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## Abstract

Strong, tough and almost fully dense Hi-Nicalon/BN/SiC fiber reinforced celsian matrix composites have been fabricated by impregnation of the fiber tows with the matrix slurry, winding on a drum, stacking the prepreg tapes in the desired orientation, and hot pressing. The monoclinic celsian phase in the matrix was produced *in situ*, during hot pressing, from a mixed oxide precursor. The unidirectional composites having ~42 volume percent of fibers exhibited graceful failure with extensive fiber pullout in three-point bend tests at room temperature. Values of first matrix cracking stress and strain were 435 ± 35 MPa and 0.27 ± 0.01 %, respectively, and ultimate strengths of 900 ± 60 MPa were observed. The Young's modulus of the composites was 165 ± 5 GPa.

## I. Introduction

Ceramic matrix composites are strong, tough, environmentally stable, light in weight, and have the ability to withstand high operating temperatures. This makes them viable candidate materials for high temperature structural applications in aerospace, utilities, and transportation industries. Various glass-ceramic matrices reinforced with continuous ceramic fibers have been developed[1,2] over the last two decades. Barium aluminosilicate with monoclinic celsian phase is one of the most refractory glass-ceramic.[1] It has a melting point of >1700°C, is phase stable to ~1600°C, and is oxidation resistant. Processing and properties of celsian glass-ceramic matrix composites reinforced with large diameter CVD SiC monofilament[3-5] multifilament small diameter Nicalon[6], and HPZ[7] fibers have been described earlier. In order to achieve stoichiometric celsian composition, the matrix is synthesized[8] by solid state reaction between the metal oxides. The objective of the present

study was to characterize the room temperature mechanical properties of Hi-Nicalon fiber-reinforced celsian matrix composites. Monoclinic celsian in the matrix was produced from the mixed metal oxides, *in situ*, during hot pressing of the composite. Strong, tough, and almost fully dense unidirectional fiber-reinforced composites were obtained.

## II. Materials and Experimental Procedure

Polymer derived Hi-Nicalon fiber tows (1800 denier, 500 filaments/tow) with low oxygen content from Nippon Carbon Co. were used as the reinforcement[9-10]. Hi-Nicalon fibers having a duplex surface layer of BN overcoated with SiC were used in the present study. The fiber coatings were applied by a commercial vendor using a continuous chemical vapor deposition (CVD) reactor. The BN coating was deposited at ~1000°C utilizing a proprietary precursor and was amorphous to partly turbostratic in nature. A thin overcoating of SiC was also deposited by CVD onto the BN-coated fibers. The SiC layer was crystalline. The nominal coating thicknesses were 0.4 μm for BN, and 0.3 μm for SiC. The BN interfacial layer acts as a weak, crack deflecting phase, while the SiC overcoat acts as a barrier to diffusion of boron from BN into the oxide matrix and also prevents diffusion of matrix elements into the fiber.

The matrix of 0.75BaO-0.25SrO-$Al_2O_3$-2$SiO_2$ (BSAS)composition was synthesized by a solid-state reaction method[8]. The starting materials used were $BaCO_3$ (Alfa Products), $SrCO_3$(Alfa Products), $Al_2O_3$ (Baikowski International Corp., high purity CR 30), and $SiO_2$ (Cerac Inc., 99.9% purity, -325 mesh) powders. Appropriate quantities of various powders were slurry mixed and ball milled for ~24 h using alumina milling media. The mixed powder was calcined at ~900 - 910°C to decompose the carbonates into oxides, followed by cooling to room temperature and grinding. TGA analysis of this calcined powder showed no further weight loss indicating complete decomposition of the metal carbonates during the calcination step. The calcined powder consisted[8] of mainly $SiO_2$ (α-quartz) and $BaAl_2O_4$ phases with small amounts of $Ba_2SiO_4$, α-$Al_2O_3$, and $Ba_2Sr_2Al_2O_7$ also present. This powder was made into a slurry by dispersing it in an organic solvent along with organic

additives as binder, surfactant, deflocculant and plasticizer followed by ball milling .

