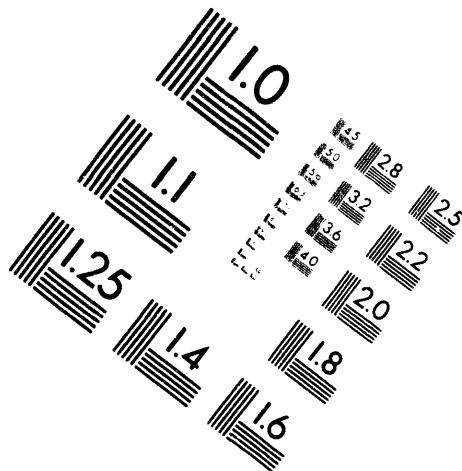




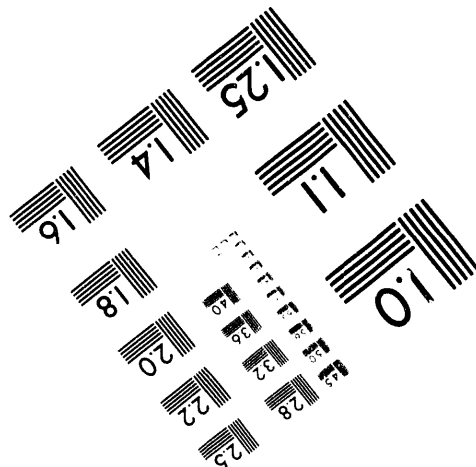
1100 Wayne Avenue, Suite 1100  
Silver Spring, Maryland 20910  
301/587-8202



A horizontal ruler with two scales. The top scale is marked from 1 to 15 mm. The bottom scale is marked from 1 to 5 cm.

Resolution Test Chart Labels:

- 1.0
- 1.1
- 1.25
- 1.4
- 1.6
- 1.8
- 2.0
- 2.2
- 2.5
- 2.8
- 3.2
- 3.6
- 4.0



MANUFACTURED TO AIIM STANDARDS  
BY APPLIED IMAGE, INC.

**1 of 1**

**Title: The Thermal Conductivity of Silicon Nitride With Molybdenum  
Disilicide Additions**

**Authors:** Stephen C. Beecher  
Ralph B. Dinwiddie  
Amanda M. Abeel  
Richard A. Lowden

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## **ABSTRACT**

The room temperature thermal conductivity has been measured for a series of silicon nitride ( $\text{Si}_3\text{N}_4$ ) matrix composites with molybdenum disilicide ( $\text{MoSi}_2$ ) additions of 2, 5, 10, 25 and 50 weight percent. Included in these measurements were a pure  $\text{MoSi}_2$  sample and a  $\text{Si}_3\text{N}_4$  sample containing only sintering aids. Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and yttrium oxide ( $\text{Y}_2\text{O}_3$ ) were added as the sintering aids, at approximately 6 and 2 weight percent respectively. When the amount of  $\text{MoSi}_2$  was increased to greater than 10 weight percent, the amount of the sintering aids necessary to densify the composite was decreased. No sintering aids were added to the pure  $\text{MoSi}_2$  sample. The measured thermal conductivities of the  $\text{Si}_3\text{N}_4$  sample without  $\text{MoSi}_2$  and the pure  $\text{MoSi}_2$  sample were 36 W/m.K and 52 W/m.K respectively, which agree very well with the literature values for similar materials [1-4]. No statistically significant changes were observed in the thermal conductivity for those samples containing up to 10 weight percent  $\text{MoSi}_2$ . However, between 10 and 25 weight percent  $\text{MoSi}_2$  there was a dramatic decrease in the thermal conductivity from 37 W/m.K to 20.9 W/m.K. The thermal conductivity then increased steadily with further additions of  $\text{MoSi}_2$  up to 52 W/m.K for the pure  $\text{MoSi}_2$  specimen.

## **INTRODUCTION**

Silicon nitride is an important technological material with a wide variety of applications. These applications range from pistons, valves, valve guides, valve seats and turbocharger rotors in the automotive industry to igniters, turbine rotors and stators, hot gas ducting, bearings and seals in the aerospace and gas turbine industries. Silicon nitride possesses excellent high temperature mechanical and thermal properties such as high strength, resistance to thermal shock, resistance to chemical attack and wear, a low thermal expansion coefficient and a relatively high thermal conductivity which makes it such a versatile material.

