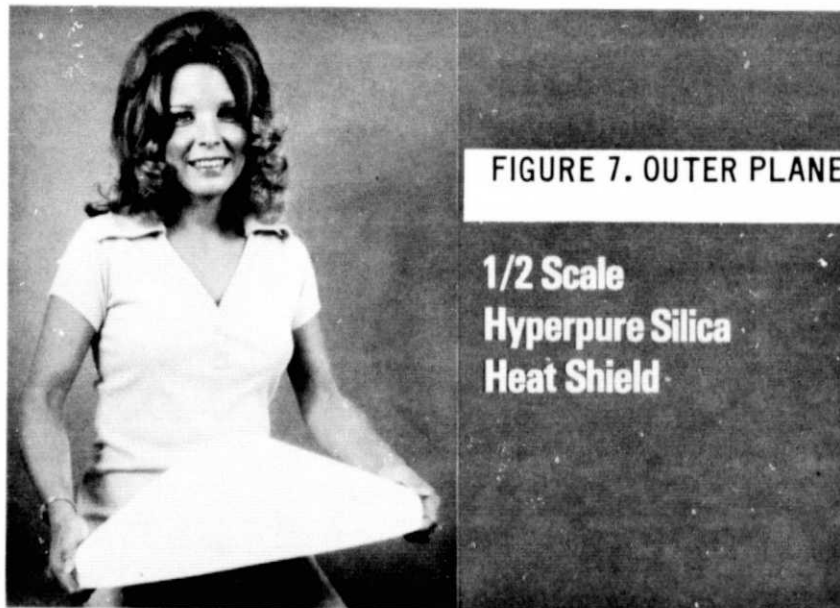
CHARACTERIZATION OF SLIP CAST SILICA

This section contains representative results of testing and studies on selected, finished high purity slip cast silica materials. Characterization of selected silica materials includes optical, physical and mechanical properties. Data on the hyperpure material is compared, where possible, to commercial high purity, slip cast vitreous silica materials.

Optical Characterization

Reflectance measurements were made at wavelengths from 0.15 to 2.3 μm in order to characterize the performance of the reflective slip cast heat shield materials. A Beckman DK-2A Integrating Sphere Reflectometer was employed to measure diffuse spectral reflectance and transmittance from 0.23 to 2.3 μm. A specially designed vacuum ultraviolet (VUV) integrating sphere reflectometer built into a high vacuum chamber was used to measure diffuse spectral reflectance from 0.15 to 0.3 μm. The results of this specially designed reflectometer are shown in Figure 8.
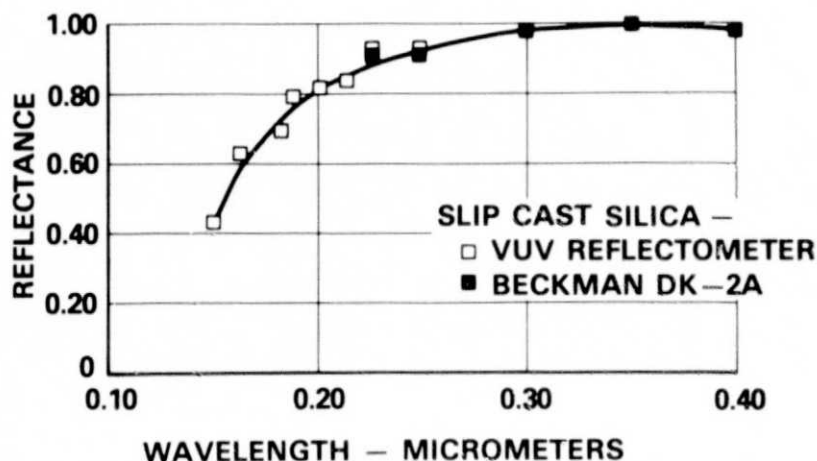

FIGURE 8. SPECIAL INSTRUMENTS DEVELOPED FOR REFLECTANCE MEASUREMENTS

To compare the reflectance with other high purity materials, several commercial slip cast materials were obtained and measured and one such representative comparison is shown in Figure 9. The Brunswick material is a strong material with a fine grain structure (see Figure 10), but evidently contains a higher impurity content