The experimental set up and the procedure used for fabrication of the fiber-reinforced celsian matrix composites were essentially the same as described earlier[11]. Tows of BN/SiC-coated Hi-Nicalon fibers were coated with the matrix precursor by passing them through a slurry and winding on a rotating drum. After drying, the prepreg tape was cut to size. Unidirectional fiber-reinforced composites were prepared by tape lay-up (12 plies) followed by warm pressing to form a "green" composite. The fugitive organics were slowly burned out of the sample in air, followed by hot pressing under vacuum in a graphite die to yield dense composites. The oxide precursor was converted into the desired monoclinic celsian phase *in situ* during hot pressing. The hot pressed fiber-reinforced composite panel was surface polished and sliced into test bars (~50.4 mm x 6.4 mm x 1.9 mm) for mechanical testing.

X-ray diffraction (XRD) patterns were recorded at room temperature using a step scan procedure (0.02°/2θ step, time per step 0.5 or 1 s) on a Phillips ADP-3600 automated diffractometer equipped with a crystal monochromator employing Cu $K_\alpha$ radiation. Density was measured from dimensions and mass as well as by the Archimedes method. Microstructures of the polished cross-sections and fracture surfaces were observed in a JEOL JSM-840A scanning electron microscope (SEM). Mechanical properties were determined from stress-strain curves recorded in three-point flexure using an Instron 4505 universal testing machine at a crosshead speed of 1.27 mm/min (0.05 in./min) and support span (L) of 40 mm. Strain gauges were glued to the tensile surfaces of the flexure test bars. Stress was calculated beam theory. The first matrix cracking stress was calculated from the stress-strain curves at the point where the curve deviates from linearity. Elastic modulus of the composite was determined from the linear portion of the stress-strain curve up to first matrix cracking using linear interpolation .

## III. Results and Discussion

The fiber volume fraction in the composites was calculated to be ~42 %. A typical

XRD pattern taken from the polished surface of the hot pressed composite is given in Fig. 1. Monoclinic celsian is the only crystalline phase detected and the undesired hexacelsian phase was not detected from XRD. This indicates that the desired, thermodynamically stable, monoclinic celsian phase is formed *in situ*, from the mixed oxides precursor, during hot pressing of the composite. Doping with SrO is known to facilitate[12,13] the formation of monoclinic celsian in the matrix.

SEM micrographs taken from the polished cross-section of a unidirectional composite are shown in Fig. 2. Uniform fiber distribution and good matrix infiltration within the fiber tows are evident. The manufacturer reports an average fiber diameter of ~14 μm, but a large variation in the diameter of the filaments within a fiber tow can be seen. The BN/SiC surface coating has been detached from some of the fibers during composite processing . This may lead to adverse reactions between the fibers and the oxide matrix at high temperature resulting in strong fiber-matrix bonding and a weak composite.

The fiber volume fraction in the composites was ~0.42.Typical stress-strain curves recorded in three-point flexure for the unidirectional BSAS matrix composites reinforced with BN/SiC-coated Hi-Nicalon fibers hot pressed at two different temperatures are shown in Fig. 3 and 4. The stress-strain curve for a hot pressed BSAS monolith is also given for comparison. The monolith shows a modulus of 96GPa, flexural strength of 131 MPa and fails in a brittle mode as expected. Both the composites show graceful failure. The values of first matrix cracking stress, $\sigma_{mc}$, the first matrix cracking strain, $\varepsilon_{mc}$, the elastic modulus, E, the ultimate strength, $\sigma_u$, and the ultimate strain, $\varepsilon_u$, of the composites hot pressed at two different temperatures are given in Table I. Values of first matrix cracking stress of 400 - 470 MPa, ultimate strength of 850 - 960 MPa and elastic modulus of 160 - 170 GPa have been observed. The measured elastic modulus is in very good agreement with a value of 169 GPa, calculated from the rule-of-mixtures ($E_c = V_m E_m + V_f E_f$ where V is the volume fraction and the subscripts c, m, and f refer to the composite, matrix, and fiber, respectively) using $E_m$ = 96 GPa[8] and $E_f$ = 270 GPa.[9,10] Values of first matrix cracking strain and the ultimate strain are ~0.26 - 0.28 % and ~0.6 - 0.8 %, respectively.

