$MoSi_2$–BASE COMPOSITE FOR ENGINE APPLICATIONS

MOHAN G. HEBSUR
NYMA Inc.
Brookpark, Ohio

and

Michael V. Nathal
NASA Lewis Research Center
Cleveland, Ohio

Introduction

The intermetallic compound $MoSi_2$ has long been known as a high temperature material that has excellent oxidation resistance and electrical/thermal conductivity. Also its low cost, high melting point (2023 °C), relatively low density (6.2 g/cm^2 versus 8 g/cm^2 for current engine materials), and ease of machining make it an attractive structural material (ref. 1). However, the use of $MoSi_2$ has been hindered because of the brittle nature of the material at low temperatures, inadequate creep resistance at high temperatures, accelerated oxidation (also known as "pest" oxidation) at temperatures between approximately 400 and 500 °C, and a coefficient of thermal expansion (CTE) that is relatively high in comparison to potential reinforcing fibers such as SiC. This CTE mismatch between the fiber and the matrix resulted in severe matrix cracking during thermal cycling.

Maloney and Hecht (ref. 2) have done extensive work on the development of continuous-fiber-reinforced $MoSi_2$-base composites to achieve high temperature creep resistance and room temperature toughness. Candidate fibers consisted of ductile refractory metal fibers and high strength ceramic fibers. Refractory metal fiber reinforcement of $MoSi_2$ matrix composites was shown to increase both creep strength and fracture toughness. The addition of about 40 vol % of SiC in the form of whiskers and particulate was shown to lower the thermal expansion of $MoSi_2$-base matrix and prevent matrix cracking in a refractory fiber-reinforced composite. However, there was a severe reaction between refractory fibers and the matrix. Matrix cracking was observed during consolidation with an SCS-6-fiber-reinforced composite, even with the matrix containing up to 40 vol % SiC (40SiC) to modify thermal expansion. The SCS-6/$MoSi_2$-40SiC composite survived five thermal cycles at 1300 °C but was completely destroyed within 100 hours of exposure to air at 500 °C.

The pesting phenomenon was caused by the formation of voluminous Mo oxides in the microcracks. During the accelerated oxidation, MoO_3 and SiO_2 were simultaneously formed in amounts determined by their concentrations in the intermetallic. The accelerated oxidation is a necessary, but not sufficient, condition for pesting. Recent improvements in the fabrication of $MoSi_2$ have led to materials with less porosity that are correspondingly less susceptible to pest attack. However, because of increased surface areas and fabrication complexities from incorporating reinforcement phases in $MoSi_2$-based composites, pesting of composite materials is still a major concern.

Earlier work (ref. 3) to develop a $MoSi_2$ matrix suitable for SiC fiber reinforcement was carried out at NASA Lewis under the High Speed Civil Transport Enabling Propulsion Materials (HSCT/EPM) program. In that work, the addition of about 30 to 50 vol % of thermodynamically stable Si_3N_4 particulate was found to improve the low temperature accelerated oxidation resistance of $MoSi_2$ by forming a Si_2ON_2 protective scale, which eliminated the catastrophic pest failure. The Si_3N_4 addition doubled the low temperature toughness and increased the high temperature creep resistance of $MoSi_2$ by 5 orders of magnitude. More important, adding Si_3N_4 significantly lowered the CTE of the $MoSi_2$ and eliminated matrix cracking in SCS-6 reinforced composites, even after thermal cycling. These encouraging preliminary results led to a joint program for further development between Pratt & Whitney, the Office of Naval Research, and NASA Lewis. The overall aim of this long-range program is to develop these composites for advanced aircraft engine applications so that they can compete with the current superalloys and

other advanced materials, primarily ceramic matrix composites (CMC's, see Fig. 1). A turbine blade outer air seal (BOAS) for the Pratt & Whitney ATEGG/JTD engine demonstrator was chosen as the first component upon which to focus. This paper briefly describes the progress made so far in developing $MoSi_2$-base hybrid composites.

Microstructure and Properties of SCS-6/$MoSi_2$-Base Composites

Figure 2 shows the transverse microstructure of the as-fabricated SCS-6 composite. Although in this case fiber distribution was not uniform, Fig. 2 clearly indicates an absence of matrix cracking. The CTE measurements made on the matrix-only plate and those made on the composites are plotted as a function of temperature in Fig. 3. The CTE's of monolithic $MoSi_2$, Si_3N_4, and SiC (ref. 2) are also included in this figure. It is clear from Fig. 3 that adding Si_3N_4 to $MoSi_2$ effectively lowered the CTE of the matrix, thereby reducing the CTE mismatch with the fibers; hence, no matrix cracks were found in the composite (Fig. 2). Figure 4 shows the SCS-6/$MoSi_2$ and SCS-6/$MoSi_2$-30Si_3N_4 composites exposed at 500^0 C. The SCS-6/$MoSi_2$ specimen, which had matrix cracks, was completely destroyed; it turned into powder within 24 cycles, whereas the SCS-6/$MoSi_2$-30 Si_3N_4 specimen was intact even after 200 cycles and did not show any pest oxide.

