Characterization and properties of controlled nucleation thermochemical deposition (CNTD) - silicon carbide

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The present investigation was undertaken to characterize the microstructure of controlled nucleation thermochemical deposition (CNTD)-SiC material and to evaluate the room-temperature and high-temperature bend strength and oxidation resistance. Utilizing the CNTD process, ultrafine grained (0.01 to 0.1 μm) SiC was deposited on W wires (0.5 mm diameter by 20 cm long) as substrates. The deposited SiC rods had superior surface smoothness and were without any macrocolumnar growth commonly found in conventional CVD material. At both room and high temperature (1200 to 1380° C), the CNTD-SiC exhibited a bend strength of ~ 200 000 psi (1380 MPa), several times higher than that of hot-pressed, sintered, or CVD SiC. The excellent retention of strength at high temperature was attributed to the high purity and fine grain size of the SiC deposit and the apparent absence of grain growth at elevated temperatures. The rates of weight change for CNTD-SiC during oxidation were lower than for NC-203 (hot-pressed SiC), higher than for GE's CVD-SiC and CVD-Si$_3$N$_4$ but considerably below those for HS-130 (hot-pressed Si$_3$N$_4$). The high-purity fully dense and stable grain size CNTD-SiC material shows potential for high-temperature structural applications, however, problem areas might include scaling the process to make larger parts, deposition on removable substrates, and the possible residual tensile stress.

1. Introduction

During recent years silicon carbide (SiC) and silicon nitride (Si$_3$N$_4$) have been identified as valuable engineering materials for high-temperature heat engine applications because of their relatively good oxidation, creep, and thermal shock resistance; and their high hardness and high strength at elevated temperatures. These materials are produced by several fabrication techniques, e.g. sintering, reaction-sintering, hot-pressing, and vapour-deposition. Among these techniques, chemical vapour deposition (CVD) can produce highly pure and dense materials which are expected to have superior high-temperature properties. Furthermore, CVD is of interest as a method of making protective coatings as well as forming complex shapes. However, CVD often results in large grains or growth cones which produce larger flaws to limit strength, and textured deposits which result in residual stresses [1].

Recently, Chemetal Corporation* has developed a process called "controlled nucleation thermochemical deposition" (CNTD) [2]. The CNTD process is generically similar to the conventional CVD process but produces exceedingly fine-grain structures and can greatly reduce or eliminate growth cones to significantly improve mechanical properties. The refined microstructure of the CNTD process results when two competing reactions are allowed to proceed under conditions of controlled chemical, thermal or fluid dynamic instability. This instability causes interruption of the columnar grain growth and subsequent renucleation; hence finer grain size. In some systems two metastable compounds are formed one of which is transient. The temporary residence of the compound serves to interrupt the epitaxy, and hence reduce texture and grain size. Other embodiments of the general process include deliberately changing the chemical potential by adjusting system parameters or mechanically disturbing the surface to stop the columnar growth.

The purpose of this work was to characterize the microstructure of the CNTD-SiC material with respect to grain structure, stoichiometry, phase analysis etc., and to evaluate the room-temperature and high-temperature fracture and oxidation behaviour.