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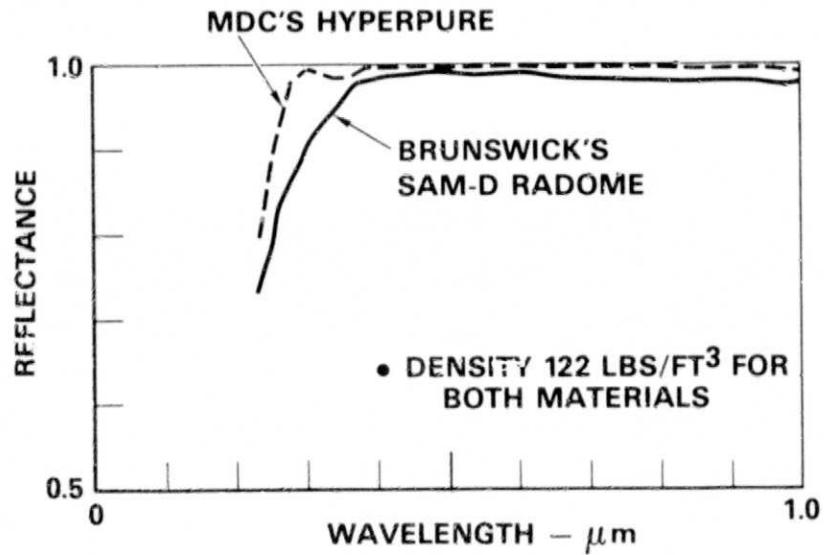as indicated by Figure 9. Similar reflectance results were obtained with other high purity materials.

FIGURE 9. COMPARISON OF TWO HIGH PURITY SLIP CAST SILICAS

- DENSITY OF BOTH 122 LBS/FT^3 (1.95 Kg/m3) (89% OF THEORETICAL DENSITY)
- SEM PHOTOGRAPHS

MAGNIFICATION → | 0.0005 IN. | ← (12.7 μm)

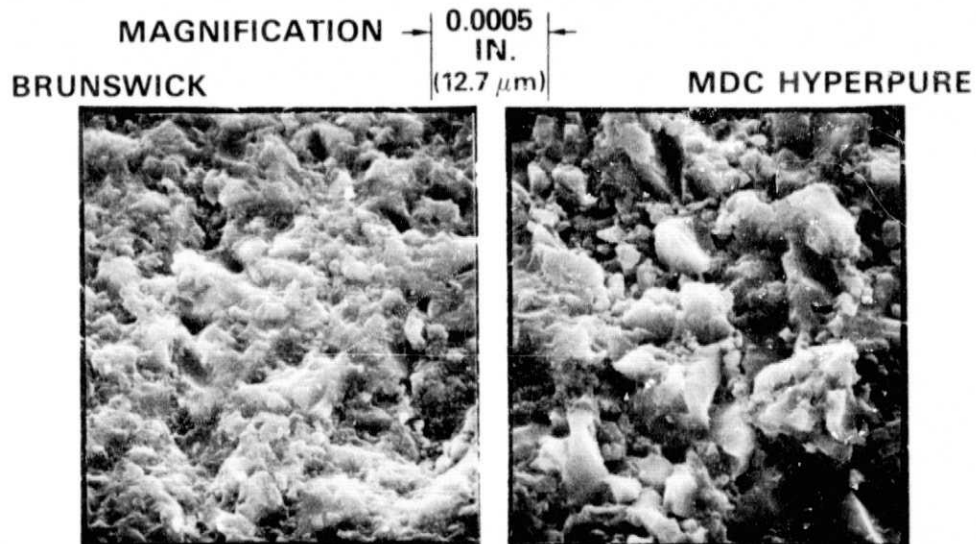BRUNSWICK   MDC HYPERPURE

FIGURE 10. MICROSTRUCTURE OF TWO SLIP CAST SILICA MATERIALS

Reflectance was also characterized as a function of process temperature for the hyperpure silica. As shown in Figure 11, reflectance is maximized (depending on desired wavelength) by firing between 2100 and 2300°F (1472 and 2760°K). Note that the strength of the material is just beginning to increase rapidly as a function of process temperature as the reflectance is peaking out.
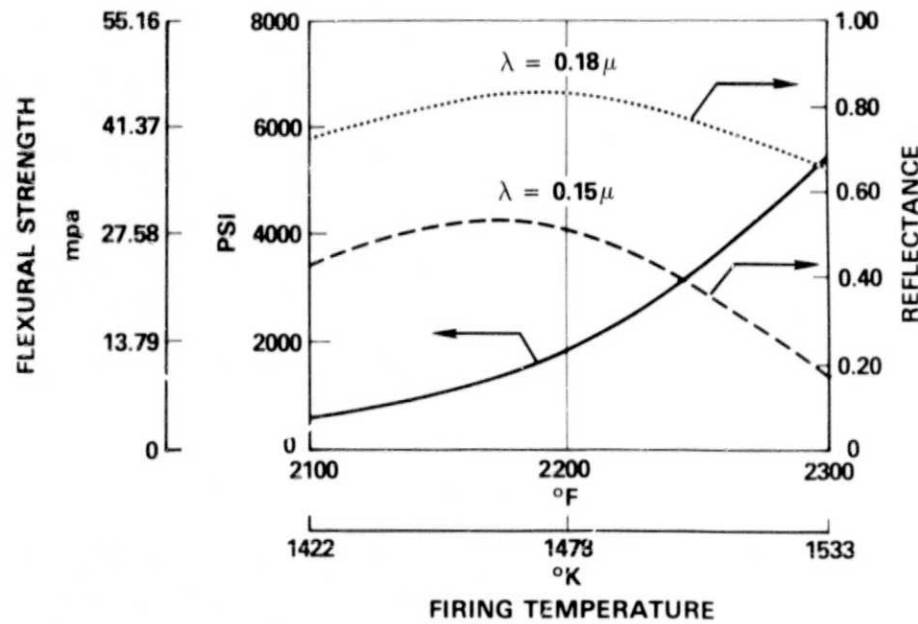