Figure 5 plots the load verses time for the SCS-6/$MoSi_2$-30Si_3N_4 monolithic, chevron-notched, 4-point- bend specimens tested at room temperature (RT). Even after testing for 2 hours, the composite specimen did not break. The critical stress intensity factor K_q, calculated from the maximum load data, was greater than 35 MPa•$m^{0.5}$. This indicates that the composite specimen was seven times tougher than the monolithic material. The toughness of the hybrid composite also increased with temperature, reaching as high as 65 MPa•$m^{0.5}$, at 1400 °C in an argon atmosphere. Charpy impact tests were conducted on ASTM standard specimens of the $MoSi_2$-50Si_3N_4 matrix and the SCS-6/$MoSi_2$-50Si_3N_4 hybrid composite between 23 (RT) and 1400 °C in air. The force-verses-time curves obtained from the Charpy impact tests indicate that much more energy is required for crack initiation in the composite specimens and that substantial energy is absorbed during crack propagation. The impact test results also showed that the impact resistance increased with an increase in temperature, and fiber reinforcement improved resistance by nearly five times, from 2.5 to 12 J (almost equal to cast Ni-base super alloys). The impact resistance of both the monolithic and the hybrid composite was superior to any material in the literature data on high temperature intermetallic or ceramic-based materials (Fig. 6).

In Fig. 7 the RT tensile stress-strain curve for SCS-6/$MoSi_2$-Si_3N_4 indicates composite-like behavior and three distinct regions: an initial linear region, followed by a nonlinear region, and a second linear region. The nonlinear region is due to matrix-cracking normal to the loading direction. The second linear region is controlled by fiber bundle strength. The carbon layer on SCS-6 fibers appears to have a significant influence on mechanical properties, particularly the tensile strain to fracture, which is a measure of composite toughness. The RT tensile stress-strain curves shown in Fig. 7 clearly demonstrate not only improved strength and toughness but also a graceful failure due to fiber pull-out. Tensile tests showed the temperature dependence of the ultimate tensile strength (see Fig. 8). For comparison, the data from SCS-6/RBSN (ref. 4) are also included. The $MoSi_2$ composite exhibits higher strength than SCS-6/RBSN at temperatures up to 900 °C; beyond that, it starts losing strength. Unlike CMC's, which have about 20 percent porosity, the $MoSi_2$-base composite is fully dense in the as-fabricated condition and, hence. exhibits a higher modulus than CMC's do. Preliminary results of stress rupture tests carried out on SCS-6 [0°]/$MoSi_2$-50Si_3N_4 composite specimens between 1000 and 1200 °C in vacuum indicated that this material is superior to Ni-base superalloys but inferior to monolithic ceramics such as AS 800 (AlliedSignal). A specimen tested at these temperatures exhibited the classical creep curve with a minimum creep rate of $2x10^{-9}$ sec^{-1}.

Advanced Processing and Fibers for Low Cost and Complex Shaped $MoSi_2$-Base Composites

Most of the outstanding strength and toughness values reported thus far were achieved with composites reinforced with SCS-6 fibers. This fiber does not have adequate creep strength at the high temperatures envisioned for $MoSi_2$, and it is too large to be bent around the sharp radii needed to make complex shapes. Finer diameter fibers would offer better cost, shape-making, creep resistance, and toughness properties. Hi-Nicalon (Nippon Carbon) is currently the best available fiber, although NASA's EPM program is developing improved SiC fibers that would be appropriate for a $MoSi_2$-Si_3N_4 matrix. In earlier studies, we used the powder cloth technique to produce composites. However, because this process is highly labor intensive and does not produce uniform fiber distribution, we recently

switched to tape casting as the powder/metallurgy method for composite fabrication. Melt infiltration and chemical vapor infiltration are popular methods for processing of CMC's because of the potential for shape making and the lower cost, but they cannot produce thickness larger than 0.25 in. Problems with segregation and porosity are also aggravated in thick specimens made by these techniques. However, composites with small diameter fibers, such as SCS-9-reinforced (75-um diam.) and coated Hi-Nicalon-reinforced (18- to 20-um diam.) $MoSi_2$-Si_3N_4 composites were successfully fabricated in thickness greater than 0.4 in. Figure 9(a) clearly illustrates the range in fiber diameter in this study. Note how switching from powder cloth to tape casting improved the fiber spacing control. Figure 9 (b) displays efficient spreading of the fiber tows and infiltration of $MoSi_2$-Si_3N_4 powder particles.