SEM micrographs of fracture surfaces from the two composites, after the three-point flexure tests, are shown in Fig. 5. Extensive fiber pullout length was observed for both samples indicating toughening behavior. Some matrix particles adhered to the pulled-out fibers. An SEM micrograph of the polished cross-section of a failed composite, after the flexure test, showing the crack propagation is presented in Fig. 6. Debonding at the fiber-matrix interface and crack deflection around the reinforcing fibers is observed indicating a tough composite. The results of this study indicate that reinforcement of celsian matrix with Hi-Nicalon fibers having a duplex BN/SiC coating results in a strong and tough composite.

## IV. Summary

Strong, tough, and almost fully dense celsian matrix composites reinforced with BN/SiC-coated Hi-Nicalon fibers have been produced. Unidirectional composites having ~42 volume percent of fibers exhibited graceful failure with extensive fiber pull out in three-point flexure test. The first matrix cracking stress of ~400 - 470 MPa and ultimate strength as high as 960 MPa have been observed. The first matrix cracking strain was ~0.26 - 0.28%. The elastic Young's modulus of the composites was measured to be ~165 GPa.

## V. Conclusion and Future Research

It may be concluded that reinforcement of the monoclinic celsian with BN/SiC-coated Hi-Nicalon fibers results in strong, tough, and almost fully dense composites.

Future research will involve the investigation of the mechanical properties (tensile strength, creep, fatigue, etc.) of unidirectional and cross-ply Hi-Nicalon/BN/SiC/Celsian composites at elevated temperatures in air and inert environments. The effects of high temperature annealing on room temperature residual strength will also be studied. The fiber-matrix interface will be characterized by electron microscopy as well as by fiber push-out and push-in tests.

## Acknowledgments

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**Table I. Room Temperature Mechanical Properties* of Hi-Nicalon/BN/SiC/Celsian Composites (Unidirectional; 12 Plies; $V_f = 0.42$)**

| Sample # | Density, ρ ($g/cm^3$) | Elastic modulus, E (GPa) | Yield stress, $\sigma_{mc}$ (MPa) | Yield strain, $\varepsilon_{mc}$ (%) | Ultimate stress, $\sigma_u$ (MPa) | Ultimate strain, $\varepsilon_u$ (%) |
|---|---|---|---|---|---|---|
| HI-NIC-BSAS-1-29-96 | 3.05 | 168<br>159 | 468<br>405 | 0.283<br>0.258 | 958<br>850 | 0.661<br>0.801 |
| HI-NIC-BSAS-1-31-96 | 3.09 | 170<br>165 | 436<br>464 | 0.264<br>0.283 | 862<br>960 | 0.583<br>0.771 |

*Measured in three-point flexure.
$\varepsilon_u$ = strain at peak load.