---

Stephen C. Beecher, Ralph B. Dinwiddie, Amanda M. Abeel and Richard A. Lowden, High Temperature Materials Laboratory, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Two of the main limitations to the use of  $\text{Si}_3\text{N}_4$  at high temperatures are creep under tension due to the presence of a glassy grain boundary phase, and a decrease in strength due to subcritical crack growth [5,6]. The intergranular glass phase is formed by the addition of sintering aids such as aluminum oxide ( $\text{Al}_2\text{O}_3$ ), magnesium oxide ( $\text{MgO}$ ) and / or yttrium oxide ( $\text{Y}_2\text{O}_3$ ) in combination with silicon dioxide ( $\text{SiO}_2$ ) which is normally present on the surface of the  $\text{Si}_3\text{N}_4$  starting powder. Modifications of the microstructure by the addition of particulates and crystallization of the grain boundary phase by heat treatment have led to the improvement in the properties of  $\text{Si}_3\text{N}_4$  [7, 8]. Another crystalline material under consideration as a second phase is molybdenum disilicide ( $\text{MoSi}_2$ ). Molybdenum disilicide possesses excellent high temperature properties with a melting point at about 2030 °C. It is thermodynamically stable with  $\text{Si}_3\text{N}_4$  at high temperatures and undergoes a brittle to ductile transition at about 1000 °C [8]. Molybdenum disilicide, a self-sacrificing oxidation material, readily reacts with oxygen to form  $\text{SiO}_2$  and  $\text{Mo}_5\text{Si}_3$  and then limits further oxygen diffusion [9]. Molybdenum disilicide particles introduced as a second phase would serve as ductile, oxidation resistant inclusions that would improve the mechanical properties of  $\text{Si}_3\text{N}_4$  at high temperatures. The purpose of this study is to determine the effects of  $\text{MoSi}_2$  additions on the thermal conductivity of hot-pressed  $\text{Si}_3\text{N}_4$  and is one component of a larger study on the properties of these composite materials (to be published elsewhere).

## FABRICATION AND CHARACTERIZATION

The  $\text{Si}_3\text{N}_4$  starting powder contained approximately 92%  $\alpha$ - phase, with an average particle size of 1  $\mu\text{m}$ , and the sintering aids,  $\text{Y}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  had average particle sizes of 3  $\mu\text{m}$  and 0.6  $\mu\text{m}$  respectively. The  $\text{Si}_3\text{N}_4$  - sintering aid mixture was batch processed using standard techniques. Initially the individual powders were mixed in the desired ratio, then vibratory milled for one hour in isopropyl alcohol using 0.25 inch diameter  $\text{Al}_2\text{O}_3$  cylinders as the milling media. After the milling procedure was complete, the mixture was wet sieved through a 325 mesh screen, dried and then dry sieved through a 325 mesh screen.

The  $\text{MoSi}_2$  powder was pre-milled to an average particle size of 1 mm and processed identically as the  $\text{Si}_3\text{N}_4$  - sintering aid material. The powders were mixed in the desired ratios and reprocessed using the same techniques. The compositions of the composites formed are shown in TABLE I. The final stage of the composite fabrication process consisted of hot-pressing the material in graphoil-lined graphite dies under vacuum at a pressure of 24 MPa and a temperature of 1600 °C for 90 minutes. Specimens approximately 3 mm thick were cut from the bulk for thermal conductivity measurements.

X-ray diffraction patterns were obtained from the 50 weight percent  $\text{MoSi}_2$  specimen. The results showed that the  $\alpha$ -phase  $\text{Si}_3\text{N}_4$  had been completely transformed into the  $\beta$ -phase. Since all of the  $\text{Si}_3\text{N}_4$  containing samples were processed at the same temperature, it was assumed that this transformation was complete in all the samples.  $\text{MoSi}_2$  was also detected as a major phase but neither  $\text{Y}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  were detected. However, oxygen apatite ( $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$ ) was detected as a minor phase.

TABLE I. COMPOSITION OF THE Si<sub>3</sub>N<sub>4</sub> / MoSi<sub>2</sub> COMPOSITES.