FIGURE 11. STRENGTH & REFLECTANCE ARE A FUNCTION OF FIRING TEMPERATURE

One portion of this program has just been completed, where reflectance of the hyperpure slip cast silica was measured as a function of temperature. As can be seen in Figure 12, no change in reflectance was noted from room temperature up to the process temperature (about 2250°F) (1505°K). This data will be utilized in constructing the thermal analysis model and still should be extended higher to the vaporization temperature of silica, to further assist in the thermal analysis of the ablating zone of the heat shield. Details of this work are being documented in a final report which is almost completed.

Another optical property which is attainable with this hyperpure slip cast material is transparency. This property of the bulk material has no use as a reflective heat shield material but may have other industrial uses. Figure 13 shows the relative transparency of three different slip cast parts. The first on the left, is as cast and is quite nontransparent, while the other two specimens
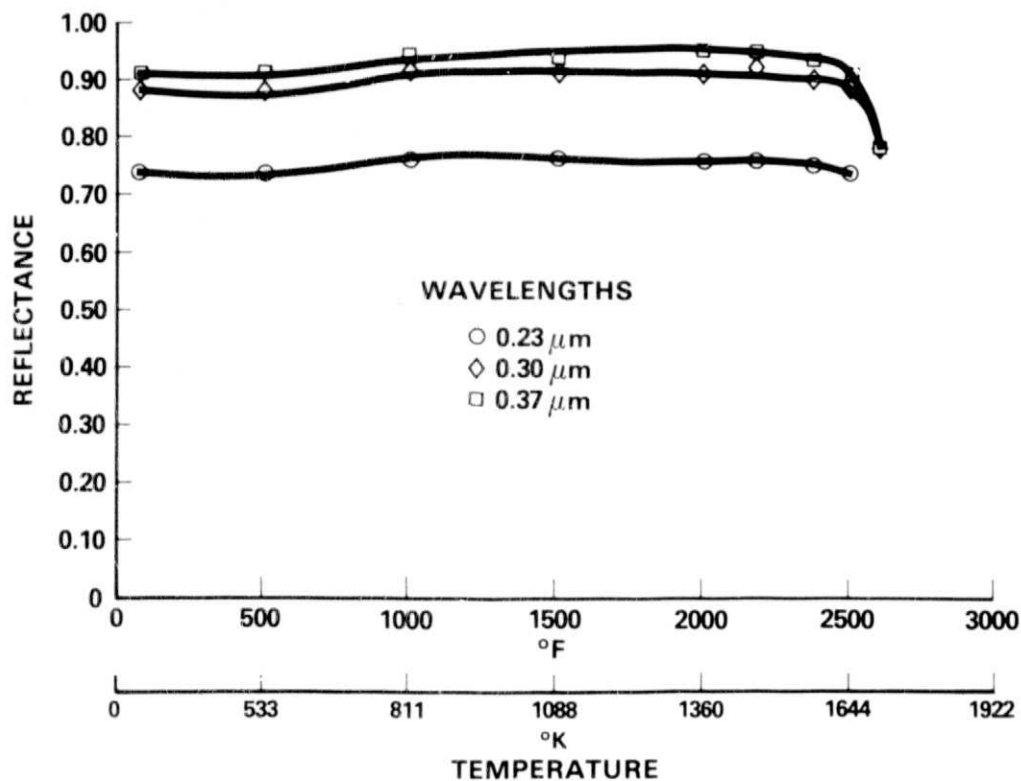
FIGURE 12. SMALL CHANGES IN REFLECTANCE AS A FUNCTION OF TEMPERATURE UP TO SINTERING TEMPERATURE
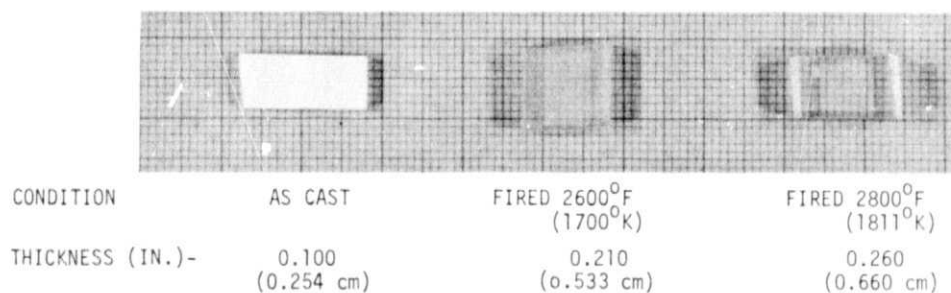