As part of a study to investigate the influence of fiber diameter and architecture on mechanical behavior, tensile and fracture toughness tests were conducted on specimens of SCS-6-, SCS-9-, and BN/SiC-coated Hi-Nicalon/$MoSi_2$-$50Si_3N_4$ hybrid composites at RT (Fig. 10 (a) and (b)). Testing in the [0°] direction produced the highest strength (700 to 1000 MPa) and total strain (1.2 percent) to failure. Testing in the [90°] direction produced the lowest ultimate tensile strength, only 72 MPa, and strain (0.04 percent) to failure fora SCS-6-reinforced composite. The Hi-Nicalon-reinforced composite exhibited high strength and strain to failure in the [0°/90°] direction (about 60 percent of unidirectional values). RT fracture toughness also followed the same trend (Fig. 10 (a)). The SEM micrograph of fracture surfaces shows more fiber pullout in the Hi-Nicalon-reinforced composite than in the SCS-6 reinforced composite (Fig. 10(b)). The Hi-Nicalon/$MoSi_2$-Si_3N_4 in the [0°/90°] direction has a higher fracture toughness value than Hi-Nicalon/SiC, the CMC's, and Hi-Nicalon/Si_3N_4 in the [0°] direction (see Fig. 10 (c)). Because the CMC's were processed at much higher temperatures, the fibers were degraded, thereby decreasing the toughness; Hi-Nicalon/$MoSi_2$-Si_3N_4 was processed at lower temperatures and, therefore, exhibited lower toughness.

Conclusions

A wide spectrum of mechanical and environmental properties have been measured in order to establish feasibility of an $MoSi_2$-base composite with Si_3N_4 particulate and SiC fibers.The high impact resistance of the composite is of particular note , as it was a key property of interest listed by Pratt & Whitney. Processing issues have also been addressed in order to lower cost and improve shape making capability. These results indicate that this composite system remains competitive with other ceramics as potential replacement for superalloys.

Acknowledgments

The authors would like to acknowledge the Office of Naval Research, Washington, DC, and Pratt & Whitney Aircraft, West Palm Beach, FL, for financial support. Help received from Drs. P. Bartolotta and M. Verrilli during mechanical testing is also gratefully acknowledged.

References

1. Vasudevan, A.K.; and Petrovic, J.J.: A Comparative Overview of Molybdenum Disilicide Composites: High Temperature Structural Silicides. Proceedings of the High Temperature Structural Silicides Workshop, Gaithersburg, MD, 1991, pp 1-17.

2. Maloney, M.J.; and Hecht, R.J.: Development of Continuous-Fiber-Reinforced $MoSi_2$-Base Composites. Proceedings of the High Temperature Structural Silicides Workshop, Gaithersburg, MD, 1991, pp. 19-31.

3 Hebsur, M.G.: Pest Resistant and Low CTE $MoSi_2$-Matrix for High Temperature Structural Applications. Mat. Res. Soc. Symp. Proc., vol. 350, 1994, pp. 177-182.

4. Bhatt, R.T.; and Phillips, R.E.: Laminate Behavior for SiC Fiber-Reinforced Reaction-Bonded Silicon Nitride Matrix Composites, NASA TM–101350, 1988.

5. Nakano, K. et al.: SiC- and Si_3N_4-Matrix Composites According to the Hot-Pressing, High Temperature Ceramic-Matrix Composites II. Manufacturing and Materials Development, A.G. Evans and R. N. Nasalin, eds., American Ceramic Society, 1995, pp. 215-229.

$SiC/MoSi_2$ COMPOSITE
NASA/P&W/ONR PROGRAM

- **OVERALL OBJECTIVE:**
  To provide R & D support to complement Pratt and Whitney's larger effort of developing IMC Blade Outer Air Seals (BOAS) for ATEGG/JTD Engines.

- **SPECIFIC OBJECTIVE:**
  To investigate the technical feasibility of SiC continuous fiber reinforced $MoSi_2$-base hybrid composites (IMC). This material system offers the potential for improved properties over the current baseline SiC particulate reinforced $(MoW)Si_2$-system. The longer range goal is cost reduction through processing.