2. Experimental procedures

Test specimens were obtained from Chemetal Corporation. The experimental system used by Chemetal for deposition is schematically shown in Fig. 1. The main deposition chamber was an air-cooled 75 mm diameter quartz chamber. Tungsten wires of 0.5 mm diameter by 20 cm long were used as substrates. Argon-, hydrogen-, silicon-, and carbon-bearing gases were introduced through an injector at the top of the chamber. A clamshell heater was used to regulate the pre-heat temperature of the reactant stream. The temperature in the reactant stream was monitored by a thermocouple 1.27 cm from the filament and filament temperature was measured with a micro-optical pyrometer. Methyltrichlorosilane (MTS) was selected as the source of both carbon and silicon. A gas metering system was used for MTS in which argon was used as the carrier gas. The carrier gas was passed through a vessel containing MTS, the amount of MTS carried being dependent upon the vapour pressure of the liquid. Subsequently, the mixed stream was monitored through the use of an electronic mass flow meter. The MTS flow was determined by difference between the mixed stream and the carrier gas. Weight measurements of the MTS vessel before and after experiments served as an additional
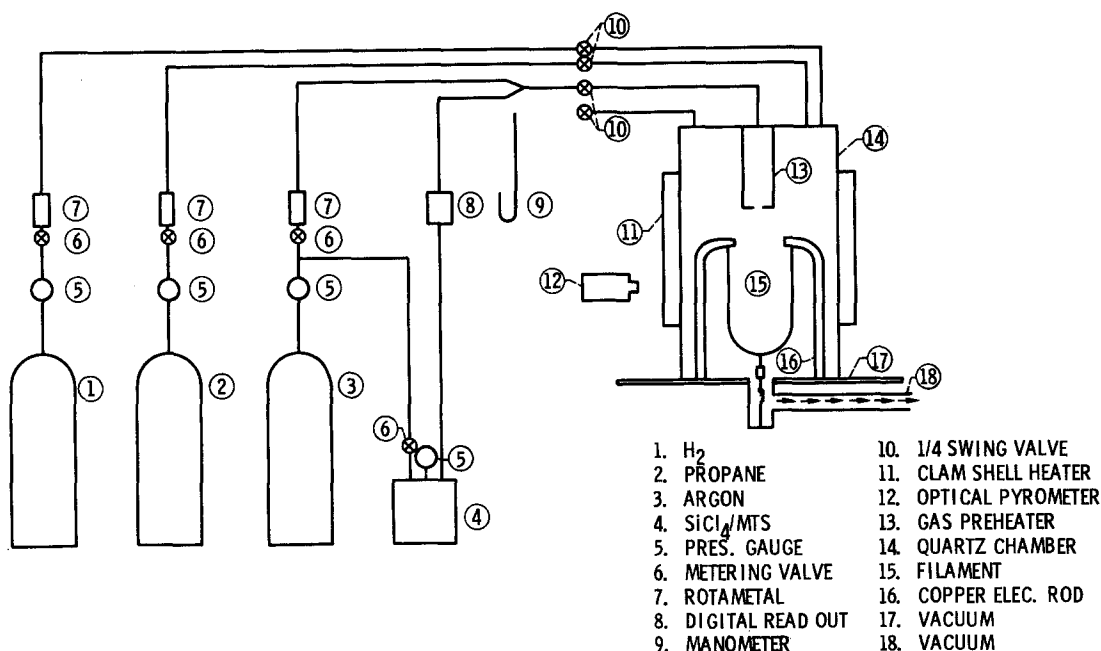

1. H_2	10. 1/4 SWING VALVE
2. PROPANE	11. CLAM SHELL HEATER
3. ARGON	12. OPTICAL PYROMETER
4. $SiCl_4$/MTS	13. GAS PREHEATER
5. PRES. GAUGE	14. QUARTZ CHAMBER
6. METERING VALVE	15. FILAMENT
7. ROTAMETAL	16. COPPER ELEC. ROD
8. DIGITAL READ OUT	17. VACUUM
9. MANOMETER	18. VACUUM

Figure 1 Gas flow schematic for CNTD-SiC (Courtesy of Chemetal Corporation, Pacoima, CA).

TABLE I Modulus of rupture test parameters for CNTD silicon carbide

Organization	Type of test	Outer span (cm)	Inner span (cm)	Loading rate (cm min^{-1})
NASA-Lewis	Four-point	1.90	0.95	0.05
NRL	Three-point	0.90		0.13

check on actual gas flows. The selection of deposition run time was made by monitoring power requirements to get deposits of 0.5 to 0.64 mm thick.

The resultant SiC deposits, rods ~ 1.5 mm or more in diameter on W filaments, were characterized by optical and electron microscopy for surface topography, and by spectrographic and X-ray diffraction for phase and composition identification. Microstructure analyses were conducted on polished and etched surfaces, fractured surfaces and on thin sections. Modulus of rupture measurements were made using both three- (Naval Research Laboratory) and four-point (NASA – Lewis Research Center) bend tests. Mechanical parameters employed by the different investigators during MOR test are listed in Table I. Fractographic analysis was conducted by optical and scanning electron microscopy to determine the nature of the fracture origins and to calculate fracture energy from the size of the observed flaws and the strength. For oxidation tests, coupons of the CNTD-SiC material were diamond sawed from thin discs (31 mm diameter by 2 mm thick) which had been deposited on graphite. The coupons were suspended from sapphire hooks in the constant temperature (within ± 0.5° C) zone of a controlled atmosphere furnace. Oxidation was carried out at 1550° C for 24 h in 150 Torr dry oxygen.

Bend tests were conducted in air at room temperature on as-deposited, abraded, oxidized, and abraded and oxidized specimens. The oxidation treatment was 1200° C in air for 100 h. The abrasion treatment was accomplished by moving the rods length-wise in and out of 320 or 600 grit SiC paper (dry) which was held between the thumb and opposing finger. Bend tests of as-deposited specimens at 1200 and 1380° C were conducted in air by four-point bending.