Weight% MoSi <sub>2</sub>	Weight% Si <sub>3</sub> N <sub>4</sub>	Weight% Y <sub>2</sub> O <sub>3</sub>	Weight% Al <sub>2</sub> O <sub>3</sub>
0	92.0	6.0	2.0
2	90.0	6.0	2.0
5	87.0	5.7	2.3
10	82.0	6.0	2.0
25	68.0	4.5	2.5
50	46.0	3.0	1.0
100	0.0	0.0	0.0

Scanning electron microscopy was performed on three of the MoSi<sub>2</sub> containing samples to characterize the overall general microstructure. It was found that for the 2, 5 and 10 weight percent MoSi<sub>2</sub> samples, the MoSi<sub>2</sub> particles were randomly distributed throughout the structure and that both the size and number increased with increasing content. It was assumed that this characterization could be extended to the remaining MoSi<sub>2</sub> composites.

Transmission electron microscopy was performed on the 2 and 10 weight percent MoSi<sub>2</sub> composites with a Hitachi HF-2000 TEM microscope equipped with a field emission gun (FEG). The FEG was used to perform Energy Dispersive Spectroscopy (EDS) so as to analyze the phases and grain boundaries of the two samples. The results confirmed that the  $\alpha$ -phase Si<sub>3</sub>N<sub>4</sub> was completely transformed into the  $\beta$ -phase and showed that there are both crystalline and amorphous pockets surrounding the Si<sub>3</sub>N<sub>4</sub> grains and a continuous glass film at the grain boundaries. The EDS spectra of these phases for both samples showed that there were only Al, Si and O at the grain boundaries and no Mo. Molybdenum was not found in either the amorphous or the secondary crystalline phases of the 2 weight percent MoSi<sub>2</sub> specimen. However, there were more amorphous pockets found in the 10 weight percent MoSi<sub>2</sub> specimen and small, round Mo-containing particles were commonly found within these pockets. No analysis was performed to determine the phase of these particles.

The density,  $\rho_{\text{meas}}$ , of each sample was determined by measuring its mass and dimensions and then compared to the theoretical density,  $\rho_{\text{th}}$ , to determine the porosity of each sample. The theoretical density was calculated from the amount of the crystalline phases included in the initial composite. It is assumed that the differences between the measured and theoretical density are attributable only to porosity and not to changes in the composition or microstructure of the phases. The values for density and porosity are shown in TABLE II.

## EXPERIMENTAL PROCEDURE

The room temperature thermal conductivity,  $\kappa$ , of the composites was determined by measuring the thermal diffusivity,  $\alpha$ , using a pulse diffusivity technique based upon a method proposed by Parker *et. al.* [10]. The thermal

TABLE II. THE MEASURED DENSITY,  $\rho_{\text{meas}}$ , THEORETICAL DENSITY,  $\rho_{\text{th}}$  AND POROSITY OF THE  $\text{Si}_3\text{N}_4$  /  $\text{MoSi}_2$  COMPOSITES.

Weight% $\text{MoSi}_2$	$\rho_{\text{meas}}$ (gm/cm <sup>3</sup> )	$\rho_{\text{th}}$ (gm/cm <sup>3</sup> )	% Porosity
0	3.11	3.27	4.9
2	3.16	3.33	5.1
5	3.27	3.41	4.1
10	3.36	3.57	5.9
25	3.65	4.06	10.1
50	4.14	4.87	15.0
100	5.94	6.32	6.0

conductivity of a material is related to the thermal diffusivity by

$$\kappa = \rho \cdot C_p \cdot \alpha \quad (1)$$

where  $\rho$  is the density and  $C_p$  is the specific heat. The specific heat of a composite material can be calculated from the component specific heats and weight percents by the relationship

$$C_p = \sum_{i=1}^n C_i w_i \quad (2)$$

where  $n$  is the number of components[11]. It is assumed there have been no interactions between the components. The specific heat capacities for the constituents of these composite materials are shown in TABLE III [12].

## RESULTS AND DISCUSSION

The results of the X-ray, TEM and SEM characterization of these composite materials show that changes in the constituent phases have taken place as a result of processing. The fundamental assumption in composite theory is that the material properties of the constituent phases do not change when the composite is formed.