Fig. 1

SEM-BSI OF AS-FABRICATED SCS-6/$MoSi_2$-30Si_3N_4 COMPOSITE SHOWING NO MATRIX CRACKING

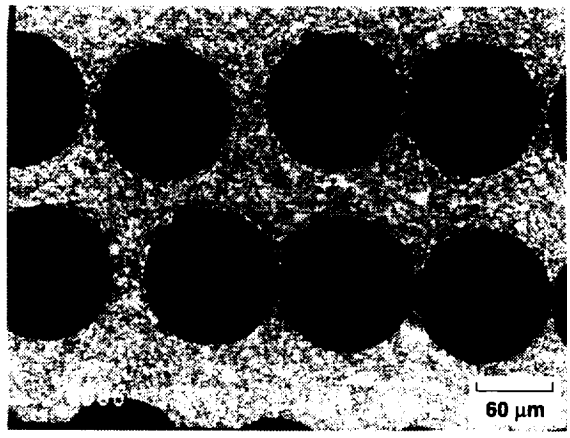


Fig. 2

CTE OF $MoSi_2$ REDUCED EFFECTIVELY BY THE ADDITION OF FINE Si_3N_4 PARTICULATE

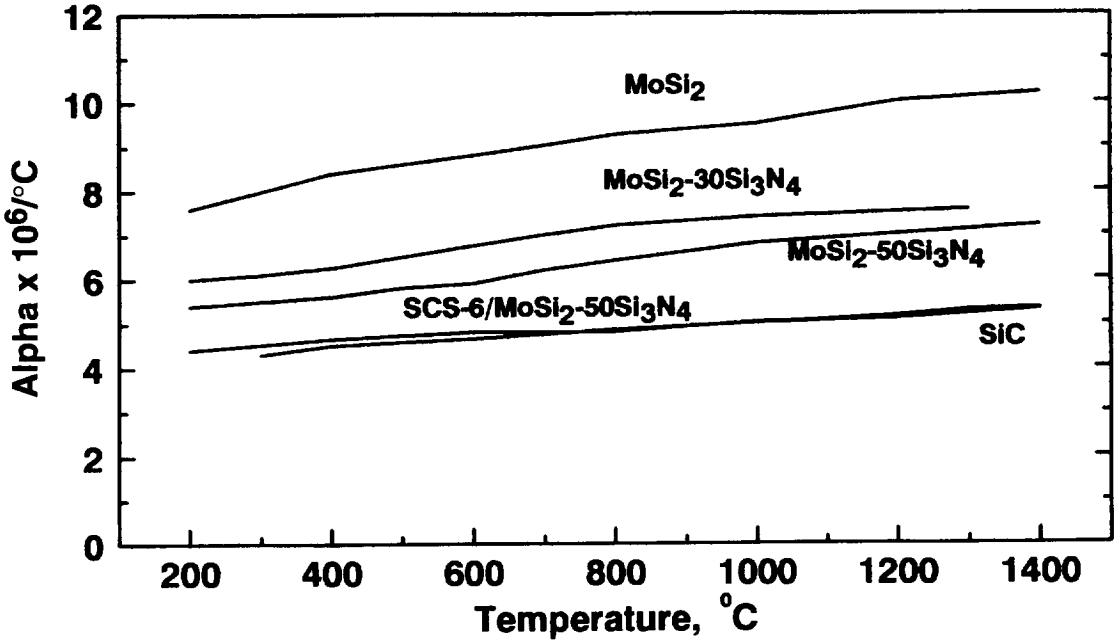
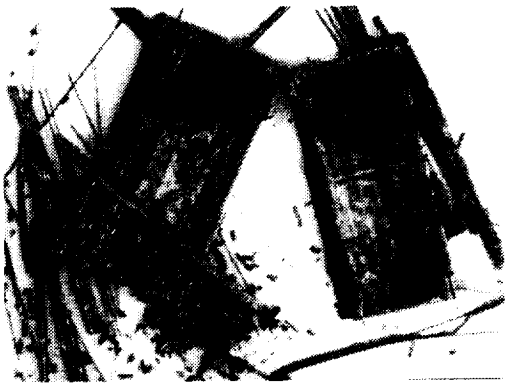