3. Results and discussion
3.1. Characterization
Spectrographic analysis of the as-deposited CNTD silicon carbide indicated only minor impurities

such as Al 240 ppm, B 250 ppm, Cr 70 ppm, Cu 90 ppm, and Fe 110 ppm. X-ray examination indicated that the material was mostly β-SiC with some free silicon suggesting a need for further improvement in the deposition process. Chemetal reported [2] that the deposition temperature, deposition pressure, and the mixture ratios are of some significance in determining stoichiometry and deposition rate. For example, at temperatures above 1300° C, carbon deposition was enhanced and tended to cause a coarse-grained nodular deposit. On the other hand, hydrogen partial pressures appeared to increase the percentage of free silicon.

Figs. 2 and 3 show differences in the as-deposited surface and grain structure obtained by CVD and CNTD deposition of SiC. Note the textured surface (Fig. 2a) and the coarse columnar grain structure (Fig. 3a) for the conventionally deposited CVD-SiC in contrast to the smooth surface topography of as-deposited CNTD-SiC (Fig. 2b) and its extremely fine grain structure (Fig. 3b). Examination by reflected light microscopy of polished sections both parallel and transverse to the CNTD deposition direction revealed very similar to sub-micron size grains. A typical example of this microstructure (transverse section) is shown in Fig. 4. Microstructural examination by transmission electron micrograph showed that the as-deposited CNTD crystallites ranged in size from 0.01 to 0.1 μm as shown in Fig. 5. The smaller crystallites appeared equiaxed, however, the larger ones were elongated in the growth direction and showed numerous stacking faults. No grain growth was observed in specimens annealed up to 1365° C for 100 h in vacuum this indicating a very stable grain size in this material.

3.2. Properties
3.2.1. Room temperature strength and fracture
The results summarized in Fig. 6, indicate average as-deposited four-point bend strengths, typically in the range of 200 000 psi (1400 MPa) with con-
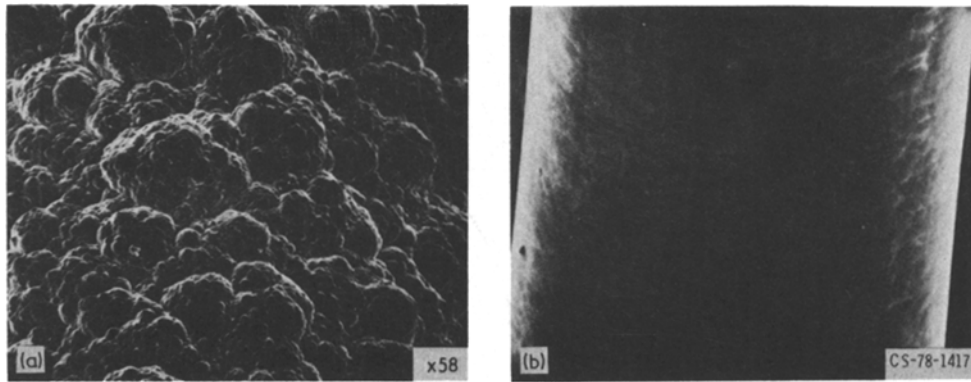
Figure 2 As-deposited surface topography of (a) Chemital CVD-silicon carbide (b) CNTD-silicon carbide.

siderable scatter, e.g. coefficients of variations of 50%. The three-point average bend strength was 250 000 psi (1725 MPa) with even more scatter. Light abrasion with dry 600 grit SiC-paper (primarily in a direction parallel with the length of the rod, i.e. the least detrimental direction of abrasion) reduced the average three-point bend strength to about 140 000 psi (950 MPa). More severe abrasion, e.g. with dry 320 grit SiC-paper, gave an average three-point bend strength of about 80 000 psi (550 MPa). After oxidation of the as-deposited rods at 1200° C for 100 h, an average three-point bend strength of 135 000 psi (924 MPa) was determined. On the other hand, oxidation of rods after abrasion with either 600 or 320 grit SiC-paper, gave an average three-point bend strength of about 190 000 psi (1300 MPa).

