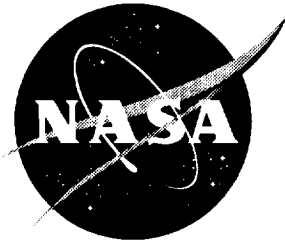


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Derek D. Hass, B. Durga Prasad, David E. Glass, and Karl E. Wiedemann  
*Analytical Services & Materials, Inc., Hampton, Virginia*

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# Reflective Coating on Fibrous Insulation for Reduced Heat Transfer

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Analytical Services and Materials, Inc.  
107 Research Drive  
Hampton, VA 23666

## Abstract

Radiative heat transfer through fibrous insulation used in thermal protection systems (TPS) is significant at high temperatures (1200°C). Decreasing the radiative heat transfer through the fibrous insulation can thus have a major impact on the insulating ability of the TPS. Reflective coatings applied directly to the individual fibers in fibrous insulation should decrease the radiative heat transfer leading to an insulation with decreased effective thermal conductivity. Coatings with high infrared reflectance have been developed using sol-gel techniques. Using this technique, uniform coatings can be applied to fibrous insulation without an appreciable increase in insulation weight or density. Scanning electron microscopy, Fourier Transform infrared spectroscopy, and ellipsometry have been performed to evaluate coating performance.

## Nomenclature

b	back scattered fraction
d	film thickness
$I_r$	reference reflected intensity
$I_s$	reference reflected intensity
L	medium thickness
N	number density of fibers
n	index of refraction
$n_H$	high refractive index
$n_L$	low refractive index
$n_1$	film refractive index
$n_2$	substrate refractive index
$Q_c$	extinction efficiency
$Q_s$	scattering efficiency
r	fiber radius
z	number of coating layers
$\lambda$	wavelength
$\rho$	reflectance
$\tau$	transmittance

## Introduction

The reusable launch vehicle (RLV) currently under development for advanced space applications will require thermal protection performance exceeding that required on past vehicles. One option being considered for this application is a metallic thermal protection systems (TPS), as shown in Figure 1, where fibrous insulation is placed between an Inconel 617 honeycomb external panel and a titanium honeycomb internal panel. The fibrous insulation provides an extremely lightweight insulator between the honeycomb sandwich panels. Saffil<sup>®</sup> insulation (~ 96% Al<sub>2</sub>O<sub>3</sub>, ~ 4% SiO<sub>2</sub>, with a mean fiber diameter of 3 μm) is an attractive insulation for this system since it provides an excellent combination of low weight, negligible weight loss below 1700°C, and low thermal conductivity. Despite Saffil's<sup>®</sup> already excellent properties, further advancement may still be necessary to meet future design requirements. Therefore, any technique which can further enhance the low thermal conductivity of Saffil<sup>®</sup> without drastically increasing its weight will advance current technology.

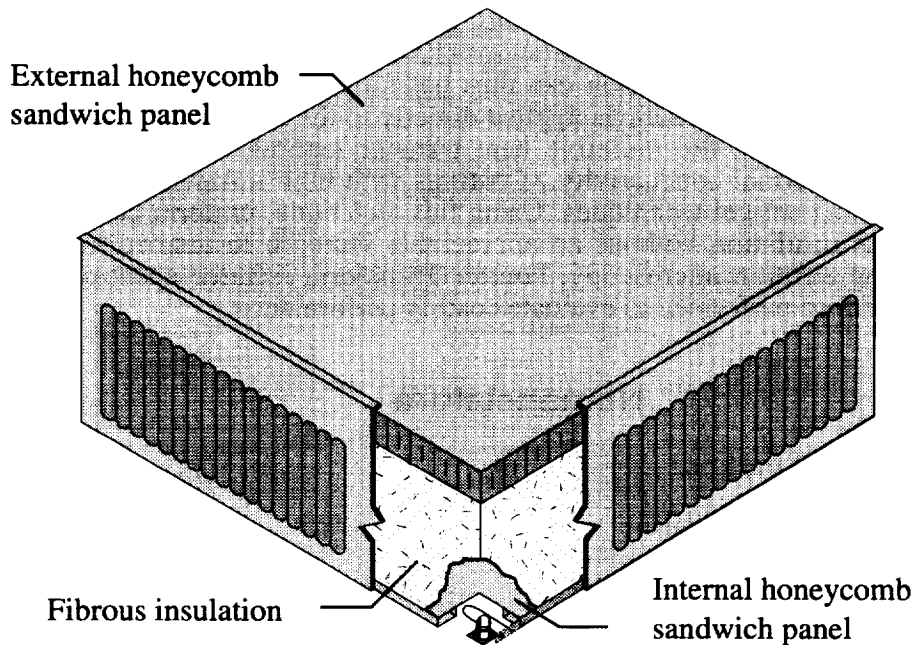


Figure 1: Schematic diagram of metallic thermal protection system with fibrous insulation between honeycomb panels.

The heat transfer through fibrous insulation is composed of conduction, convection, and radiation contributions. The importance of the radiation component increases with temperature, and is important even at the relatively low temperatures experienced in home attic insulations [1]. Thermal radiation accounts for 40-50% of the total heat transfer in light weight fibrous insulation at moderate temperatures [2]. Figure 2 shows the approximate percentage of each mode of heat transfer in fibrous insulation at one atmosphere. In reentry conditions (i.e. high temperature (1200°C) and vacuum pressures) the radiative contribution dominates [10-11] the heat transfer.

The interaction of thermal radiation with individual fibers in fibrous insulation has been studied by several authors. Mathes, et al. [3], determined the extinction coefficient of fibrous insulation using Mie-scattering theory with an emphasis on radiation oblique to the fibers. Lee [4] analyzed the scattering regimes of parallel fibers accounting for

dependent scattering. His results indicate that the scattering is strongly dependent on the complex index of refraction. Cunningham, et al. [5], experimentally studied the scattering of radiation by coated fibers. The fibers were 7.9  $\mu\text{m}$  mean diameter silica fibers with a 0.25  $\mu\text{m}$  coating. The experimental results compared well with theoretical predictions.

In addition to studies on the fundamentals of radiation heat transfer in fibrous insulation, several studies have been performed on methods to reduce the heat transfer through fibrous insulation. Verschoor, et al. [6], experimentally measured the effective thermal conductivity of glass fibrous insulation ranging in density from 0.5 to 8.4  $\text{lb}/\text{ft}^3$ . They determined that at low pressures, the heat transfer by radiation is very small for the 4.6  $\text{lb}/\text{ft}^3$  insulation, but becomes appreciable as the density is reduced to 0.5  $\text{lb}/\text{ft}^3$ . Solid conduction due to fiber contact was found to contribute very little to the heat transfer in the fibrous insulation studied. They suggest that the thermal conductivity can be reduced by using fibers with small diameters and high density insulation, i.e., 0.01  $\mu\text{m}$  diameter fibers in a 10  $\text{lb}/\text{ft}^3$  insulation. Thermal conductivity can also be reduced by sealing a low conductivity gas within the insulation, evacuating the insulation, or filling the pores with powders of very fine particle size. Earlier studies [7] indicate that it is possible to reduce radiative heat transfer in silica insulation by applying dielectric coatings to the fibers.