CONDITION	AS CAST	FIRED 2600°F (1700°K)	FIRED 2800°F (1811°K)
THICKNESS (IN.)-	0.100 (0.254 cm)	0.210 (o.533 cm)	0.260 (0.660 cm)

FIGURE 13. TRANSPARENT SLIP CAST SILICA

fired at 2600 and 2800°F (1700 and 1811°K) show considerable transparency. These high firing temperatures are possible, without devitrification, because of the extreme purity which has been maintained in this hyperpure fused silica. Another side-by-side comparison of the purity affects on devitrification is shown in Figure 14. Here a pure slip case material, supplied by the University of Missouri, was fired in the same furnace run as was the hyperpure silica. The McDonnell Douglas hyperpure silica on the left in Figure 14 came out clear and strong, while the other material was opaque and very weak indicating that a good deal of devitrification has taken place.

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- BOTH SINTERED SAME RUN
- SPECIMENS APPROXIMATELY ¼ INCH (0.64 cm) THICK
- BOTH SPECIMENS ARE SLIP CAST FUSED SILICA

MDC   UNIV. OF MO., ROLLA
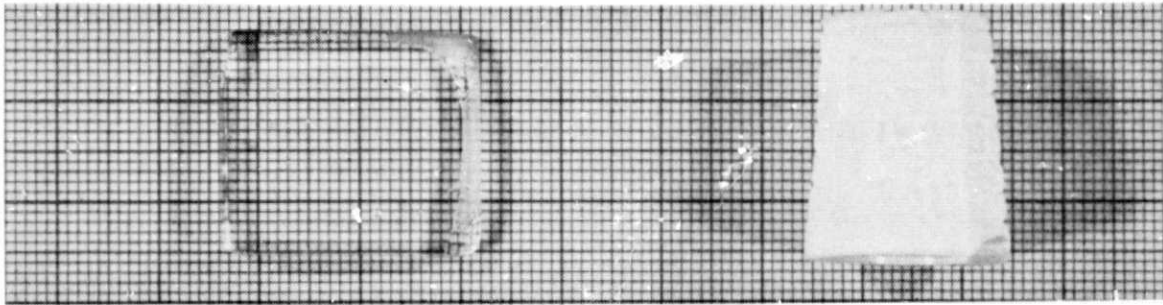HYPERPURE   HIGH PURITY