Fractographic examination of the room-temperature bend specimens provides three results. First, almost all fractures initiated from the SiC, or oxidized surface and not the W–SiC interface suggesting that the results were indicative of the behaviour of the SiC. However, the W rod often showed a fracture origin almost directly opposite that of the SiC (see Fig. 7). Fracture markings indicated that the cracks initiating at the SiC surface propagated inward towards and around the W core. The W core fractured from an origin at the point where the cracks in the SiC which proceeded around each side of the W core met, i.e. opposite to the origin in the SiC surface. This could indicate the presence of residual compressive stresses in the W or residual tensile stresses in the SiC.

The second fractographic result is insight into the strength results. While only about 20% of the failure-causing flaws could be identified in the
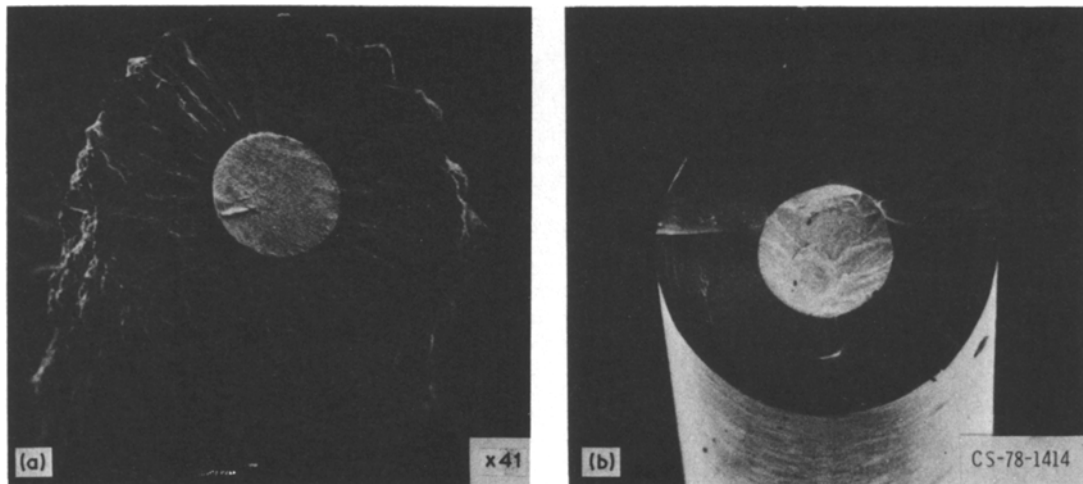

Figure 3 Fractured cross-section [2] of (a) Chemital CVD-silicon carbide showing columnar grain orientation (b) Chematal CNTD-silicon carbide showing homogeneoud non-columnar fine-grain deposit.
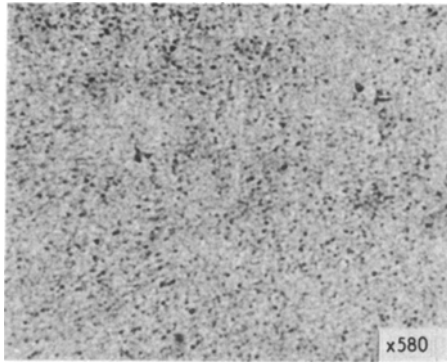
Figure 4 Microsctructures of CNTD-silicon carbide; electrolitic etch − chromic acid/HF; tranverse section.

as-deposited test rods, some of these flaws were clearly suggestive of local contact or impact damage, especially the lower strength samples. Such damage is consistent with lack of surface protection of the rods and could explain the variable as-deposited strengths. These results indicate that the as-deposited samples, i.e. without surface damage, would represent a distinctly higher strength population than the oxidized samples.

About 75% of the specific fracture origins of the abraded rods were identified. These origins were flaws characteristic of abrasion damage (see Fig. 8). Examination also showed that while
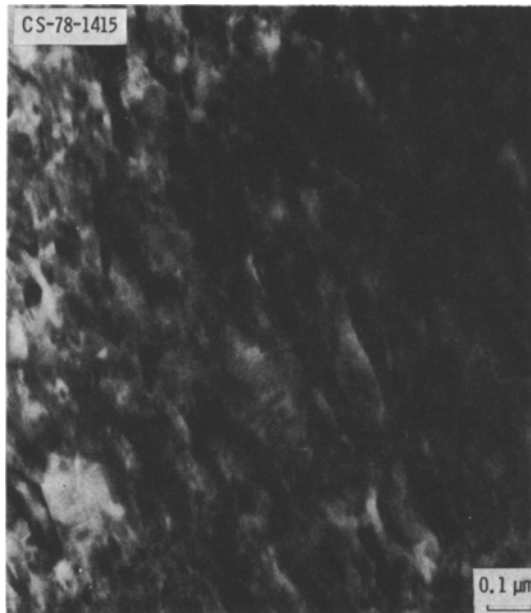

Figure 5 Transmission electron micrograph of CNTD-silicon carbide showing alignment of elongated grains associated with stacking faults.

the surface abrasion scratches were mainly parallel with the axis, some scratches were nearly perpendicular to the rod axis (Fig. 8b). These approximately perpendicular scratches were preferred sources of failure and were characteristic of the lower strength samples. This and the variable depth of the flaws are probable reasons for the variation in abraded strengths.

