Silicon-Based Ceramic-Matrix Composites for Advanced Turbine Engines: Some Degradation Issues

Linus U.J.T. Ogbuji

Dynacs Engineering Co.
NASA-Glenn Research Center
Cleveland, OH 44122, USA

Abstract

SiC/BN/SiC composites are designed to take advantage of the high specific strengths and moduli of non-oxide ceramics, and their excellent resistance to creep, chemical attack, and oxidation – while circumventing the brittleness inherent in ceramics. Hence, these composites have the potential to take turbine engines of the future to higher operating temperatures than is achievable with metal alloys. However, these composites remain developmental and more work needs to be done to optimize processing techniques. This paper highlights the lingering issue of pest degradation in these materials and shows that it results from vestiges of processing steps and can thus be minimized or eliminated.

1.0 Introduction

Most designs for advanced turbine engines of the future call for wall temperatures above 1400°C at the hottest sections (e.g. combustor and vanes). These specifications are driven by the thermodynamics of efficiency in the internal combustion engine [1], as well as by increasingly stringent emission mandates (requiring higher temperatures for the total combustion of NO_x and SO_x contents of propulsion fuels). Such temperatures are beyond the current and foreseeable capabilities of metallic alloys, even with aggressive cooling (which is already standard practice), especially since their protection with barrier coatings (thermal and environmental) is still at the early developmental stage. In the mean time, therefore, ceramics remain the only realistic hope for attaining the design specification of high-temperature turbine engines.

The superior properties of ceramics include higher strength and stiffness (especially at elevated temperatures), increased oxidation resistance, thermochemical stability, lower creep rates, and lower densities. Their densities (typically ~3 times lower than those of superalloys) translate into even higher specific strengths and moduli, and this is an extra premium for maximization of payload and fuel efficiency. In terms of service lifetimes, another big advantage of (non-oxide) ceramics in engine applications is shown in Fig. 1, which compares oxidation rates of superalloy constituents (including silica formers) [2] with those of SiC and Si_3N_4 [3]. It shows that the passive oxidation rates of silicon-based ceramics in a static environment are several orders of magnitude lower than those of the best metallic materials (although it must be pointed out that oxidation in an engine flame is not truly passive, nor the ambient static). Clearly, engine components made of silicon-based ceramics have the potential for superior durability in oxidizing ambients because their oxidation rates are among the lowest known.

The great drawback of ceramic materials is, of course, their inherent brittleness, which is a liability in highly stressed, moving components. Ceramic-matrix composites (CMCs) provide a way to circumvent that disadvantage, and the last two decades have witnessed concerted and widespread efforts toward their development. Unlike monolithic ceramics, CMCs are designed for damage tolerance to ensure the dissipation of significant fracture energies through compliance and deflection of cracks at the interface between fiber and matrix. The goal in CMC design is to achieve some forewarning of impending functional failure of the component – a property that is called "graceful failure." The main features of a CMC are: (1) strong and stiff fibers to bear load, (2) a matrix to transmit load as well as to protect the fibers, and (3) a weak/compliant interfacial layer (or "interphase") sandwiched between matrix and fiber. The weak interphase permits deflection of matrix cracks away from the fiber. This not only protects the fiber but also increases the crack-path and, with it, the work of fracture (i.e. toughness). In addition, the weak interphase aids the pull out of fibers broken during fracture, and the frictional resistance to pull out (sliding friction) serves to increase the work of fracture [4].

CMCs fall into two major categories: oxides and non-oxides. Each has its advantages, but oxides tend to have rather high creep rates, which make them unsuitable for prolonged applications at high-temperature; hence, oxide CMC systems are unsuitable for the long service lifetimes desired in aircraft engines and ground-based turbines. Non-oxides, on the other hand, have good creep properties and, in addition, are comprised of covalentbonded carbides, nitrides, and borides which are marked by chemical inertness in many gaseous environments [1]. Of the non-oxide CMCs the most promising by far for turbine engine applications are SiC/BN/SiC composites, comprised of BN-coated SiC fibers in SiC matrix. Nevertheless, because the intrinsic toughness of silicon nitride is higher than that for silicon carbide, efforts are continuing toward the development of composites with Si_3N_4 matrix reinforced with SiC fibers (generally referred to as "SiC/SiN" composites).

The need for load transfer through compliance as well as for crack deflection require that the interphase be weak in shear, and there are two design approaches to achieve this [5]. One method is to induce shear weakness by means of tailored porosity in the interphase. The other is to use inherently weak materials for an interphase; boron nitride (BN) and pyrolytic carbon (py-C) are especially suited to this application. Figure 2 illustrates the two approaches schematically. While a porous interphase is feasible in principle, its development has been arrested by practical difficulties, as noted elsewhere [6]. Excellent mechanical properties are achievable with a py-C interphase at room temperature and in inert environments; however, those advantages are offset by the oxidative volatility of carbon in a flame environment. Hence, a BN interphase represent the state of the art for SiC/SiC composites in turbine engine applications. While significant progress has been made with SiC/BN/SiC composites, they remain essentially in the developmental stage, especially with regard to fabrication processes, which are not yet standardized or even optimized. There is a need to assess the effects of processing conditions on the quality and consistency of these composites, with a view to improving performance.

The constituent phases in a SiC/BN/SiC composite are just silicon carbide and boron nitride; however, additives and contaminants can become incorporated, deliberately or inadvertently. Elemental silicon, carbon, and boron are native to the system and usually present, sometimes in significant quantities. They can play beneficial roles. For instance, the presence of a little Si in the BN interphase is known to boost oxidation resistance [7], while free carbon in the fiber improves creep properties, primarily by suppressing oxygen content [8]. Nevertheless, unintended components may also prove deleterious. Concern over the oxidative volatility of free carbon, mentioned above, is at the heart of the work reported in this paper.