Fig. 3

SILICON NITRIDE ADDITION TOTALLY ELIMINATED PESTING IN MOLY DISILICIDE-BASE COMPOSITES

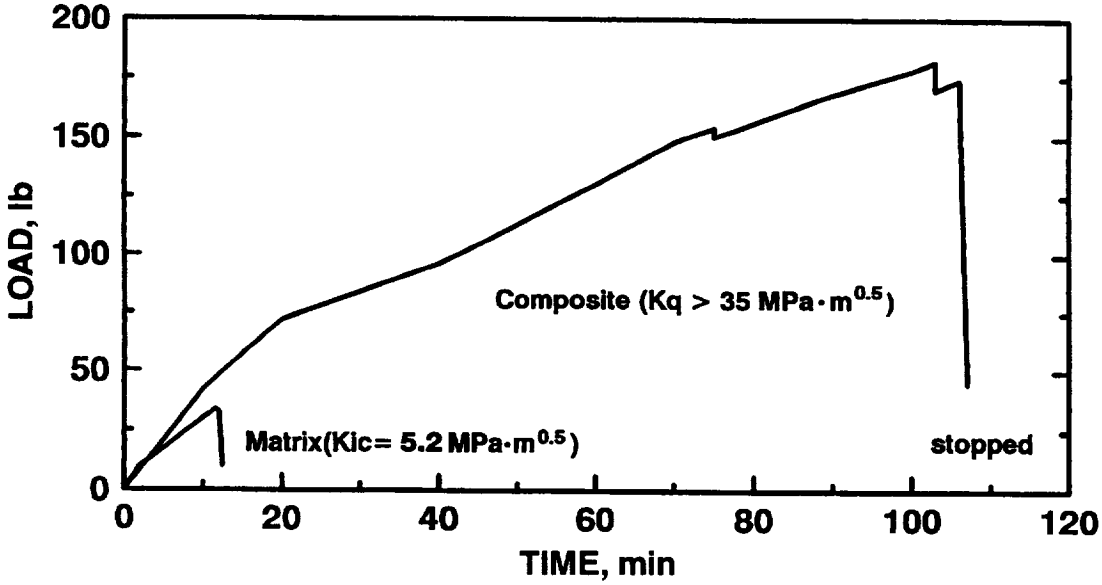


SCS-6/$MoSi_2$
500 °C/24 cycles
Pested

SCS-6/$MoSi_2$-Si_3N_4
500 °C/200 cycles
No pesting

Fig. 4

SCS-6/$MoSi_2$-Si_3N_4 COMPOSITE EXHIBITS SUPERIOR TOUGHNESS BEHAVIOR AT ROOM TEMPERATURE



STRAIN RATE = $1.2x10^{-5}$ s^{-1}

Fig. 5