Most of the fracture origins in oxidized specimens could be located. In bodies with less oxidation or more severe abrasion, fracture origins from remnants of abrasion flaws were found. Otherwise, the characteristic features were origins at cracks and especially at bubbles in the oxide scale (Fig. 9) similar to observations in Si_3N_4 [3]. These results are consistent with the lowering of the as-deposited strength and the raising of abraded strength by oxidation. Thus, the cracks and bubbles are larger and more severe than the flaws in as-deposited rods (except for some large flaws apparently resulting from handling) but are of about the same size or smaller than abrasion flaws. The lack of complete elimination of abrasion flaws or elimination of handling damage in all oxidized specimens appears to be a factor in the scatter of the oxidized strength. Thus more complete oxidation might raise strengths to an optimum somewhat above the as-oxidized strength level reported here. However, since the bubbles and cracks are limited by, and appeared to be related to, the thickness of the oxide layer, thicker layers produced by longer time or higher temperatures oxidation could reduce strengths below the expected optimum level, and possibly even below the levels observed in the present tests.

The third fractographic result is that the fracture energies calculated from the size of the observed critical defects and the strength, (assuming the Young's modulus for hot-pressed SiC), though showing a fairly wide scatter, were much lower, than that found for other SiC bodies (6 to 9 versus about $20 \, J \, m^{-2}$). Correction of strengths for a few specimens where the fracture origin was clearly a substantial distance around the rod periphery from the point of maximum tensile stress (as indicated by fracture mirror anisotropy) served only to reduce the scatter of calculated fracture energies.

The low and variable fracture energies noted above suggest a variable residual tensile stress of approximately 100 000 psi (690 MPa). Such residual tensile stresses in the SiC might also be the cause

○ AS DEPOSITED
△ ABRADED 600 GRIT
□ ABRADED 320 GRIT
▽ ABRADED 600 AND 320 GRIT AND
   OXIDIZED (~100 hr AT ~1200° C)
◇ AS DEPOSITED AND OXIDIZED

(NUMERAL) ABOVE RANGE BARS DENOTES
NUMBER OF SPECIMENS TESTED

Figure 6 Modulus of rupture as a function of temperature for CNTD-silicon carbide rods.
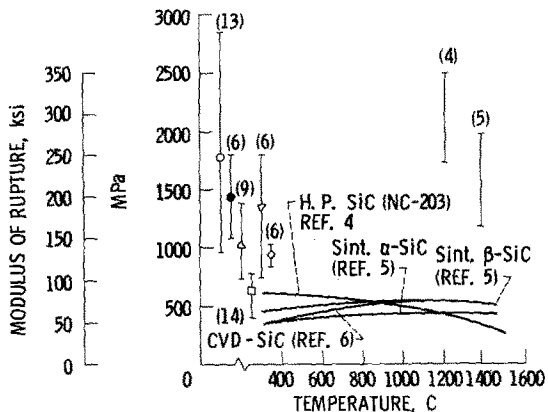
of the shattering of the SiC deposit which was observed during attempts to remove the W core by leaching. The presence of residual tensile stress is also suggested by a preliminary analysis of fracture mirror sizes, was consistent with the different locations of the fracture origins in the SiC and W, and was also consistent with the increase of strength with temperature which is discussed in the next section. While a more complete analysis is needed, the observed radial orientation of the elongated grains suggested a texture which is known to be a basic source of residual stresses in CVD bodies [1]. However,

Figure 7 SEM of fractured CNTD-SiC rod and the W-core (white) showing fracture origins directly opposite to each other.

the mismatch in expansion between the W core and the SiC cannot be ruled out as an alternate or additional sources of such stresses.