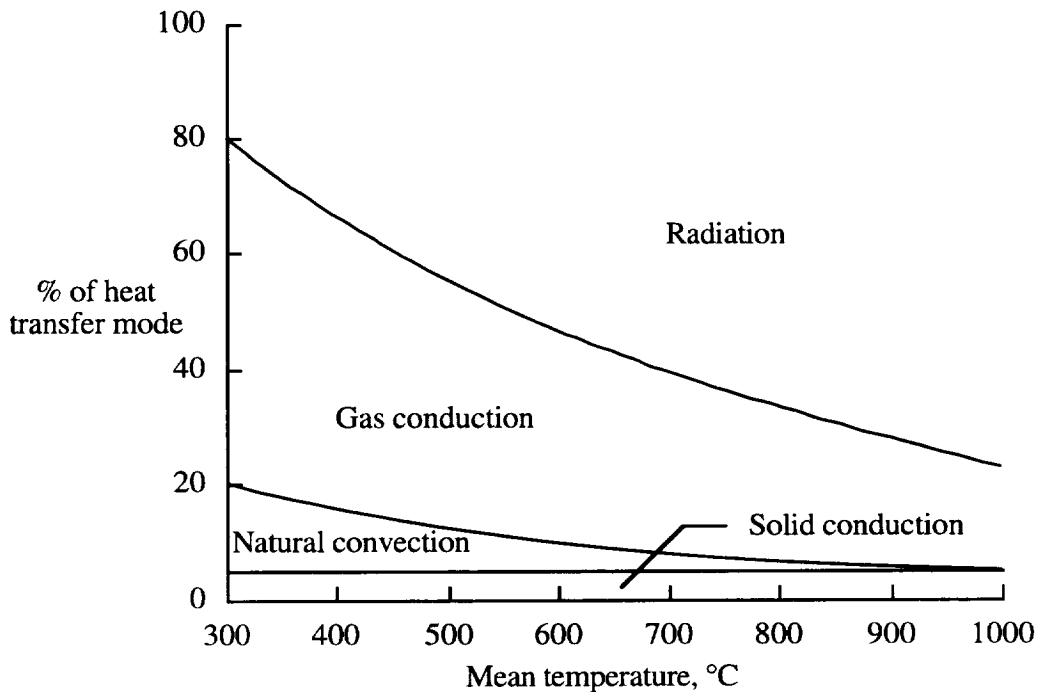


Figure 2: Contribution of each mode of heat transfer in fibrous insulation at one atmosphere.

Most glasses undergo a sharp transition from almost total transparency to total opacity in the 5 to 10  $\mu\text{m}$  infrared region depending upon the chemical composition and thickness [6]. Fibers can be opacified by variations in the chemical composition that will shift the transition to a lower wavelength. Fibrous insulation has also been opacified by the dispersion of reflective metallic particles or flakes throughout the insulation [8]. This dispersion of particles substantially increased the radiation attenuating efficiency of the fibrous insulation with very little increase in the insulation bulk density.

The thermal conductivity of fibrous insulation is dependent on temperature, air pressure, density, fiber diameter, and the optical properties of the individual fibers. The temperature, pressure, and density are all fixed by either environmental conditions or design requirements and the fiber diameter is already optimized for low thermal conductivity. As a result, altering the optical properties of the fibers presents the best opportunity for improving the thermal conductivity of the insulation. The optical properties of individual Saffil® fibers can be altered by coating the fibers with layers of a high index of refraction material [9]. Such a coating should result in an improvement in the reflectivity of the fibers and thus a decrease in the effective thermal conductivity. The radiative contribution is strongly dependent on the optical properties of the insulation fibers [12-13]. Therefore an increase in the index of refraction of the fibers should effect the thermal conductivity of the fibrous insulation.

The objective of this work was to reduce the radiative heat flux through ceramic fibrous insulation by enhancing its reflectivity. Increased reflectance can be accomplished through the development and application of reflective coatings. Several coating approaches were considered including: high index of refraction ceramic coatings, multilayer quarterwave stacks, and coatings of nanocomposite materials. Coatings were applied using a sol-gel technique which permitted a uniform coating to be applied without unwanted increases in insulation weight and density.

### Theoretical Approach

The idea of coating fibers with a reflective layer has been proposed as a means to reduce heat transfer through the insulation. Internal reflections promote the distribution of radiative energy within the medium, making the transient temperature distributions more uniform.

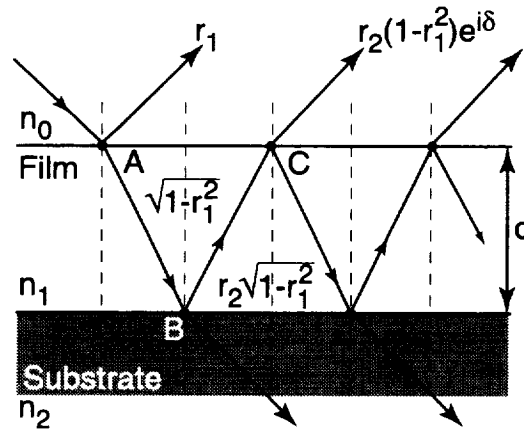


Figure 3: Reflections from a nonabsorbing, homogeneous thin film at normal incidence.

The refractive index has two effects on the temperature distributions within a medium [15]. One is that internal reflections (resulting from a high refractive index) help distribute energy within the medium, resulting in a more uniform transient temperature distribution. However, reflections from the boundaries tend to contain radiation within the medium for larger refractive indices. For optically thin layers, where the medium interaction with the thermal radiation is negligible and the temperature distribution is relatively uniform, the effect of the reflective boundaries dominates over the refractive

index effects, and increasing the refractive index will tend to keep the energy within the medium. For an optically thick medium, where the medium interaction with the thermal radiation is significant, the effect of the refractive index is more important than the reflective boundaries, and increasing the refractive index helps maintain uniform temperatures throughout the medium. Specifically, for an optical thickness less than 10, internal reflections provided by a refractive index of 2 have a substantial effect in equalizing the temperature distributions [14]. For the cases studied in reference 14 with convective heating, the more uniform temperature distribution resulted in a lower maximum temperature.

When a thin film, or coating, is applied to a material, its optical properties can be altered [16]. For the case of a nonabsorbing, homogeneous films, as shown in Figure 3, these properties will depend on film thickness,  $d$ , radiation wavelength,  $\lambda$ , and the index of refraction of the film,  $n_1$ , and substrate,  $n_2$ . From Figure 4 it can be seen that if a thin film is applied to a substrate with  $n_1 > n_2$ , then an increase in reflectance will occur. This increase will reach a maximum at a film thickness of  $\lambda/4nd$ . The reflectance has an oscillatory nature due to interference effects as a maximum occurs at  $\lambda/4, 3\lambda/4, 5\lambda/4$  etc. This result has two important effects. One is that the same coating can be both reflective and nonreflective depending on its thickness. The second is that coating reflectance is dependent on the wavelength of the media to be reflected. This means that a coating that is reflective in the visible spectrum may not be reflective to infrared radiation.

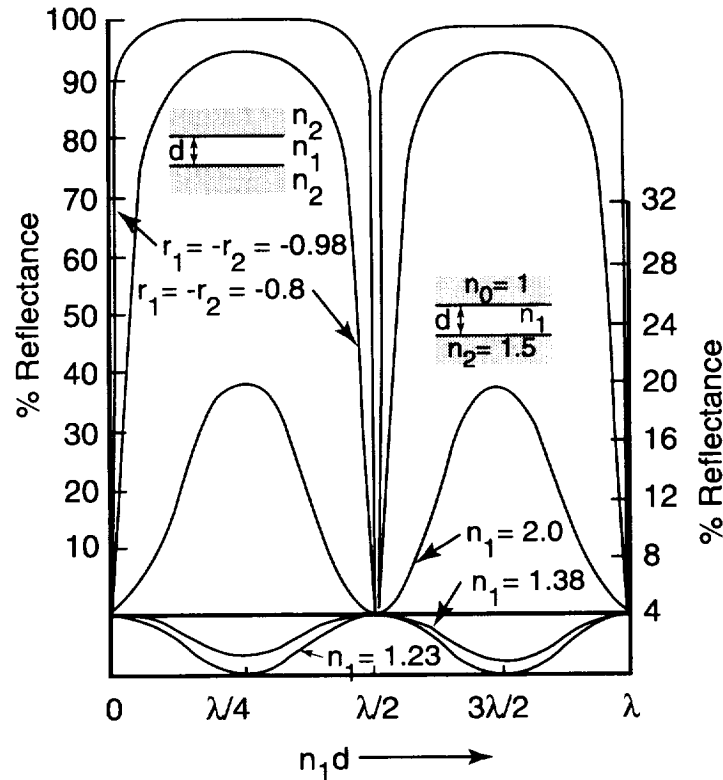


Figure 4: Reflectance as a function of  $n_1 d$  for films of various refractive index values on a glass substrate.