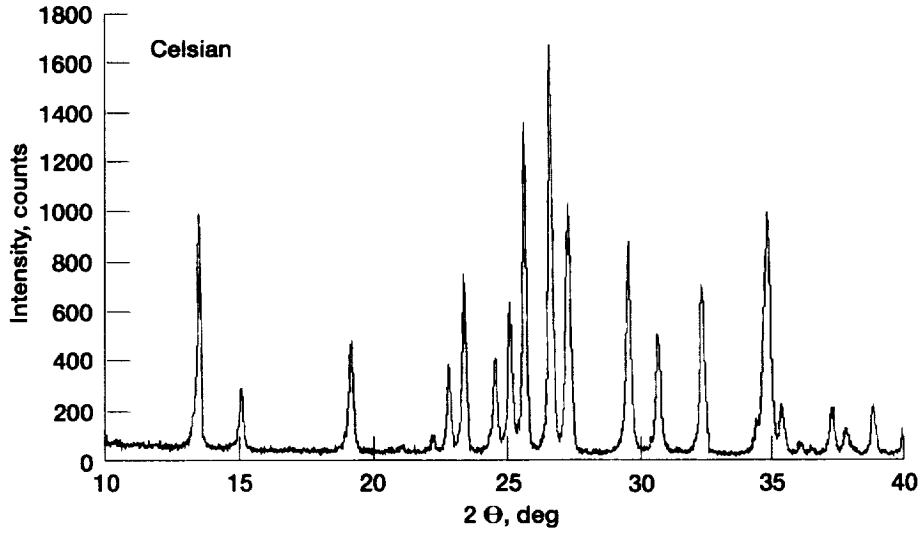


Figure 1.—Room temperature x-ray diffraction pattern from the surface of a Hi-Nicalon/BN/SiC/BSAS composite. All the peaks correspond to the monoclinic celsian phase.