CVN ENERGY vs TEMPERATURE PLOT FOR $MoSi_2$-BASE COMPOSITES COMPARED WITH OTHER MATERIALS

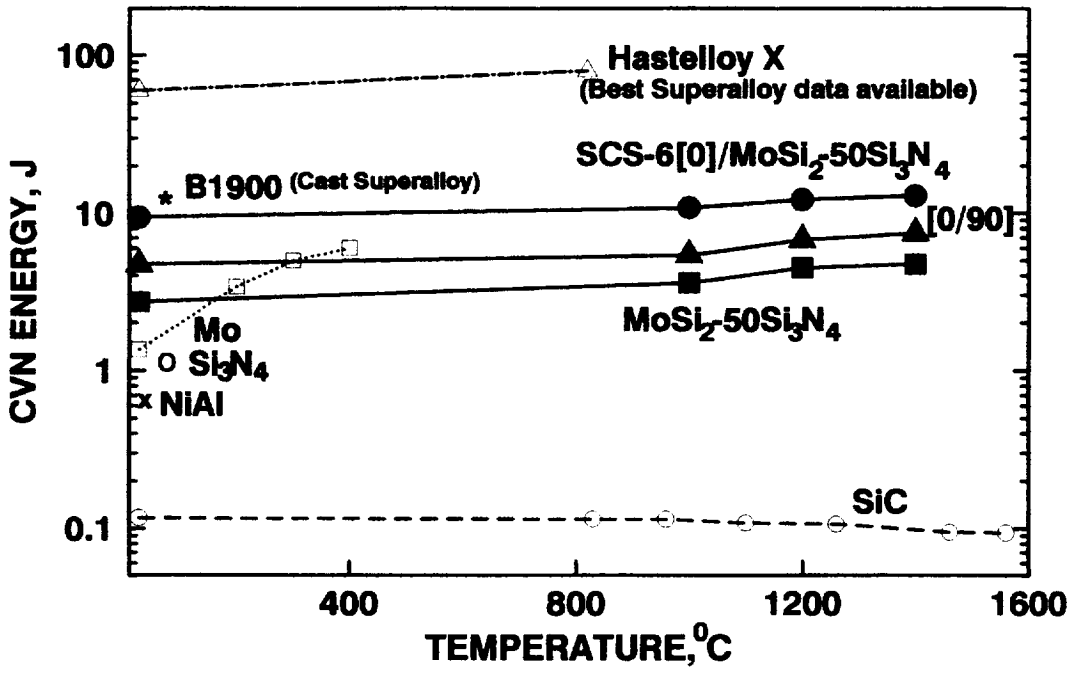


Fig. 6

ROOM TEMPERATURE STRESS-STRAIN CURVES FOR SCS-6/$MoSi_2$-30Si_3N_4 EXHIBIT A COMPOSITE LIKE BEHAVIOR

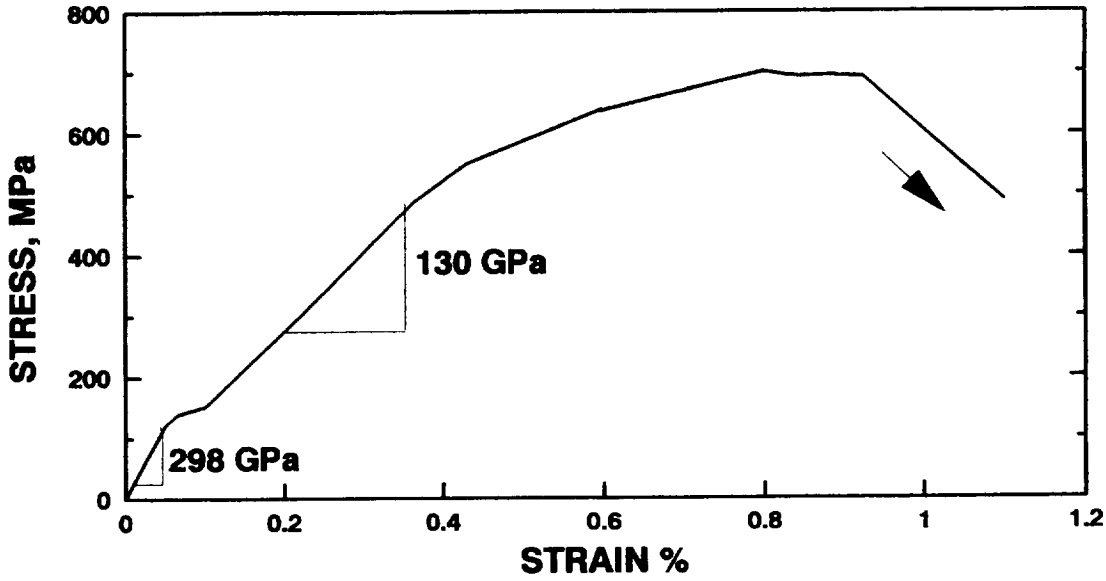


Fig. 7

TEMPERATURE DEPENDENCE OF ULTIMATE TENSILE STRENGTH OF SCS-6/$MoSi_2$-Si_3N_4 COMPOSITE

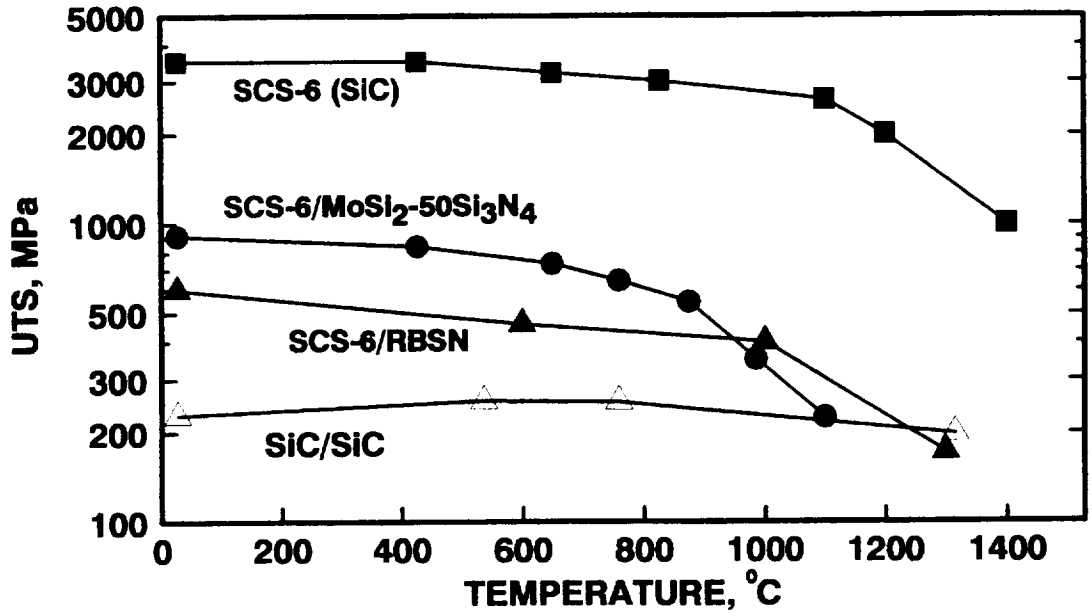
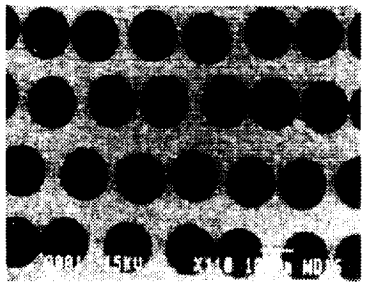