3.2.2. High-temperature strength

The high-temperature modulus of rupture values shown in Fig. 6 were determined at 1200 and 1380° C in four-point bend tests on rods with as-deposited surfaces. All testing was conducted in air with a cross-head velocity of 0.05 cm min^{-1}. During high-temperature testing, particularly at 1380° C, intermittent dips were observed in the load–deflection curve before the rods failed in the usual catastrophic manner typical of brittle failure. At catastrophic failure, both the SiC and the W core fractured into multiple pieces and the calculated strengths averaged 600 000 psi (4200 MPa). However, when the rods were unloaded and cooled immediately after the first dip in the load–deflection curve, it was found that fracture of the SiC had already occurred (Fig. 10). Thus the values plotted in Fig. 6 were calculated from the load at the first dip of the high-temperature load-deflection curve. These values, which averaged about 220 000 psi (1500 MPa) at 1380° C, are summarized in Fig. 6. Note that the average four-point bend strength at 1200° C is about 100 000 psi greater than at room temperature, which is consistent with a 100 000 psi residual tensile stress at room temperature, i.e. relaxation of the residual tensile stress at the higher temperatures could be
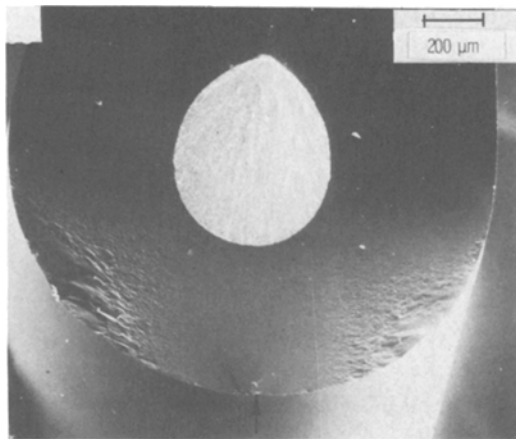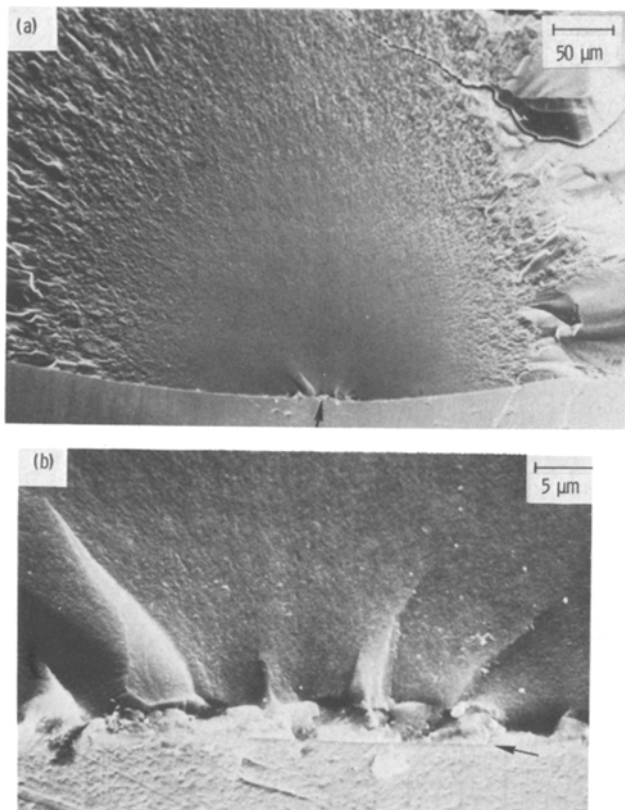
the source of increased strength at 1200° C. Note also that the high-temperature strengths are substantially higher than the 55 000 to 80 000 psi (380 to 551 MPa) for other silicon carbide bodies, fabricated by various other techniques. Furthermore, there is no noticeable strength drop at high temperatures of 1380° C when compared to room temperature. This retention of strength at high temperatures can be attributed to the high-purity fine-grained SiC deposit with superior surface smoothness produced by the CNTD process.

3.2.3. Oxidation

The oxidation kinetics (weight change) data in Fig. 11 show that the rates of weight change for the CNTD-SiC are lower than for NC-203, higher than for GE's CVD-SiC, and CVD-Si_3N_4 but considerably below those for hot-pressed Si_3N_4. Since most people feel that oxidation rates for Si-based materials are directly relatable to the composition of the oxide scale (particularly to the concentration of glass modifiers such as Fe, Mg, Ca, etc.), the results for CNTD SiC indicate that the material does not contain significant concentrations of degrading impurities. Consequently, CNTD-SiC should retain its desirable high-temperature properties for long times.