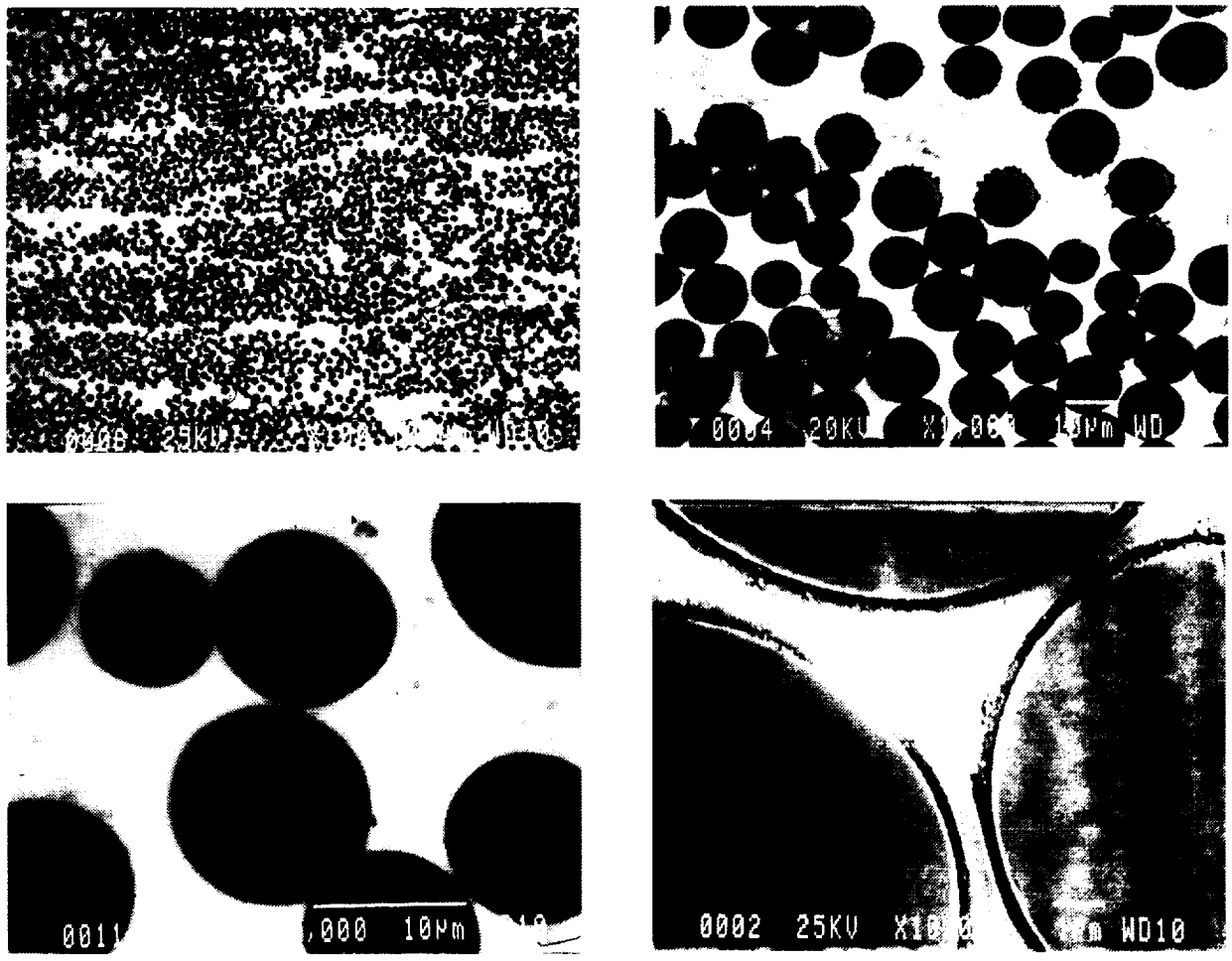


Figure 2.—SEM micrographs showing polished cross-section a unidirectional Hi-Nicalon/BN/SiC/BSAS composite.

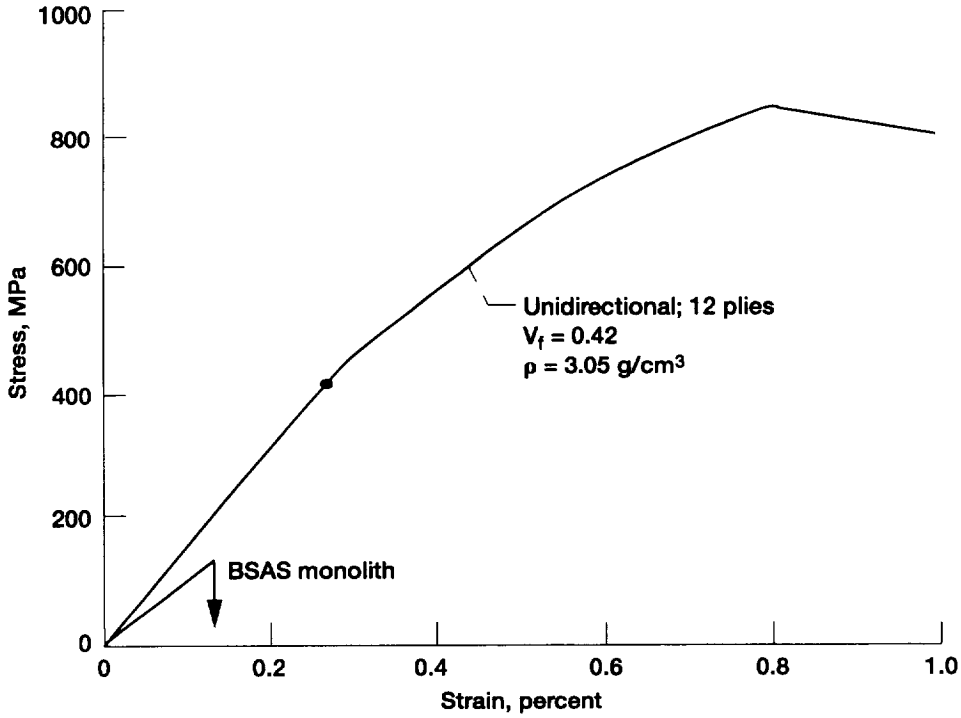


Figure 3.—Stress-strain curve recorded in three-point flexure for a unidirectional Hi-Nicalon/BN/SiC/BSAS composite hot pressed at lower temperature. Also shown are the results for a hot pressed BSAS monolith.