TABLE III. THE CONSTITUENT SPECIFIC HEAT CAPACITIES FOR THE  $\text{Si}_3\text{N}_4$  /  $\text{MoSi}_2$  COMPOSITES.

Constituent	$C_p$ (J/g.K)
$\text{Si}_3\text{N}_4$	0.715
$\text{MoSi}_2$	0.498
$\text{Y}_2\text{O}_3$	0.454
$\text{Al}_2\text{O}_3$	0.776

This assumption has been violated for these materials. The results from X-ray diffraction show that  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  do not appear in the final composite but have formed part of the secondary crystalline and amorphous phases. In order to predict the effective thermal conductivity of a composite, the constituent volume fractions and thermal conductivities must be known. Since we do not have this information on the processed constituents then composite thermal conductivity modeling would not be applicable.

The  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  phases comprise a small fraction of the original starting material in the formation of the composite, at most 8 weight percent. It was assumed that even though these two phases decomposed to form other phases of unknown specific heat and weight percent, the secondary phase contribution to the specific heat of the new phases is the same as for the original starting materials. With this assumption in mind, the calculated composite specific heat for each sample determined from Equation 2 is shown in TABLE IV. Also shown in TABLE IV are the measured thermal diffusivity and the thermal conductivity,  $\kappa_{\text{meas}}$ , calculated with Equation 1.

The results of the density measurements have shown that these materials have varying degrees of porosity. In order to compare the thermal conductivity of these materials the effect of the differing degrees of porosity on the thermal conductivity must be adjusted to the zero porosity value. The application of composite thermal conductivity theory to adjust for the effect of porosity is valid since we can use the surrogate matrix method where all the constituent phases are considered to be the matrix of unknown conductivity and the pores as a randomly dispersed phase [13]. Maxwell's model can be written as

$$\kappa_{\text{zp}} = \kappa_{\text{meas}} \left\{ \frac{1 + v_d / 2}{1 - v_d} \right\} \quad (3)$$

where  $\kappa_{\text{zp}}$  is the thermal conductivity adjusted for zero porosity and  $v_d$  is the pore volume fraction [14]. The thermal conductivity of the pores is assumed to be zero. The thermal conductivity of the composites adjusted to the zero porosity values are shown in TABLE V and graphically in Figure 1.

TABLE IV. THE COMPOSITE SPECIFIC HEAT, THE MEASURED THERMAL DIFFUSIVITY AND MEASURED THERMAL CONDUCTIVITY FOR THE  $\text{Si}_3\text{N}_4$  /  $\text{MoSi}_2$  COMPOSITES.

Weight % $\text{MoSi}_2$	$C_p$ (J/g.K)	$\alpha$ ( $\text{cm}^2/\text{sec}$ )	$\kappa_{\text{meas}}$ (W/m.K)
0	0.70	0.165	35.9
2	0.696	0.162	35.6
5	0.691	0.162	36.6
10	0.679	0.162	37.0
25	0.650	0.088	20.9
50	0.600	0.119	29.6
100	0.498	0.174	51.5



TABLE V. THE THERMAL CONDUCTIVITY OF THE  $\text{Si}_3\text{N}_4$  /  $\text{MoSi}_2$  COMPOSITES ADJUSTED FOR ZERO POROSITY.

Weight % $\text{MoSi}_2$	$\kappa_{zp}$ (W/m.K)
0	38.7
2	38.5
5	38.9
10	40.5
25	24.4
50	37.4
100	56.4

As shown in Figure 1 there appears to be a slight increase in the thermal conductivity as the amount of  $\text{MoSi}_2$  is increased from 0 to 10 weight percent although this increase is less than the experimental error for these four samples. This increase could be attributed to a decrease in the amount of the amorphous phase at the grain boundaries between the  $\text{Si}_3\text{N}_4$  grains and the increase in the amount of  $\text{MoSi}_2$  present. The reason for the sudden decrease in the thermal conductivity for the sample containing 25 weight percent  $\text{MoSi}_2$  has yet to be identified; however it has been hypothesized that the unidentified Mo-containing spherical particles found in the 10 weight percent  $\text{MoSi}_2$  specimen may also be found in greater concentrations in the 25 weight percent specimen and have a much more deleterious effect. One of the reasons that this effect may not have been observed in the 10 weight percent specimen is that the particles were found in the amorphous pockets between the  $\text{Si}_3\text{N}_4$  grains. The thermal conductivity increased for the remaining samples when the amount of  $\text{MoSi}_2$  was increased.