To substantially increase the reflectivity of the individual fibers in insulation systems, coatings must be developed which have a high index of refraction,  $n$ . Ceramic materials, specifically oxides, however, offer the ability to modestly increase the effective

n value for the insulation fibers. Using sol-gel techniques, oxides can be applied to fibrous insulation to produce reflective coatings (if  $n_{\text{coating}} > 1.7$ ). These oxide coatings can also be applied in multilayer quarterwave stacks or used as a matrix material for nanocomposite materials to yield coating systems with improved reflectance over single oxide films. Several approaches have been explored with the details described below.

### **High Index of Refraction Coating**

The simplest approach for a reflective coating is a material with an index of refraction higher than the base fibers. This will result in an increase in reflectance which is dependent on the index of refraction of the coating, the thickness of the coating, and the wavelength of the media to be reflected. As shown above in Figure 3, the reflectance increase is dependent on the coating thickness. Therefore, it is important to obtain a thickness approaching  $nd = \lambda/4$  to obtain maximum reflectance. In addition, it can be seen that as the wavelength of the media to be reflected increases, so does the coating thickness required to obtain the maximum reflectance. At the expected temperatures of the insulation in the thermal protection systems, near infrared reflectance is required (1-5  $\mu\text{m}$ ). The required wavelength creates a potential problem in that the coating thicknesses required to substantially increase the reflectance may lead to an unacceptable increase in weight. As a result, coating approaches which can produce a higher reflectance at lower thickness values may be needed.

### **Multilayer Quarterwave Stack**

Since the high reflectance of a single film is due to the constructive interference of the thermal radiation reflected at both surfaces, the reflectance can be enhanced by phase agreement of the reflected radiation from multiple coating layers. This requires a stack of alternating high (H) and low (L) refractive index layers. Next to the substrate is the usual high index layer so that the stacking order is HLHLHLHL... For z layers, it has been calculated that the maximum reflectance is given by [17]

$$\rho = \left[ \frac{n_H^{z+1} - n_L^{z-1} n_2}{n_H^{z+1} + n_L^{z-1} n_2} \right]^2 \quad (1)$$

where  $n_H$ ,  $n_L$ , and  $n_2$  are the high, low, and substrate indices, respectively.

Improved reflectance over a single high index of refraction layer can be achieved using multilayer quarterwave stacks. The effect increases as the difference between the index of refraction increases with the effective index of refraction expressed as;

$$n_{\text{eff}} = (n_H^{z+1} / n_L^{z-1})^{1/2}$$

where  $n_H$  is the index of refraction for the high index layer and  $n_L$  is the index of refraction for the low index layer. The average index of refraction values for some of the high-temperature ceramic oxides are presented in Table 1 [18]. On comparison, both  $\text{TiO}_2$  and  $\text{ZrO}_2$  oxides meet the requirement of high-temperature stability and high index of refraction. On the other hand,  $\text{SiO}_2$  has a low index of refraction. Therefore,  $\text{TiO}_2$  (H) -  $\text{SiO}_2$  (L) and  $\text{ZrO}_2$  (H) -  $\text{SiO}_2$  (L) combinations were chosen to examine reflective characteristics. When considering metal oxides, titania ( $n=2.61$ ) and silica ( $n=1.54$ ) offer the largest difference in index of refraction. For a three layer quarterwave stack consisting of  $\text{TiO}_2$  and  $\text{SiO}_2$  the effective index of refraction is given as:



$$n_{\text{eff}} = (2.61^4 / 1.54^2)^{1/2} = 4.42$$

This approach has interest due to the high theoretical reflectance possible. However, there are several disadvantages. The greatest, for the case of Saffil® insulation where the fiber diameters are relatively small, is that three quarterwave layers (the minimum necessary) leads to a large increase in weight (especially for wavelengths greater than 2 μm) and these layers are also difficult to adequately apply to the fibers. In addition, obtaining a coating of a specified thickness is difficult to quantify so that quality control becomes an issue. As a result, this concept does not entirely meet the specified criteria, and therefore a concept that will give improved reflectance without increasing the coating thickness and complexity is still desired.

Table 1: Index of Refraction of Several Metal Oxides [18]

Ceramic Material	Index of Refraction
TiO <sub>2</sub>	2.61
Ta <sub>2</sub> O <sub>5</sub>	2.50
Fe <sub>2</sub> O <sub>3</sub>	2.35
ZrO <sub>2</sub>	2.10
Al <sub>2</sub> O <sub>3</sub>	1.70
SiO <sub>2</sub>	1.54

### ***Nanocomposite Layers***

The need for high reflectance with a simple, low weight coating may be satisfied by the development of nanocomposite layers. These materials consist of nano-sized particles in a ceramic matrix. This can lead to non-linear optical properties which may show decreases in the transmissivity of the material [19-20]. The major advantage of such an approach is the potential for a relatively high coating reflectance/thickness ratio. A favorable ratio would allow for an adequate increase in fiber reflectance without an unacceptable weight gain or the need to apply multiple layer coatings. In addition, if an acceptable increase in reflectance can be achieved at thicknesses less than λ/4, then not only is the weight increase limited, but non uniform thicknesses in the coating can be tolerated to some degree. If a coating with a thickness of λ/4 is used, any variation in thickness will lead to a decrease in the total reflectivity due to the peak in reflectance at λ/4. However, thinner coatings, away from the reflectance peak, would not be effected by thickness variations since a thinner coating in one region would result in a thicker coating in another, and the average reflectivity would remain similar to a uniform layer thickness throughout. Due to the difficult nature of applying coatings to fibrous insulation, precise control over coating thickness and uniformity is marginal at best. As a result, a coating which is not critically dependent on thickness and uniformity offers a big advantage. A large variety of nanocomposite coatings are possible with limitations set mostly by finding suitable sol-gel chemistries to obtain the nanosized particles required. Systems that show promise include TiO<sub>2</sub>(Pt) and SiO<sub>2</sub>(Pd), with the TiO<sub>2</sub>(Pt) being the most easily applied to the insulation fibers at present.

Some possible drawbacks of this concept exist. One is the unknown thermal stability of these coatings. With the high service temperatures experienced, the possibility of particle growth leading to a decrease in reflectivity over time exists. Another possible disadvantage is that an increase in absorption may occur in these layers. Despite these uncertainties, this approach appears to be the most promising of the three

described since it offers the possibility of coatings which yield an effective reflectance increase without altering the attractive properties of Saffil<sup>®</sup> insulation.

### Experimental Approach

A sol-gel process was used to apply the reflective coatings to glass slides and fibrous insulation. These coatings were analyzed using optical and scanning electron microscopy to determine coating uniformity and look for the presence of defects. Fourier Transform infrared (FTIR) spectroscopy was used to determine the transmissivity of coated slides and fibers for the initial screening of several coatings, and ellipsometry was used to study its optical properties. The details of sol preparation of SiO<sub>2</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub> (Pt) and the steps involved in coating these sols on glass coupons and ceramic insulation are now described.

#### Sol-gel Process

The necessary requirements for applying reflective coatings to fibrous insulation can be met by the sol-gel process. The process offers several unique properties including the ability to use a wide range of compositions and the ability to apply coatings to complex substrates. Both make this process advantageous for this research.

The high and low refractive index layers were applied by a sol-gel process. A sol-gel process involves the formation of a homogenous solution of raw materials and the gelation of the solution to form a porous amorphous oxide. Upon firing, densification may proceed to give a glass of a polycrystalline ceramic. Organometallic compounds such as alkoxides are usually dissolved in alcohol to give a homogeneous solution. Oxide materials are formed from hydrolysis and condensation processes that result from the addition of water or exposure to the atmosphere.