X-ray diffraction analysis of an oxidized surface showed that the scale was made up of crystallites of α-cristobalite in a glassy matrix. Since the scale was of high purity, the oxygen transport through the continuous glass phase would be expected to be very slow.

4. Conclusions

Utilizing the controlled nucleation thermochemical deposition (CNTD) process, ultrafine-grained SiC has been deposited with superior surface smoothness and without the macro-columnar growth commonly found in conventional CVD material. At both room and high temperature, the CNTD-SiC with as-deposited surfaces exhibited a bend strength of 200 000 psi (1390 MPa) or more. This is significantly higher than for SiC made by conventional sintering, hot-pressing or CVD processes. Room-temperature strengths are significantly reduced by abrasion, but are still comparable to or greater than the strength of unabraded
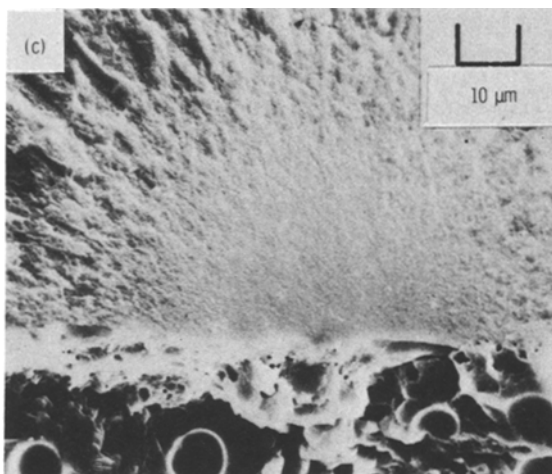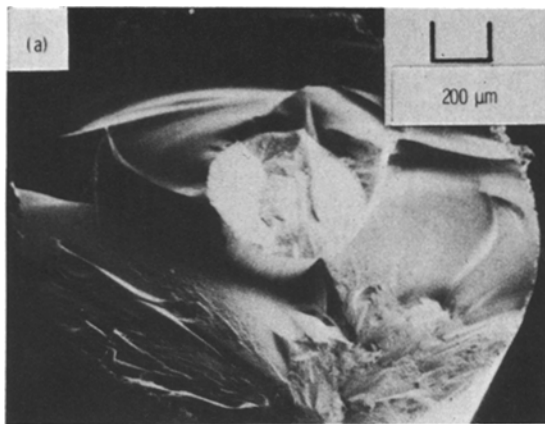
Figure 9 SEM of room temperature fracture of CNTD-SiC oxidized for 100 h at 1200° C, σ_f 146 ksi (1000 MPa).

material produced by conventional processes. Furthermore, while oxidation may have raised the strength of previously abraded rods, it also appears that the oxide scale might have been the source of critical flaws.

Several factors suggested variable residual tensile stresses of the order of 100 000 psi (690 MPa). The reduction or elimination of this residual tensile stress could correspondingly raise room-temperature strengths.

The excellent retention of strength at high temperatures is attributed to the high purity and fine grain size of the SiC deposit made by CNTD process. The rates of weight change for CNTD-SiC during oxidation are lower than for NC-203 (hot-pressed SiC), higher than for GE's CVD-SiC, and CVD-Si$_3$N$_4$, but considerably below those for hot-pressed Si$_3$N$_4$ (HS-130). Since the material was of high purity, was fully dense, and did not exhibit grain growth at elevated temperatures, it should retain its desirable high-temperature properties for long times. The material shows
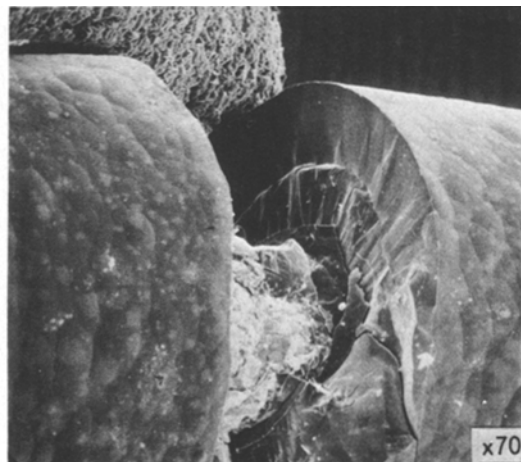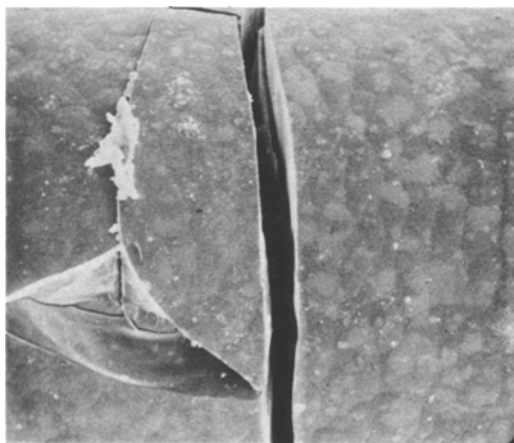