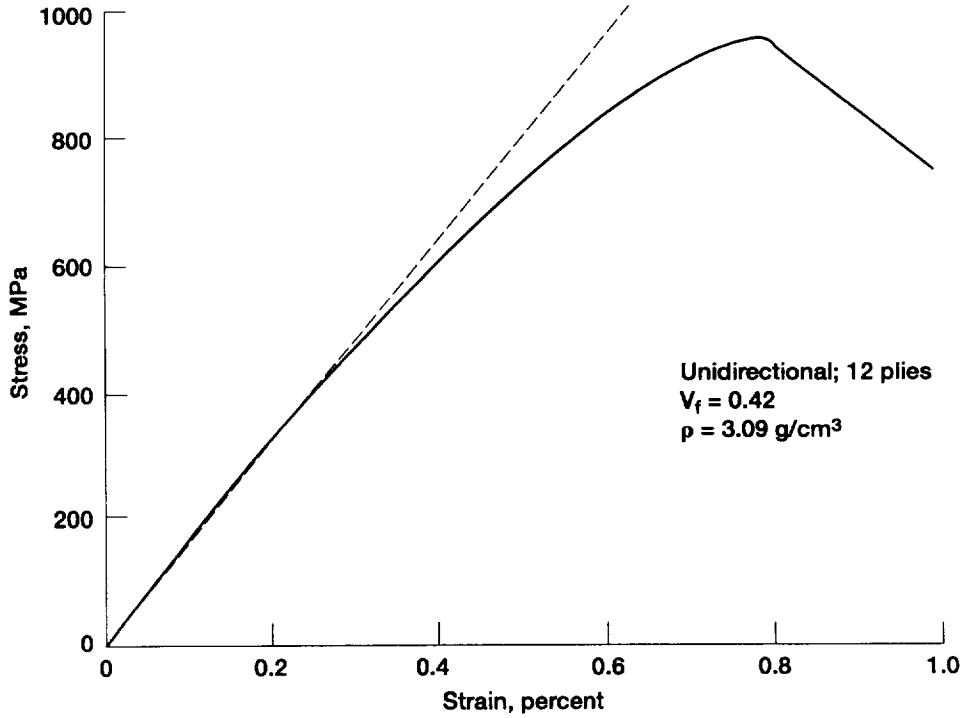


Figure 4.—Stress-strain curve recorded in three-point flexure for a unidirectional Hi-Nicalon/BN/SiC/BSAS composite hot pressed at higher temperature.

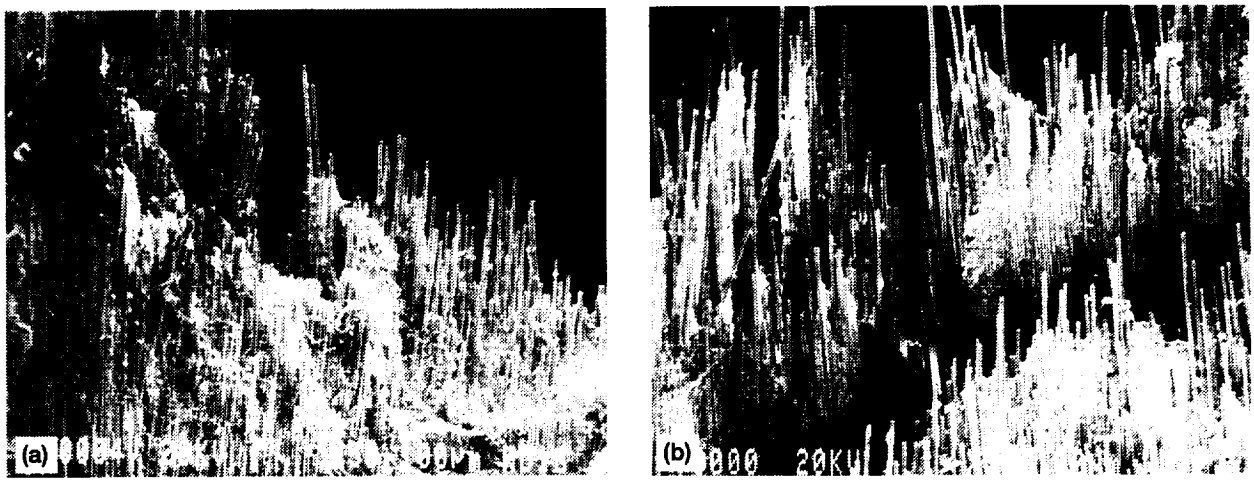


Figure 5.—SEM micrographs from the fracture surfaces of unidirectional Hi-Nicalon/BN/SiC/BSAS composites showing extensive fiber pullout; (a) hot pressed at lower temperature, (b) hot pressed at higher temperature.

Figure 6.—SEM micrograph from the polished cross-section of a failed unidirectional Nicalon/BN/SiC/BSAS composite after the flexure test showing fiber/matrix debonding, crack propagation and crack deflection around the fibers.

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