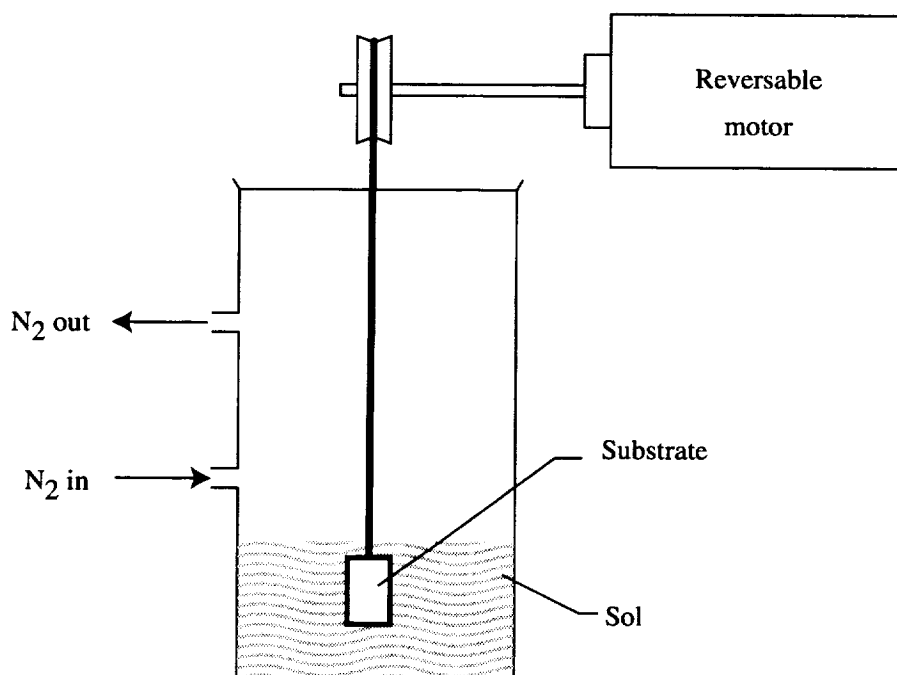
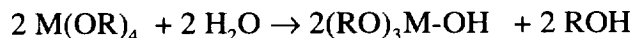
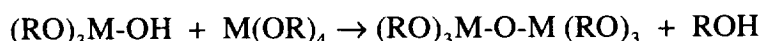
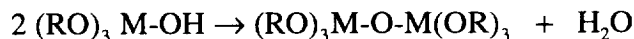


Figure 5: Schematic diagram of the sol gel coating apparatus

The most common sol-gel process for oxide preparation uses monomeric compounds [normally alkoxides  $M(OR)_n$ ] of network forming elements (e.g.,  $M = Si, Ti$ ) as glass precursors, where R is an alkyl group [21]. In alcohol/water solutions, the alkoxide groups are removed step-wise by acid or base catalyzed hydrolysis reactions, and are replaced by hydroxyl groups.



Subsequent condensation reactions involving the hydroxyl groups yield networks composed of inorganic oxide (M-O-M) linkages.



Depending on solution conditions, e.g., pH, water concentration, temperature, solvent, etc., continued condensation reactions result in polymers exhibiting a complete spectrum of structures ranging from primarily linear, entangled chains, to discrete clusters, to fully condensed colloidal particles. For porosity free coatings, linear chain structures are desired.

Table 2: Weight of Chemicals Used in Sol Preparation

Material		Weight, g		
		SiO <sub>2</sub>	TiO <sub>2</sub>	TiO <sub>2</sub> (Pt)
Beaker 'A'				
1	Methanol	10.000	20.000	20.000
2	HNO <sub>3</sub>	1.500	-	-
3	Deionized Water	3.600	-	-
4	2,4, Pentadionate	-	4.840	4.840
5	Tetra Ethoxy Silane	16.833	-	-
6	Titanium Isopropoxide	-	11.240	11.240
7	Dihydrogen Hexachloroplatinate	-	-	8.000
Beaker 'B'				
1	Triton X-100	0.200	0.200	0.200
2	Methanol	40.000	40.000	40.000
3	Methyl Ethyl Ketone (MEK)	40.000	40.000	40.000
4	Methyl Ethoxyacetate	-	8.000	8.000

### **SiO<sub>2</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>(Pt) Sol Preparation**

In this study, tetraethoxysilane (TEOS), titanium isopropoxide and dihydrogenhexachloroplatinate precursors were used to make colloidal suspensions of SiO<sub>2</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>(Pt), respectively. The mixing of solutions was done in two parts. The first solution (beaker 'A') consisted of alkoxides and acid catalysts or other complex forming substances in alcohol. The silica sols were catalyzed using nitric acid and the titania used 2,4 pentadionate. The second solution (beaker 'B') consisted of a surfactant

(Triton X-100) used to improve surface wetting, methyl alcohol, and methyl ethyl ketone (MEK). The chemicals in beakers 'A' were thoroughly mixed on a magnetic stirrer for 30 minutes at which point the contents of beaker 'B' were added to beaker 'A'. The total volume of beaker B could be used to control the sol dilution which in turn effected final coating thickness. The resulting sol was mixed for at least 60 minutes before the coating process. The chemicals required to make 0.1 moles of SiO<sub>2</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub> (Pt) sols are presented in Table 2.

### **Reflective Coatings on Glass Slides**

Glass slides were cleaned with alcohol, dipped in the sol and pulled out at a slow rate. The coated glass slide was then dried in an oven at 70°C for 15 minutes and cured at 600°C for 5 minutes. The transmissivity of the coated glass slides were obtained by Fourier Transform Infrared (FTIR) spectroscopy and compared with uncoated slides. Ellipsometry was performed to determine the index of refraction and thickness of the coatings.

### **Reflective Coatings on Ceramic Fibrous Insulation**

Once coatings showed effective optical properties on glass slides, they were applied to the fibrous insulation. The insulation used in thermal protection systems offered a coating substrate that was much more complex than coating glass slides. As a result, the conversion from coating glass slides to fibrous insulation without dramatically altering the advantageous properties of the insulation was a critical step in this research.

Several coating approaches were attempted and yielded an assortment of defects. The approaches attempted and the defects observed are summarized in Table 3 and Table 4.

Table 3: Techniques for Application of Reflective Coatings to Fibrous Insulation

Techniques	Comments
Dipping + Drying (70°C + 25°C)	Excessive crust formation
Dipping + Drying with temperature gradient	Non uniform coating + Excessive crust formation
Dipping + Vacuum drying (25°C)	Excessive crust formation
Soak In + Drying with temperature gradient	Non uniform coating + Excessive crust formation
Soak In + Drying (70°C)	Non uniform coating
Spraying + Drying (70°C)	Non uniform coating
Dipping + Excess adsorption + Low temperature drying	Good uniform coating + Limited crust formation

Applying the reflective coatings using the traditional technique of dipping, drying, and curing was not found to be effective and led to several defects. The most serious being a crust formation on the outer edges of the coated insulation. This effect was due to the presence of excess sol after the dipping of the insulation and its migration to the sample edges during drying. This crust led to excessive weight gains and increased density. As a result, other techniques were needed for satisfactory results. Several techniques were attempted including controlled temperature gradient drying, soaking in the sol using a pipette for application, spraying, and removal of the excess sol via the application of an absorbing layer after dipping. Thermal gradients, soaking, and spraying

were all found to produce non-uniform coatings. However, it was found that by placing an absorbent material on the outer edges of the Saffil® after dipping and before drying, a uniform semi-crust free layer could be produced. As a result, the use of an absorbent material to remove excess sol from the dipped Saffil® was considered the critical step in the coating process.

Table 4: Coating Defects Observed During Application of Coatings to Fibrous Insulation

Defects	Cause	Solution
Crust Formation	Excess Sol + Rapid Drying	Absorbing Layer + Room Temp. Drying
Excessive Weight Gain	Excess Sol	Absorbing Layer
Increased Density	Excess Sol	Absorbing Layer
Bridging Defects	Sol Dilution + Coating Approach	Increase Dilution + Simple Approach
Crystal Formation	Sol Composition	2,4, Pentadionate Complex Former

Two other defects, however, still persisted. The first was the formation of "bridging" defects. These defects occurred when two or more fibers were in close contact and the coating material effectively bridged two individual fibers instead of uniformly coating them. Such defects were excessive when "thicker" sols were used, but could be improved by increasing the sol dilution. However, when multilayer coatings were applied, these defects again became excessive since small defects after one layer led to increasingly larger defects with each successive layer. Due to these defects, coatings consisting of only one layer were preferred.