FIGURE 14. PURITY AFFECTS DEVITRIFICATION

Physical Properties

Most of the important physical properties of the hyperpure slip cast fused silica can be varied by process temperature. Since the purity level is so high in this material, our process temperature is not limited by devitrification as are other slip cast fused silicas. Examples of how firing temperature can affect physical properties are shown in Figures 15 and 16. In Figure 15, open and total
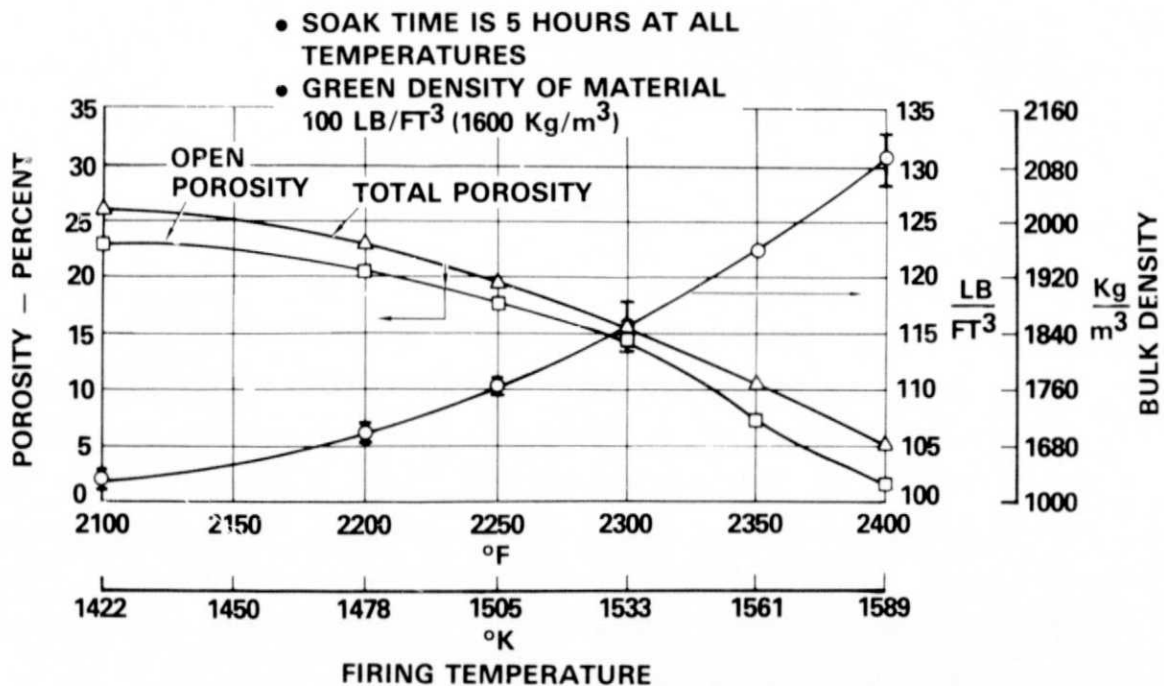

FIGURE 15. POROSITY AND BULK DENSITY OF HYPERPURE SLIP CAST FUSED
SILICA AS A FUNCTION OF SINTERING TEMPERATURES

porosity are shown as a function of firing temperature. Note that a non-water-absorbing product can be obtained by firing five hours at just slightly over 2400°F 1589°K. In Figure 16 linear shirnkage is shown as a function of process temperature for three different kinds of products; a material which has been optimized for reflectance for a Jupiter atmospheric entry, a zero water absorbing material but still opaque because of closed pores, and third, a high clarity, clear fused silica glass. Processing times and furnace atmospheres were also varied to produce these three different products.
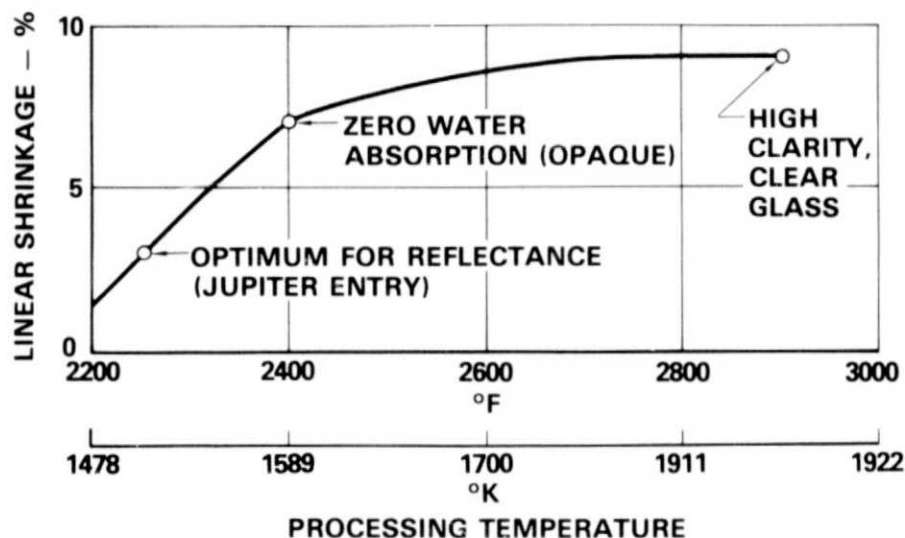