Figure 10 SEM of as-deposited CNTD-SiC rod fractured at 1380° C showing cracks in SiC, σ_f 169 ksi (1167 MPa).
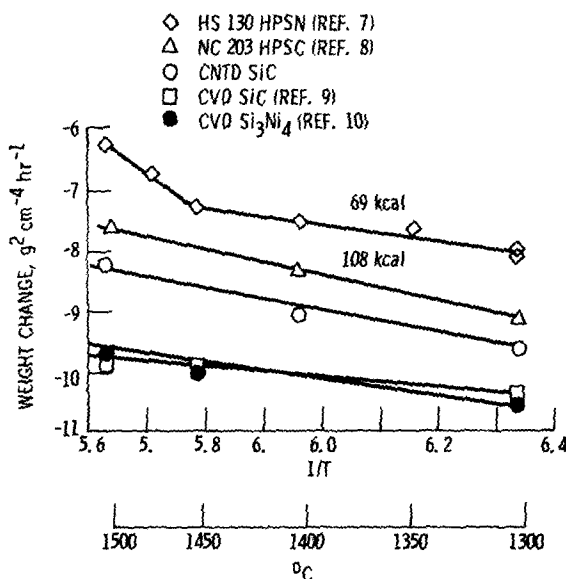
◇ HS 130 HPSN (REF. 7)
△ NC 203 HPSC (REF. 8)
○ CNTD SiC
□ CVD SiC (REF. 9)
● CVD Si_3Ni_4 (REF. 10)

Figure 11 Oxidation behaviour of SiC and Si_3N_4 materials. Log K_p weight change versus $1/T$; 150 mm dry O_2.

potential for future use; however, some potential problem areas are scaling the process to make larger parts, deposition on removable substrates, and the possible residual tensile stress.

References

1. F. I. BARATTA, *Amer. Ceram. Soc. Bull.* 57 (1978) 806.
2. R. A. HOLZL, "Investigation of CNTD Mechanism and Its Effect on Microstructural Properties in Silicon Carbide", Special Topical Report, Chemetal Corp., Pacoima, California, AFOSR; *Contract No. F49620-77-C-0036*, July (1977).
3. S. W. FREIMAN, J. J. MECHOLSKY, W. J. McDONOUGH and R. W. RICE, in "Ceramics for High Performance Applications", Vol. II, edited by J. J. Burke, E. N. Lenoe, and R. N. Katz, (Brook Hill, Chestnut Hill, Mass., 1977) pp. 1069–76.
4. D. C. LARSEN and G. C. WALTHER, Property Screening and Evaluation of Ceramic Turbine Engine Materials, in IITRI-D6114-ITR-36 (IIT Research Institute, Chicago, Illinois, 1978) p. 20.
5. *Idem,* Property Screening and Evaluation of Ceramic Turbine Engine Materials, IITRI-D6114-ITR-30 (IIT Research Institute, Chicago, Illinois, 1978).
6. A. F. McLEAN, E. A. FISHER and R. J. BRATTON, "Brittle Materials Design, High Temperature Gas Turbine", AMMRC-CTR-72-19 (Army Materials and Mechanics Research Center, Watertown, Mass., 1972) p. 109.
7. W. C. TRIPP and H. C. GRAHAM, *J. Amer. Ceram. Soc.* 59 (1976) 399.
8. J. W. HINZE, W. C. TRIPP and H. C. GRAHAM, High Temperature Oxidation of Hot Pressed Silicon Carbide, in "Mass Transport Phenomena in Ceramics", Materials Science Research, Vol. 9, edited by A. R. Cooper and A. H. Heuer (Plenum Press, New York, 1975) pp. 409–19.
9. H. C. GRAHAM, Air Force Materials Laboratory, Wright Patterson AFB – Ohio, private communication, April, 1978.
10. J. J. GEBHARDT, R. A. TANZILLI and T. A. HARRIS, *J. Electrochem. Soc.* 123 (1976) 1678.