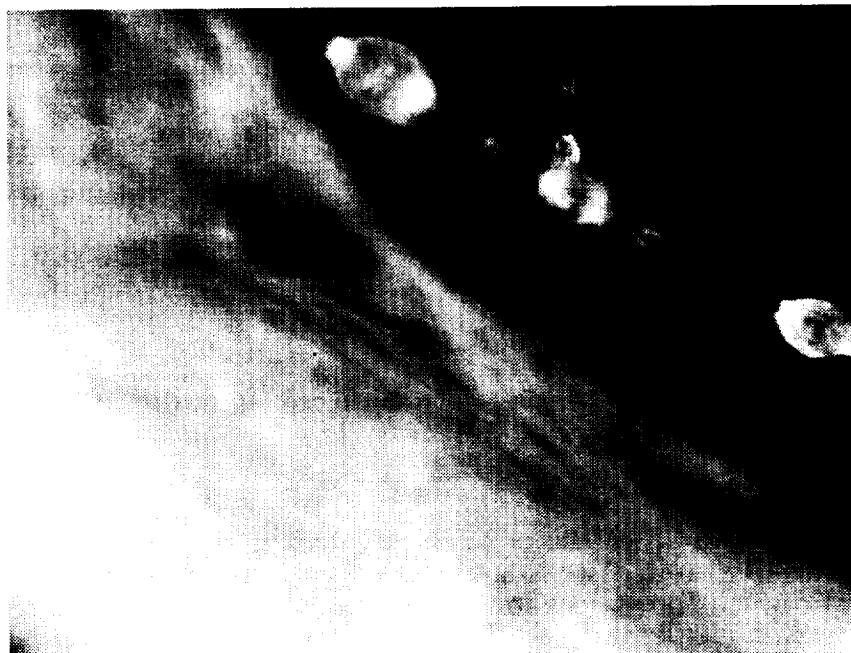
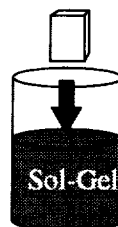


Figure 6: Crystalline formations observed after applying sol-gel coatings to Saffil® insulation.

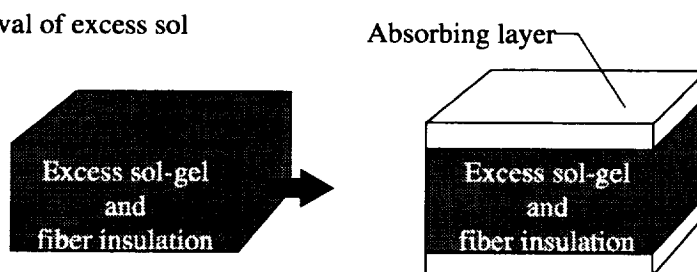
The final defect observed was the presence of crystallites in the insulation after firing. These defects are shown in Figure 6. The presence of these crystals was not desired since they increased the insulation weight without improving the fiber reflectivity. It was found, however, that by replacing acid catalysts with a complex forming substance (2,4, Pentadionate) that these defects could be avoided.

The final process consisted of dipping the Saffil® insulation into the sol and removing it at a controlled rate. Absorbing layers were then placed on the top and bottom of the infiltrated piece of insulation to remove excess sol and leave the individual fibers coated. The insulation was dried for 24 hours at room temperature or below. The lower the temperature, the less sol migration occurred due to capillary effects. The insulation was then fired at 1000°C for 1 hour to form a crystalline coating. This process is shown schematically in Figure 7.

1) Dip insulation in sol-gel



2) Removal of excess sol



3) Low temperature drying

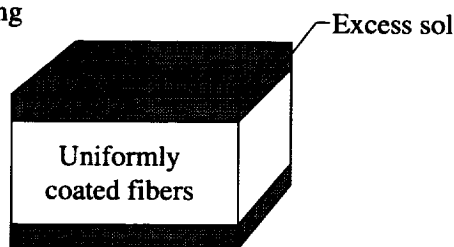


Figure 7: Final procedure for applying sol-gel derived coatings to Saffil® insulation.

## Results

$\text{SiO}_2/\text{TiO}_2$  and  $\text{SiO}_2/\text{ZrO}_2$  multilayer coatings enhanced the reflectance of glass slides. Application of a  $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$  trilayer and a single  $\text{TiO}_2$  layer on Saffil samples resulted in reduced transmittance values compared to uncoated Saffil samples. A single nanocomposite layer of  $\text{TiO}_2/\text{Pt}$  on glass slides and Saffil samples also reduced the transmittance values compared to uncoated samples. Further measurements on the coated Saffil by a guarded hot plate technique may be required to validate these coatings for final application in TPS.

## Reflectance Measurements on Glass Slides

Specular reflectance spectra from  $\text{ZrO}_2/\text{SiO}_2$  and  $\text{TiO}_2/\text{SiO}_2$  combinations were obtained by FTIR spectroscopy. Specular reflectance was obtained as a function of wave number. Figure 8 shows the spectral characteristics of multilayer stacks formed by alternating 11 layers of  $\text{SiO}_2$  and  $\text{TiO}_2$  on a glass slide. The infrared region of the spectrum encompasses radiation with wavenumbers ranging from about 12,800 to  $10\text{ cm}^{-1}$  (wavelengths from 0.78 to 1000  $\mu\text{m}$ ). Since most of the blackbody radiant energy of interest occurs below wavenumbers of  $2000\text{ cm}^{-1}$  (below wavelengths 5  $\mu\text{m}$ ), the maximum wavenumber of interest shown on the figures is  $2000\text{ cm}^{-1}$ . As shown in Figure 8, the reflectance was increased by greater than 100% in the infrared (IR) region by the application of sol-gel multi-layer  $\text{TiO}_2/\text{SiO}_2$  coatings. The measured total reflectance values for  $\text{ZrO}_2/\text{SiO}_2$  (11 layer stack),  $\text{TiO}_2/\text{SiO}_2$  (11 layer stack), and  $\text{TiO}_2/\text{SiO}_2$  (21 layer stack) are 16.65%, 18.30%, and 26.30%, respectively at a wavelength of  $4000\text{ cm}^{-1}$  (wavelength 2.5  $\mu\text{m}$ ). In general, the reflectance of the  $\text{ZrO}_2/\text{SiO}_2$  combination was observed to be smaller than that of the  $\text{TiO}_2/\text{SiO}_2$  combination for an equal number of total layers. Also, it has been observed that the reflectivity increases with an increase in the total number of layers for wavenumbers less than  $2000\text{ cm}^{-1}$ .

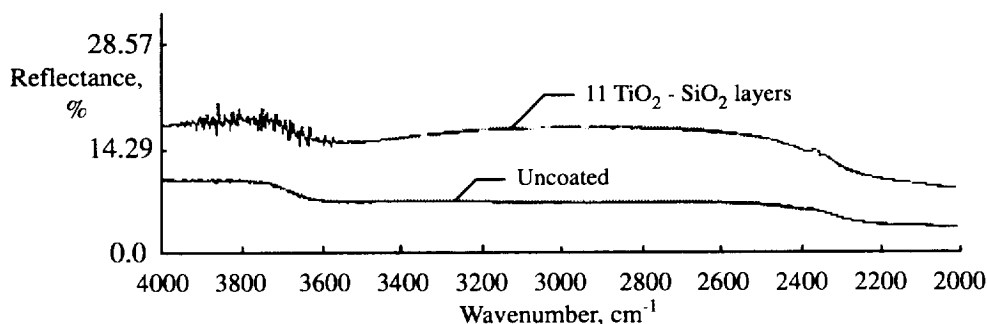


Figure 8: Spectral characteristics of uncoated and coated glass slide.