FIGURE 16. VARIOUS FORMS AND PROCESSING CHARACTERISTICS OF HYPERPURE SLIP CAST FUSED SILICA

Mechanical Properties

Average flexural strengths of as high as 7,000 psi (48.27 MPa) have been measured as shown in Figure 17. Again, firing temperature is the processing variable which results in the greatest variation in mechanical properties. These room temperature strengt measurements are conservative since the specimen size is small (surface grinding defects are an appreciable part of the cross-sectional area). We have not yet optimized the strength of the hyperpure slip cast material by using such techniques as optimum particle packing. One example of the improvement possible using various sized particles, is shown in Figure 18 where appreciable improvements have been made in the "green" strength of two of our hyperpure silicas. The concentration of "fines" (under 2 μm) is the major factor which can improve the unfired strength of the material.
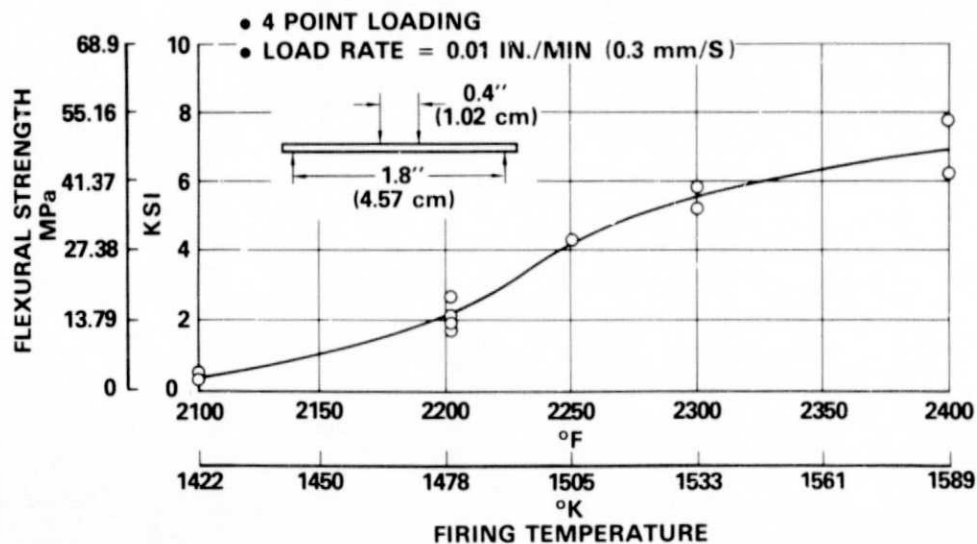
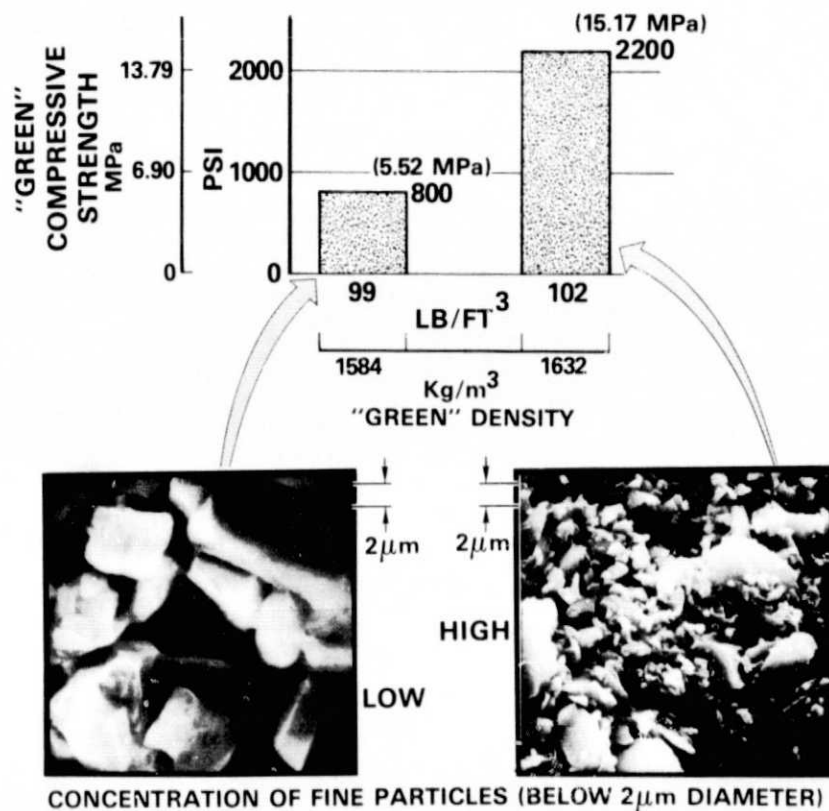FIGURE 17. FLEXURAL STRENGTH OF SLIP CAST HYPERPURE FUSED SILICA AS A FUNCTION OF FIRING TEMPERATURE

FIGURE 18. STRENGTH IMPROVEMENT IN DRY, SLIP CAST, HYPERPURE FUSED SILICA

CURRENT EFFORT

Recent findings have caused a minor redirection of the program toward increasing the toughness of our hyperpure silica heat shield material. Detailed stress analyses show that for a Jupiter entry a safety factor of only 1.25 is obtained using the latest material properties which is marginal for a brittle material.