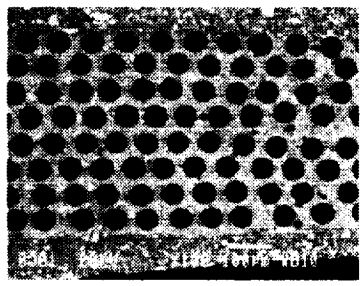
Fig. 8

PROCESS DEVELOPMENT FOR $MoSi_2$-Si_3N_4/SiC HYBRID COMPOSITES

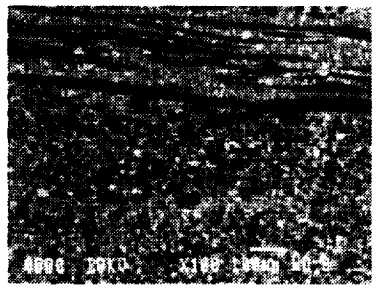
- Finer Diameters for Near-Net Shape Capability
- Improved Fiber Spacing Control
- Potential for Lower Cost



1993 Status
SCS-6 Fibers
150 μm diameter
(Powder Cloth Process)



1995 Status
SCS-9 Fibers
75 μm diameter
(Tape Cast)



1995 Status
Hi-Nicalon
20 μm diameter
(Tape Cast)

Fig. 9(a)

BN/SiC COATED Hi-NICALON/$MoSi_2$-50Si_3N_4 COMPOSITE SHOWING GOOD INFILTRATION

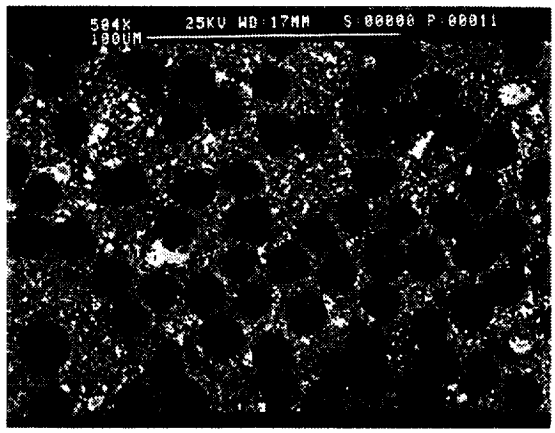
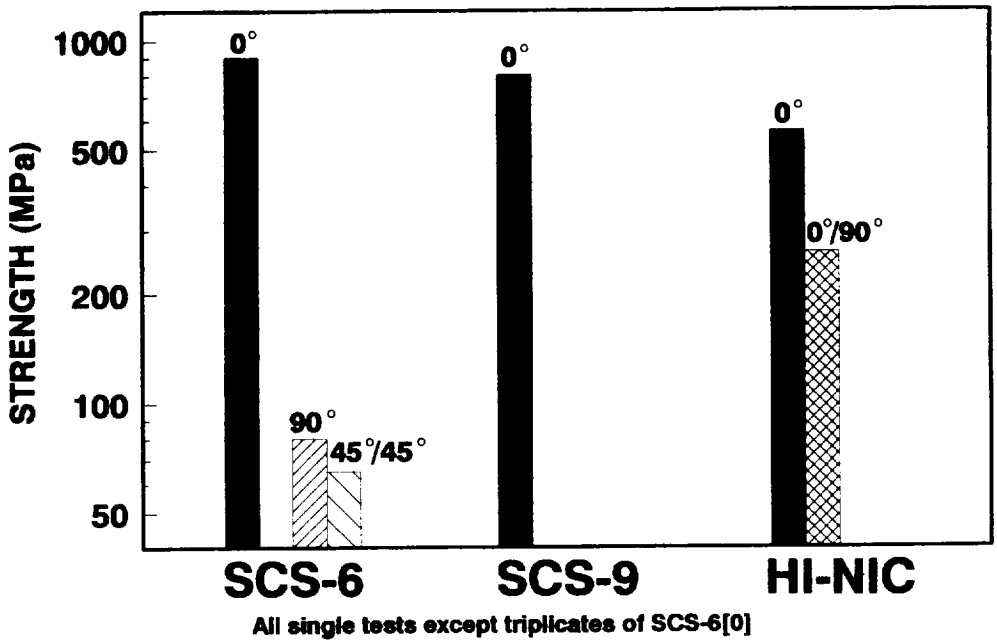


Fig. 9(b)

INFLUENCE OF FIBER DIAMETER AND ARCHITECTURE ON RT TENSILE STRENGTH OF $MoSi_2$-BASE COMPOSITES



All single tests except triplicates of SCS-6[0]

Fig. 10(a)