## Transmittance Measurements on Saffil Samples

The initial approach to obtaining a reflective coating was to coat the fibers with alternating layers of a high and a low refractive index coating. The two materials used for the coatings were  $\text{TiO}_2$  and  $\text{SiO}_2$ . To evaluate the effectiveness of the coating, a thin ply of Saffil<sup>®</sup> (~0.64 mm thick) was coated with a reflective coating. Six specimens were coated with varying coatings, and along with two uncoated controls (one heat treated like the coated samples and one not heat treated), were sent to NASA Lewis for testing. The eight samples and their respective weight gains are shown in Table 5. The last two samples, with 25 and 36 % weight gain, are obviously unacceptable.

At NASA Lewis, the transmittance of each specimen was determined. The specimen was placed between a black body source at  $1075^\circ\text{C}$  ( $1966^\circ\text{F}$ ) and a spectrometer. The transmittance is defined as the ratio of the radiation intensity detected at the spectrometer with the sample between the blackbody and the spectrometer and the radiation intensity with no sample between the blackbody and the spectrometer. The specimen was approximately  $50^\circ\text{C}$ , and thus contributed little emission to the transmittance. A chopper was used to assist in the measurements.

Table 5: Samples Tested for Transmittance and Respective Weight Gains

Sample	% weight gain
Uncoated	0
Uncoated and heated treated	0
TiO <sub>2</sub>	1.19
TiO <sub>2</sub>	4.34
TiO <sub>2</sub>	7.9
TiO <sub>2</sub> / SiO <sub>2</sub> / TiO <sub>2</sub>	4.7
TiO <sub>2</sub> / SiO <sub>2</sub> / TiO <sub>2</sub>	25
TiO <sub>2</sub> / SiO <sub>2</sub> / TiO <sub>2</sub> / SiO <sub>2</sub> / TiO <sub>2</sub>	36

The results of the tests are shown in Figure 9 for the eight specimens. Two controls were used. One was Saffil® as delivered by the manufacturer. The second control was uncoated Saffil® that had been exposed to the same heat treatment cycles as the coated fibers. The transmittance was nearly identical for the two cases, and therefore only the heat treated control is shown here. The six specimens with coated fibers permitted an evaluation of the number of layers of coating and the thickness of the coating. From Figure 9, it is evident that the transmittance of Saffil® is highly wavelength dependent, and for the 0.64-mm-thick sample tested here, is approximately 2% below 7 μm, 10-30% between 7 and 11 μm, and 0% above 11 μm. Coating the fibers provided a significant decrease in the transmittance between 7 and 11 μm.

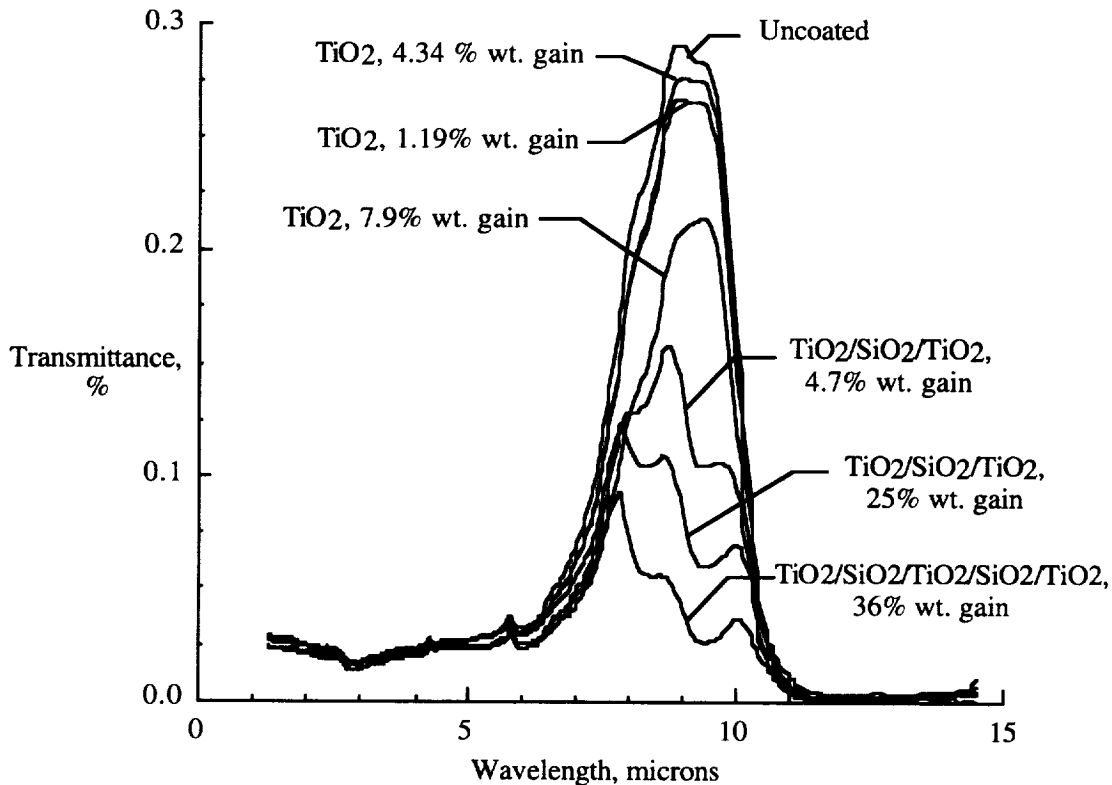


Figure 9: Transmittance of coated and uncoated Saffil® as a function of wavelength



The effect of the reflective coating can best be seen by comparing the curves in Figure 9 for a single layer of  $\text{TiO}_2$  (1.19%, 4.34%, and 7.9% weight gain) and a tri-layer of  $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ . As would be expected, increasing the mass in the one layer coating decreases the transmittance. (The transmittance for the 1.19% and 4.34% weight gain are opposite the expected trends, but this is likely due to measurement uncertainties, such as variations in sample thickness.) The tri-layer coating with a 4.7% weight gain shows a significant reduction in transmittance versus the single layer coating of approximately the same mass. Increasing the mass gain of the single layer coating to 7.9% still results in a higher transmittance than for the tri-layer with a 4.7% weight gain. The tri-layer coating with a 4.7% weight gain appears to be the optimum coating of the ones tested. These results seem to indicate that the approach of increasing the reflectance by alternating layers of high and low index of refraction materials can decrease the amount of thermal radiation transmitted through fibrous insulation.

The diffuse, or hemispherical, transmittance of coated and uncoated Saffil<sup>®</sup> insulation was determined at NASA Langley to be between 0.45 and 1.9  $\mu\text{m}$ , and the results are shown in Figure 10. An integrating sphere was used to obtain the diffuse transmittance by collecting all of the scattered radiation. This is in contrast to specular measurements where only radiation that travels straight through the sample is measured. The coated sample is the tri-layer coated sample with a 4.7% weight gain that was evaluated at NASA Lewis. The diffuse transmittance shows a significant reduction in the low wavelength range due to coating the fibers.