Stress Analysis

Several detailed stress analyses have been conducted recently using the best available properties of the hyperpure material. Figure 19 shows where large tensile stresses occur in a silica heat shield during maximum aerodynamic deceleration during a Jupiter atmospheric entry. The predicted ultimate stresses (factor of safety = 1.25) result from applied inertial and aerodynamic pressure loads combined with loads induced by an appropriate temperature gradient through the thickness of the heat shield. The largest stress (1413 psi) (9.743 MPa) results primarily from mechanical flexure of the heat shield and structure under the aerodynamic pressure loading. The stresses at the aft edge (1179 psi) (8.129 MPa) and near the nose (1180 psi) (8.136 MPa) result primarily from the temperature gradient.

- JUPITER NOMINAL ENTRY — MAXIMUM DECELERATION
- LOADS AND STRESSES ARE ULTIMATE
- TYPICAL STRUCTURAL SUPPORT SYSTEM

MERIDIONAL CROSS SECTION SHOWN

STRUCTURAL SUPPORT

SILICA HEAT SHIELD

σ_t = 1179 PSI 8.129 MPa

σ_t = 1413 PSI 9.743 MPa

σ_t = 1180 PSI 8.136 MPa

SURFACE TEMPERATURE = 4800°F 2922°K

BONDLINE TEMPERATURE = 70°F 294°K

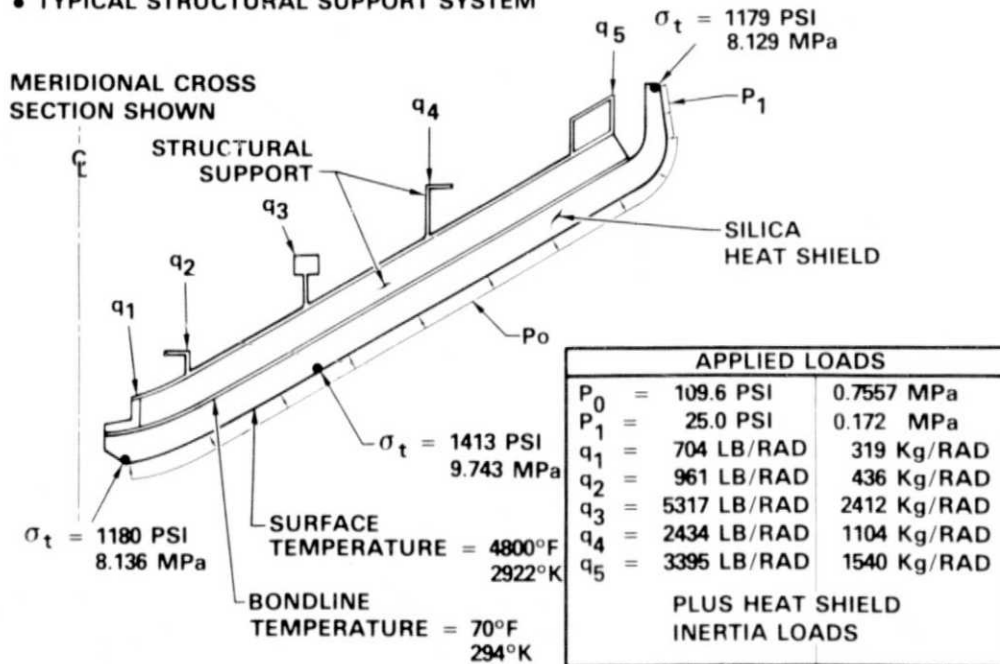| APPLIED LOADS		
P_0 =	109.6 PSI	0.7557 MPa
P_1 =	25.0 PSI	0.172 MPa
q_1 =	704 LB/RAD	319 Kg/RAD
q_2 =	961 LB/RAD	436 Kg/RAD
q_3 =	5317 LB/RAD	2412 Kg/RAD
q_4 =	2434 LB/RAD	1104 Kg/RAD
q_5 =	3395 LB/RAD	1540 Kg/RAD
PLUS HEAT SHIELD INERTIA LOADS		

FIGURE 19. PREDICTED TENSILE STRESSES IN A SILICA HEAT SHIELD

Improved mechanical property results will become available since we are also measuring properties of the hyperpure slip cast material as a function of temperature. This property determination work is about one-half completed.