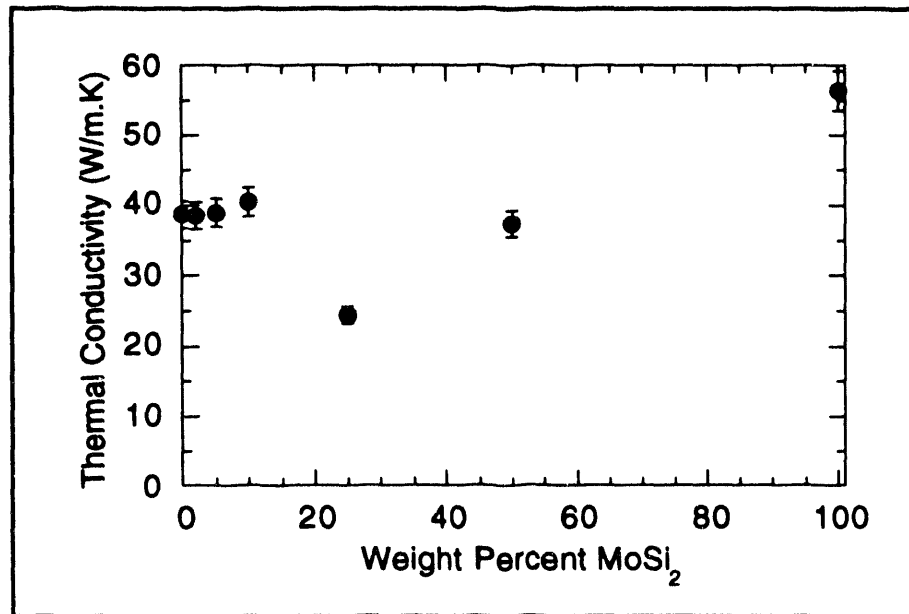


Figure 1. The thermal conductivity of the  $\text{Si}_3\text{N}_4$  /  $\text{MoSi}_2$  composites adjusted to zero porosity value.

This increase was expected; however, it appears that the increase is almost linear which was not expected. The overall trend in the thermal conductivity as a function of MoSi<sub>2</sub> content shows that composite thermal conductivity models would not be applicable for predicting the effective thermal conductivity of the composite from the constituent thermal conductivity.

## SUMMARY AND CONCLUSIONS

We have measured the room temperature thermal conductivity for a series of Si<sub>3</sub>N<sub>4</sub> / MoSi<sub>2</sub> composite materials. The variation in the thermal conductivity with increasing MoSi<sub>2</sub> concentrations indicated that changes occurred in these materials as a result of processing. X-ray diffraction patterns obtained from the 50 weight percent MoSi<sub>2</sub> specimen indicated that there were no Al<sub>2</sub>O<sub>3</sub> or Y<sub>2</sub>O<sub>3</sub> phases present in the processed material. These compounds were originally added to the Si<sub>3</sub>N<sub>4</sub> powder as sintering aids. Oxygen apatite was detected as a minor phase although none was present in the starting materials. The X-ray analysis also showed that the original  $\alpha$ -phase of the Si<sub>3</sub>N<sub>4</sub> component had transformed into the  $\beta$ -phase as a result of processing. TEM analysis was performed on two samples and confirmed that the  $\alpha$ -phase had transformed into the  $\beta$ -phase. The analysis of the 10 weight percent MoSi<sub>2</sub> specimen also showed small Mo-containing particles of unknown composition found in glass pockets between the Si<sub>3</sub>N<sub>4</sub> grains where the Al, Y and Si were also found. SEM studies of 3 samples showed the formation of an amorphous phase at the Si<sub>3</sub>N<sub>4</sub> grain boundaries and small pockets of glass between grains.