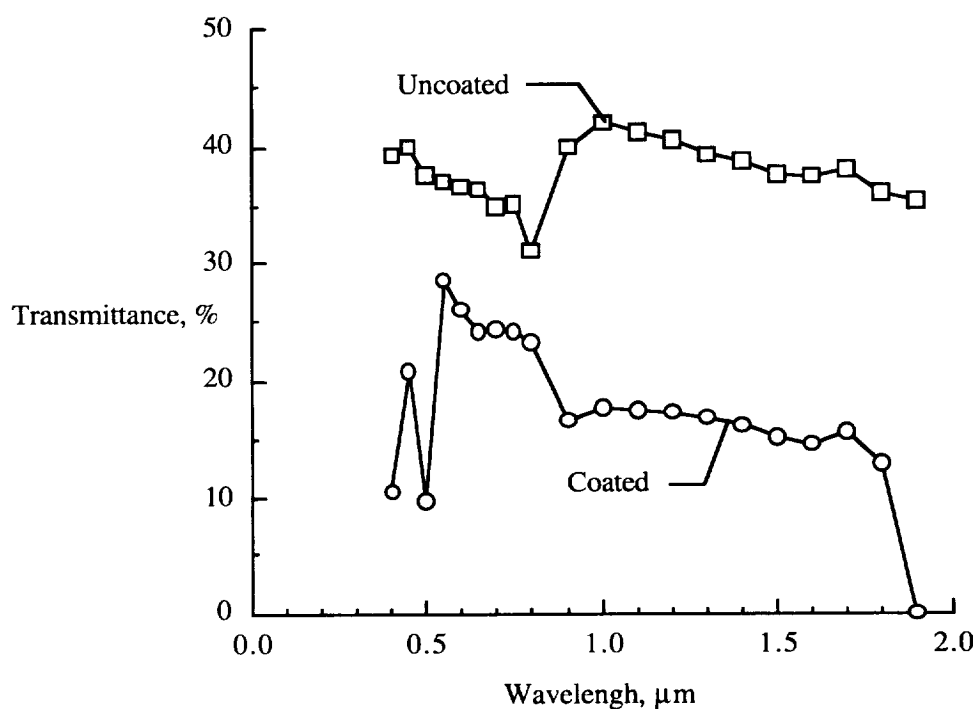


Figure 10: Diffuse transmittance of coated and uncoated Saffil<sup>®</sup> insulation.

Diffuse transmittance measurements were also made on the catalytic grade of Saffil<sup>®</sup>. The catalytic grade contains porous fibers, and thus has a lower density. In addition, the maximum use temperature (with no significant shrinkage) is 1300°C, down from 1700°C for the conventional LD matte material. Three samples of Saffil<sup>®</sup> were

coated. Two were coated with a tri-layer of  $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ , and one was coated with a single layer of  $\text{TiO}_2$ . The two samples that were coated with the tri-layer were coated with the same coating, and thus should have similar attenuation effects on the thermal radiation. The transmittance of the coated and uncoated catalytic grade Saffil<sup>®</sup> is shown in Figure 11 between 0.45 and 1.9  $\mu\text{m}$ .

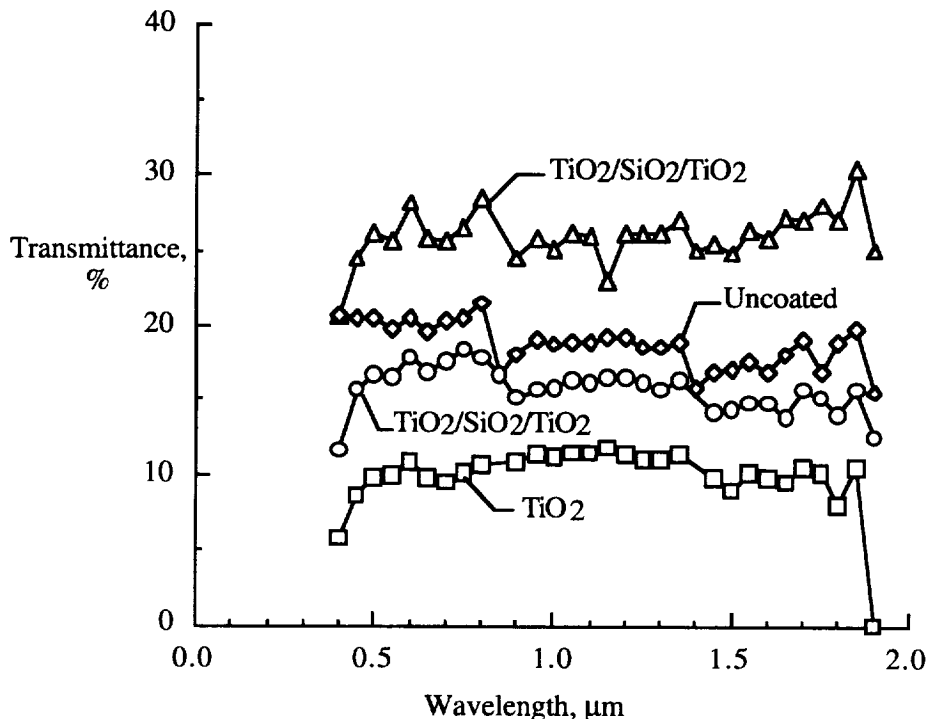


Figure 11: Diffuse transmittance of coated and uncoated catalytic grade Saffil<sup>®</sup>.

The thickness of the samples was different for each specimen, and thus the transmittance data alone is not sufficient to interpret the results. The extinction coefficient takes into account the transmittance and the thickness, and can thus be used to compare the different samples. Table 6 shows the extinction coefficient for each of the four Saffil<sup>®</sup> specimens. The extinction coefficient of the  $\text{TiO}_2$  coated and uncoated sample are similar, indicating that the single layer coating provides negligible benefit. The two samples with the tri-layer provided significant benefit compared to the uncoated Saffil<sup>®</sup>. Though the transmittance is different for the two coated samples, the extinction coefficients are similar. The extinction coefficients shown here are for diffuse radiation and are a function of the wavelength at which the measurements are made.

Finally, a thicker piece of Saffil<sup>®</sup>, approximately 0.25-in. thick, was coated to determine the effectiveness of applying the coating uniformly through the thickness. After the sample was coated, layers were peeled apart and the transmittance was measured. A sketch of the sample and the individual layers is shown in Figure 12. All of the layers except layer 2 were approximately the same thickness.

Table 6: Extinction Coefficient of Coated and Uncoated Catalytic Grade Saffil®

Coating	Avg. Transmittance	Thickness, m	Extinction Coefficient, m <sup>-1</sup>
Uncoated	0.19	$1.85 \times 10^{-3}$	895
TiO <sub>2</sub>	0.1	$2.67 \times 10^{-3}$	863
TiO <sub>2</sub> / SiO <sub>2</sub> / TiO <sub>2</sub>			
Sample 1	0.16	$1.47 \times 10^{-3}$	1244
Sample 2	0.27	$1.14 \times 10^{-3}$	1145

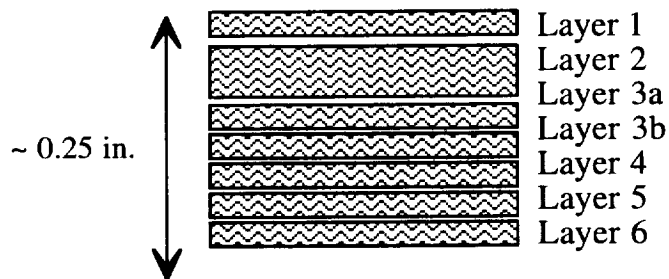


Figure 12: Sketch of the thick piece of coated Saffil®.

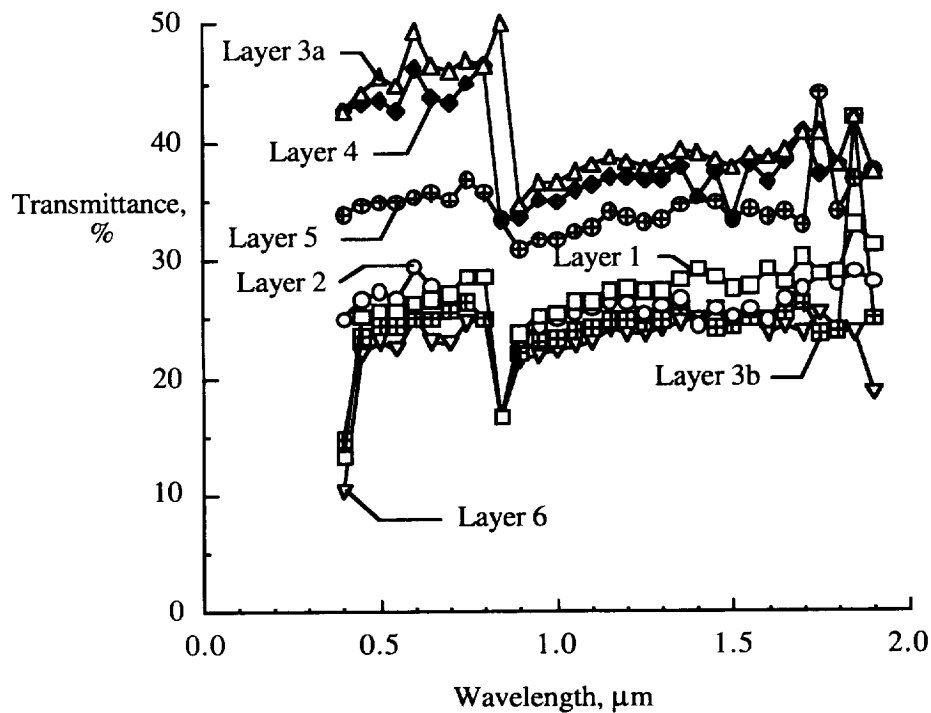


Figure 13: Diffuse transmittance of individual layers of coated Saffil®.