Tougher Material Development

We are currently developing a tougher (toughness being the area under the tensile stress-strain curve) silica material, by incorporating silica fibers into the formulation. Figure 20 shows our preliminary test results showing higher mechanical strains at failure with increasing silica fiber concentration. These are various types of silica materials and are therefore not directly comparable, but we feel it is a valid trend. Fiber concentrations of 25 percent have been obtained to date and we expect that 50 percent concentrations are possible using the casting approach. Two other approaches are also being worked to incorporate fibers into the heat shield material but these are just beginning and there is no progress to report.
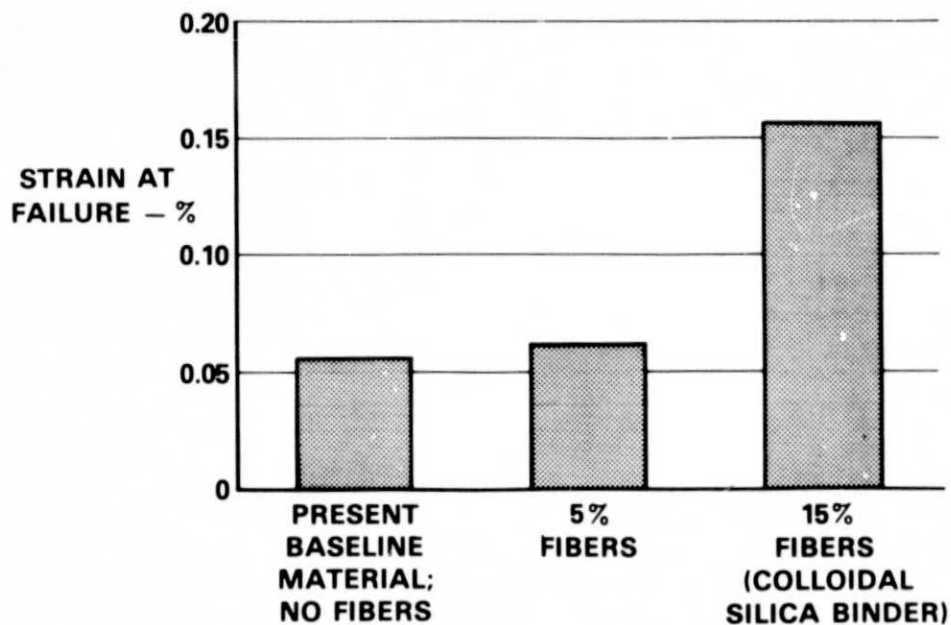
FIGURE 20. PRELIMINARY COMPARISON OF TOUGHER FUSED SILICA MATERIALS

CONCLUSIONS

Probes entering the atmospheres of the outer planets, such as Jupiter, will require heat shielding capable of withstanding convective and radiative heating environments much more severe than current experience. With radiative heating being predominant over convective heating in some cases, a different approach to heat shielding was suggested by NASA Ames in 1971. A heat shield that reflects the radiation, to prevent it from being absorbed, would result in an appreciably lighter heat shield compared to a non-reflecting heat shield. This concept was proven by arc jet/radiant lamp testing using white and black Teflon.

As an extension of this work with Teflon, silica was chosen for use as the reflecting heat shield material for planetary probe vehicles. Many different forms of silica were evaluated, and only one form of silica was available with the purity level (1 ppm total metals) required for maximum reflectance. This form is the synthetic type such as is manufactured by Dynasil Corporation and others.

Various forms of silica were also evaluated as candidate heat shield materials along with appropriate processing methods. These forms included cloth, yarns, loose fibers, grains, and binders. Very tough and strong composites were made, compared to all granular formulations, using high fiber concentrations and colloidal silica binders, however, neither fibers or colloids are available with the high purity levels required for maximum reflectance.

Slip casting was selected as the fabrication method which would yield a hyper-pure reflective heat shield, consistent with processing methods which could be scaled up to full size (35 inch) (88.90 cm) diameter heat shields. A half scale shield was built which, after completion, has a reflectance of 0.99 from wavelengths of 0.4 to 1.2 μm. A very critical processing step in producing a crack-free cast shield is drying, and this problem is eliminated by slow humidity drying and the addition of large grains of silica to the slip. This and other key processing steps were verified by successfully producing both 1/6 scale and 1/2 scale heat shields.

Both mechanical and optical properties are now being measured as a function of

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temperature on the reflectance optimized slip cast material. Preliminary stress analyses, using limited data now available, have revealed that the heat shield can survive a Jupiter entry with a safety factor of 1.5. It is desirable to have a higher safety factor considering the brittleness of this material. The desirability of having a shield with a higher safety factor has slightly redirected the program to produce a highly reflective material, having a higher strain-at-failure (or a tougher material). The results of this effort to date have been encouraging. The tougher material is produced by the incorporation of hyperpure silica fibers into the slip formulation.

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(2) Allen, H. J., "Gass Dynamics Problems of Space Vehicles," Proceedings of the NASA/University Converence on the Science and Technology of Space Exploration, November 1-3, 1962, Chicago, Illinois.

(3) Blome, J. C., Drennan, D. N., Schmitt, R. J., High Purity Silica Reflective Heat Shield Development, Final Report, NASA CR 137617, October 1974.