The effect of all these changes was that the fundamental assumption for the application of composite thermal conductivity models had been violated and would not give meaningful results. However, since the concentration of the sintering aids was small, it was assumed that their contribution to the specific heat remained constant and composite theory could be used to determine the composite specific heat. This assumption allowed us to determine the thermal conductivity with the result that the measured thermal conductivity values for the Si<sub>3</sub>N<sub>4</sub> and MoSi<sub>2</sub> samples, 36 W/m.K and 52 W/m.K respectively, agree well with values found in the literature. The thermal conductivity for those samples with 10 weight percent MoSi<sub>2</sub> and less showed little variation and gave almost the same values within experimental error. The decrease in the thermal conductivity for the 25 weight percent MoSi<sub>2</sub> specimen has yet to be explained but may be due to the formation of the Mo-containing phase found in the 10 weight percent specimen but at larger concentrations.

In conclusion our results show that the experimental determination of the thermal conductivity for some composite materials is recommended. Composite thermal conductivity models are inadequate in giving meaningful predictions when processing conditions result in reactions between the components.

## ACKNOWLEDGMENTS

Research sponsored by the U. S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program under contract DE-AC05-84OR21400, managed by Martin Marietta Energy Systems, Inc. and by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute for Science and Education.

The authors would like to thank Karen Leshkivich for supplying the samples, Karren L. More for the TEM and SEM characterization and Camden R. Hubbard for the X-ray analysis.

## REFERENCES

1. Powell, R., and R. P. Tye, 1969. "The Thermal and Electrical Thermal Conductivities of Some Metallic Compounds," in Thermal Conductivity, Proceedings of the Eighth Conference, C. Y. Ho and R. E. Taylor, ed. New York: Plenum Press, pp. 575-583.
2. George, W., 1973. "Thermal Property measurements on Silicon Nitride and Silicon Carbide Ceramics between 290 and 700 K." Proceedings of the British Ceramic Society, 22:147-167.
3. Sanchez, L., 1992. "Electrical, Mechanical and Thermal Characterization of a Cofired, Multilayer Substrate Processed from Sol-Gel Silica." Ceramic Engineering Science Proceedings, 9(11-12):1590-1602.
4. Bose, S., and R. J. Hecht, 1992. "Thermal properties of MoSi<sub>2</sub> and SiC whisker reinforced MoSi<sub>2</sub>." Journal of Material Science, 27:2749-2752.
5. Lange, F. F., 1974. "High-Temperature Strength Behavior of Hot-Pressed Si<sub>3</sub>N<sub>4</sub>: Evidence for Subcritical Crack Growth." Journal of the American Ceramic Society, 57(2):84-87.
6. More, K. L., D. A. Koester, and R. F. Davis, 1991. "Microstructural Characterization of a Creep-Deformed SiC Whisker-Reinforced Si<sub>3</sub>N<sub>4</sub>." Ultramicroscopy, 37:263-278.
7. Weston, J. E., P. L. Pratt, and C. H. Steele, 1978. "Crystallization of Grain Boundary Phases in Hot-Pressed Silicon Nitride Materials." Journal of Material Science, 13:2137-2146.
8. Petrovic, J., and R. Honnell, 1990. "MoSi<sub>2</sub> Particle Reinforced SiC and Si<sub>3</sub>N<sub>4</sub> Matrix Composites." Journal of Material Science Letters, 9:1083-1084.

9. Sasaki, S., H. Shimura, K. Hasegawa, and K. Hirano, 1992. "Laser Assisted Plasma Coating for Carbon Matrix Composites." in 4th International Symposium on Ceramic Materials and Components For Engines ed. London:Elsevier Science Publishers, LTD., 409-415.
10. Parker, W. J., R. J. Jenkins, C. P. Butler, and G. L. Abbott, 1961. "Flash Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity." Journal of Applied Physics., 32(9):1679-1684.
11. Lee T. Y. R., and R. E. Taylor, 1978. "Thermal Diffusivity of Dispersed Materials.", Transactions of the ASME., 100:720-724.
12. Touloukian, Y. S., and E. H. Buyco, 1970. "Specific Heat Nonmetallic Solids," The TPRC Data Series. Thermophysical Properties of Matter. Volume 5, New York, Plenum.
13. Beecher, S. C., 1990. Thermal Transport Properties of Selected Advanced Ceramic Composites, Ph.D. Thesis, University of Delaware.
14. Maxwell, J. C., 1904. A Treatise on Electricity and Magnetism. Volume 1 3rd Edition, Oxford:Clarendon Press, pp. 435 - 440.

**DATE**

**FILMED**

**10 / 13 / 94**

**END**