INFLUENCE OF FIBER DIAMETER AND ARCHITECTURE ON RT FRACTURE TOUGHNESS OF $MoSi_2$-BASE COMPOSITES

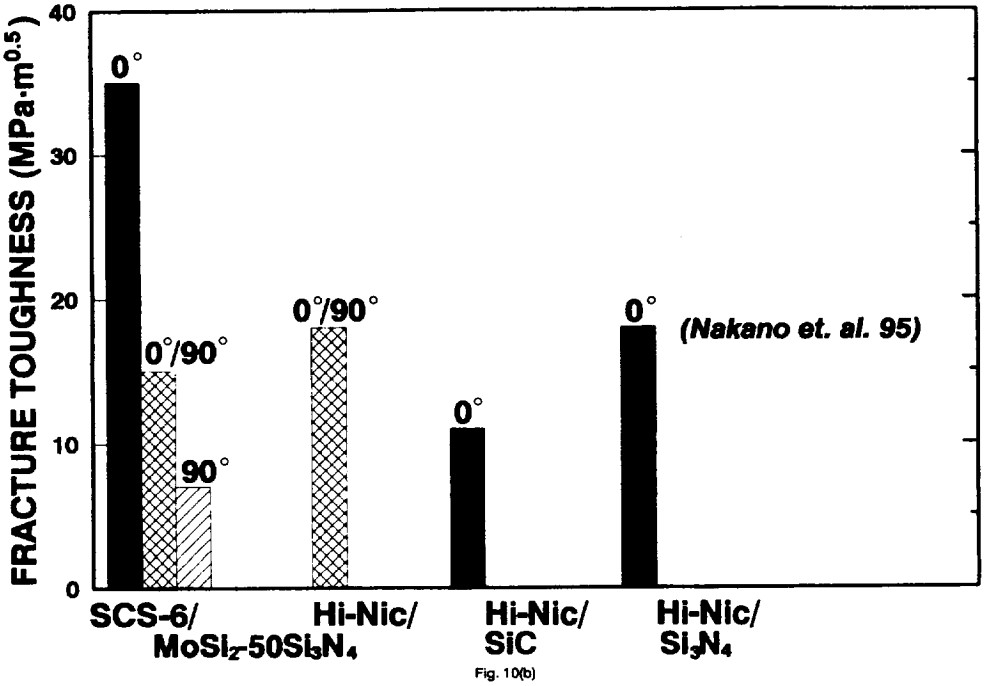
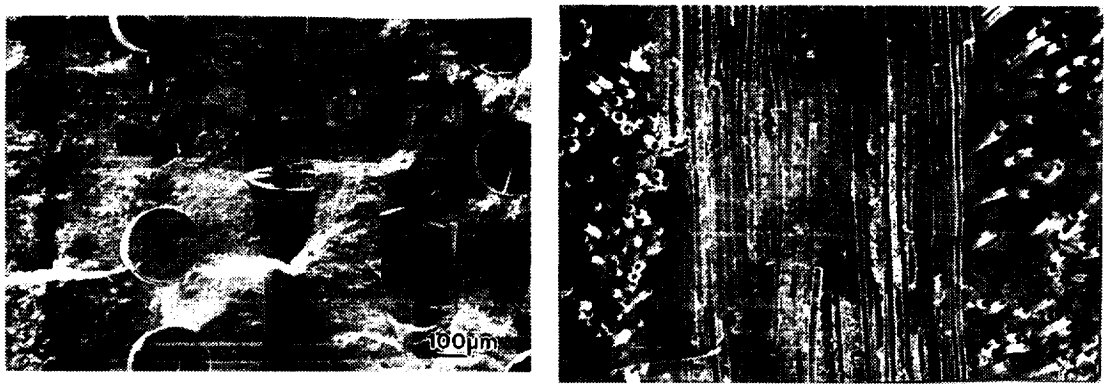


Fig. 10(b)

SEM-SE IMAGES OF RT FRACTURE TOUGHNESS TESTED SPECIMENS



SCS-6 [0/90°] BN/SiC/Hi-Nic [0/90°]

$MoSi_2$-50Si_3N_4 MATRIX

Fig. 10(c)

SUMMARY

HYBRID COMPOSITE:
($MoSi_2$+Si_3N_4 particulate + continuous SiC fibers)

- **Si_3N_4 particulate**
  - **Eliminated pest**
  - **Improved creep and oxidation resistance**
  - **Lowered CTE and density**
  - **Doubled the RT fracture toughness**

- **SiC fibers**
  - **Increased toughness at all temperatures**
  - **Increased UTS and allowed "graceful failure"**
  - **Improved impact resistance five-fold**
  - **Tensile creep properties evaluated**
  - **Tensile and toughness evaluated as a function of fiber architecture and diameter**

- **Processing**
  Larger and thicker composites fabricated with improved fiber spacing and finer diameter fibers by tape casting technique

Fig. 11

CONCLUSION

- $MoSi_2$-base hybrid composites remain competitive with state-of-art ceramics as replacement for superalloys in jet engines

FUTURE PLANS

- Continue exploring lower cost processing of hybrid composites
- Continue $MoSi_2$-Si_3N_4 development
- Mechanical properties evaluation
- Optimizing fiber coatings

Fig. 12