The diffuse transmittance of the different layers is shown in Figure 13 between 0.45 and 1.9 μm for the seven different layers. As in the previous case, the transmittance of the Saffil® is dependent on the sample thickness. Table 7 shows the extinction coefficient of each layer. The extinction coefficient accounts for the sample thickness, and thus can

be used to evaluate the uniformity of the coating through the thickness. The uncertainty in the extinction coefficient calculations is quite large due to the large uncertainty in the thickness measurement.

Table 7: Extinction Coefficient of Coated Saffil®

Layer	Avg. Transmittance	Thickness*, m	Extinction Coefficient, m <sup>-1</sup>
1	0.27	8.89 x 10 <sup>-4</sup>	1473
2	0.27	1.78 x 10 <sup>-3</sup>	736
3a	0.37	8.89 x 10 <sup>-4</sup>	1118
3b	0.25	8.89 x 10 <sup>-4</sup>	1559
4	0.36	8.89 x 10 <sup>-4</sup>	1149
5	0.35	8.89 x 10 <sup>-4</sup>	1181
6	0.24	8.89 x 10 <sup>-4</sup>	1605

\* Thickness measurements contain large uncertainties.

No pattern or trend appears to be present in the extinction coefficient values. One might expect the outer layers to be coated with heavier coatings and the inner layers with less coating, resulting in low extinction coefficients in the inside and high extinction coefficients on the outside layers. However, the transmittance measurements do not indicate a clear distinction between inner and outer layers of Saffil®.

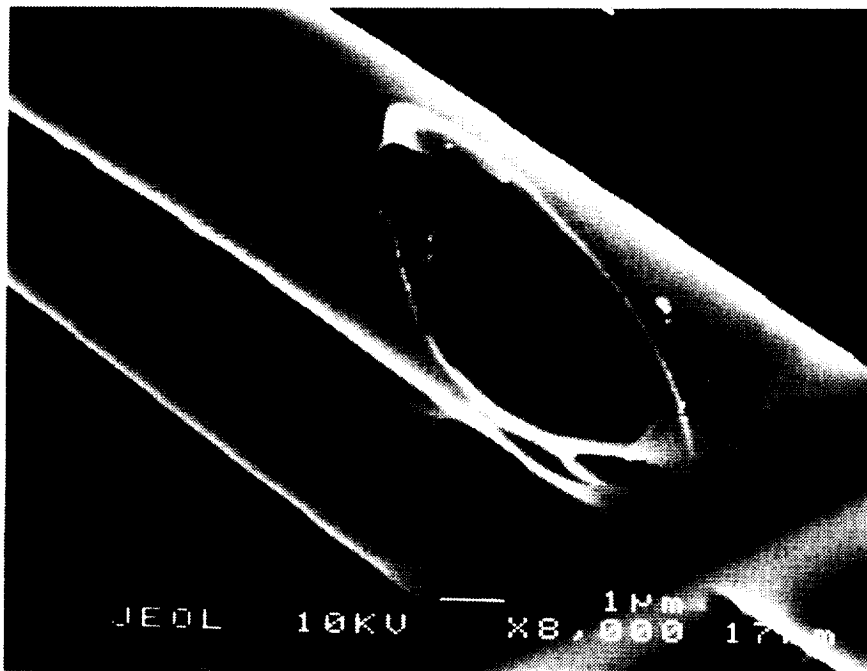


Figure 14: SEM image of Saffil® insulation coated with TiO<sub>2</sub>.

The appearance of fibrous insulation coated with TiO<sub>2</sub> was investigated using a scanning electron microscope (SEM). The analysis revealed that the Saffil® fibers were uniformly coated with TiO<sub>2</sub> over most (approximately 95%) of the fiber surface area.

Uncoated areas appeared to be due to fiber touching. Such defects are unavoidable due to the nature of the substrate and are shown in Figure 14.

### **Nanocomposite Reflective Coatings**

The incorporation of fine noble metallic particles into a ceramic matrix has been known to bring about enhanced optical properties of matrix materials [19-20]. TiO<sub>2</sub> (Pt) composites were prepared by mixing an alkoxide of titanium and platinum complex. The incorporation of Pt into TiO<sub>2</sub> matrix followed by thermal treatment at 650°C resulted in a dramatic change in the optical properties.

The transmissivity of quartz slides and Saffil<sup>®</sup> insulation coated with single layers of TiO<sub>2</sub> and TiO<sub>2</sub>(Pt) was investigated using FTIR techniques. The results revealed that TiO<sub>2</sub>(Pt) coatings reduced the transmissivity of the quartz slide approximately 20%. A coating containing TiO<sub>2</sub> did not have as great an effect on the transmissivity. Saffil<sup>®</sup> insulation coated with TiO<sub>2</sub>(Pt) also resulted in a decrease in transmissivity compared with uncoated insulation. However, these measurements are complicated by density variations throughout a sample of Saffil<sup>®</sup> insulation. These variations have been found to lead to a wide range in the measured transmissivity of samples measured at various points on the sample. Efforts to eliminate this problem involved the use of a special sample holder which allowed the sample to be measured at the same point on the sample before and after coating. These attempts drastically decreased the variability in the measurements, but not to a level where these results can be taken qualitatively.

### **Specimens Coated for Conductivity Measurements**

Saffil samples 4 in. x 4 in. x ~0.2" thick were prepared for guarded hot plate measurements. Three different coatings were selected for thermal evaluation using the guarded hot plate technique. These coatings are TiO<sub>2</sub>(Pt), TiO<sub>2</sub>, and TiO<sub>2</sub>/SiO<sub>2</sub>/TiO<sub>2</sub>. Coatings were applied on the fibrous Saffil specimens according to the procedure described earlier. The edges of the samples were trimmed to avoid edge effects due to coating in thermal measurements. The weight gain due to coating materials were measured and the results are presented in Table 8.

Table 8. Test Matrix for Guarded Hot Plate Measurements.

Coating Type	% Weight Gain	No. Specimens
Uncoated	0.0	2
TiO <sub>2</sub>	3.8	2
TiO <sub>2</sub> (Pt)	9.3	2
TiO <sub>2</sub> /SiO <sub>2</sub> /TiO <sub>2</sub>	14.5	2
SiO <sub>2</sub>	7.0	2

### **Conclusions**

The objective of this research was to determine if reflective coatings could be applied to a fibrous insulation and what effect they would have on the thermal conductivity of the insulation. Application of a coating onto fibrous insulation could not be done using conventional techniques due to the complex nature of the substrate. As a result, reflective coatings were developed using sol-gel techniques. It was found that sol-gel could be used to apply a coating to the individual fibers in Saffil<sup>®</sup> insulation using a

procedure in which a sample was dipped in a sol, had the excess sol removed by the application of an absorbing layer, dried at low temperature, and cured at 1000°C. SEM measurements confirmed that an effective coating had been applied to the fibers. Transmissivity measurements showed that the coating was effective in decreasing the transmissivity of the insulation. However, uncertainty in this data was large. Future measurements using ellipsometry and a guarded hot plate will determine the index of refraction of the coatings and the thermal conductivity of the insulation to answer existing questions on the validity of this technique.

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