2.0 Procedure

Our SiC/BN/SiC composites were obtained from the Carborundum Co. of Niagara Falls NY, and AlliedSignal Composites, Inc. (now Honeywell) of Newark DE, USA. Some of the samples differed in their reinforcing fibers, which were either Hi-Nicalon^{TM} (Nippon Carbon Co.) or Sylramic^{TM} (Dow Corning Co.). Both fibers are polycrystalline silicon carbide, but they are made in different ways and differ in microstructure and purity, O_2 and C contents especially. The Sylramic^{TM} fiber is stoichiometric, but the Hi-Nicalon^{TM} fiber contains 30-40% excess carbon. The matrix in both varieties was melt-infiltrated silicon carbide (MI-SiC), made by infiltration of molten Si into carbon preform.

Screening tests showed that most of the various SiC/BN/SiC composites in our turbine engine programs had excellent mechanical properties, but that some became degraded in oxidizing environments at intermediate temperatures (600-1100°C), thus raising an issue of "pesting". A pre-disposing factor was indicated and our investigation focused on the possibility of an adventitious carbon film on the fiber, which underlies the BN interphase and undermines its resistance to oxidation. Such a film could build up by precipitation from carbon-rich Hi-Nicalon^{TM} fibers, or in other systems from incomplete removal of fiber sizing (the coating used to protect fibers from handling damage -- and which is supposed to burn off during matrix incorporation).

The SiC/BN/SiC composites were machined into tensile bars, with fiber and interphase ends exposed at the cut edges to interaction with oxidants. Some were oxidized in the flame of a burner rig operating at atmospheric pressure (and hence called an atmospheric-pressure burner rig, or APBR); others were oxidized in a tube furnace with a controlled mix of oxidants. The APBR was operated by burning Jet-A fuel at flame velocities of 0.1 to 0.3 Mach to simulate the combustor of a turbine engine. The tube furnace was used to study the effect of moisture content on degradation. Because results showed that sample degradation occurred in the APBR but not in a furnace of similar oxidant mix, it appeared that flame velocity was a factor in degradation. Therefore, samples were run flame speeds of 0.3, 0.2, and 0.1 Mach (the latter representing the slowest fuel flow for which we could sustain a flame). After APBR or furnace exposure the oxidized bars were tested to failure in tension to measure their residual strength and fracture strain, and then characterized by microscopy to determine operating degradation mechanisms. The results (for 0.3 Mach exposures) have been detailed elsewhere [9,10] and only a summary of the salient points is presented here, for those materials that exhibited severe pest degradation.

3.0 Results

3.1 Mechanical Properties

Of the SiC/BN/SiC varieties assessed in our program, two exhibited severe degradation of strength in the APBR between 600 and 1100°C. They were made with Hi-Nicalon^{TM} and Sylramic^{TM} fiber reinforcements, respectively, the latter being characterized by fiber sizing that probably charred to carbon during processing. The pattern of degradation in these two materials was similar, starting with interphase oxidation and leading to fiber damage. The result was to weaken and embrittle the composite in a manner akin to the "pest" oxidation of $MoSi_2$ at intermediate temperatures. Hence, 600-1100°C is considered the regime of pest degradation (or "pesting") in SiC/BN/SiC composites [9,11]. In both materials the underlying cause of pesting was inadvertent carbon film on the fiber. The results will be illustrated here mostly with Hi-Nicalon^{TM}/BN/SiC, which was studied more extensively than Sylramic^{TM}/BN/SiC. In Figure 3 the tensile stress-strain behavior of a Hi-Nicalon^{TM}/BN/SiC sample is shown in as-received condition and after a 150-hour exposure at 800°C. APBR exposure caused a ~65% loss of strength (and ~90% loss of as-received fracture strain – which is not shown in the figure).

A burner rig flame contains approximately 10% H_2O (and other oxidants, including CO, CO_2, O_2, NO_x, and SO_x, [12]), resulting from the chemistry of hydrocarbon combustion. H_2O is known to be a more severe oxidant of siliceous materials than O_2 [13], the rate of SiC oxidation in a moist oxidant being strongly dependent on the partial pressure of H_2O. Hence, the effect of moisture content on degradation of our SiC-based composites was an issue of concern. Since the APBR moisture content is constant at 10% a tube furnace was used to study the effect of moisture. The composites were exposed at 800°C in air (2.5% moisture) and in controlled mixtures of H_2O and O_2. Fig. 4 shows the residual strengths of the Hi-Nicalon™/BN/SiC samples oxidized for 150 hours at various H_2O contents. It shows that this material is highly resistant to moisture degradation. Even after 500 hours in 90% moisture this composite showed no significant loss of strength or fracture strain.

APBR exposure of the Hi-Nicalon™/BN/SiC material at 600, 800, 700, 900, 1000, and 1100°C resulted in similar degradation of mechanical properties. At 1200°C, however, the material was not significantly degraded by APBR exposure, showing that above ~1100°C silica forms rapidly enough on the surface to seal off and protect the sample from serious degradation. However, degradation occurred quickly within the pest regime: By varying the duration of APBR exposure it was found that a 15-hour of exposure at 800°C caused significant degradation (~40 % loss of strength) in the Hi-Nicalon™/BN/SiC composite.

For samples exposed in a 0.3 Mach APBR flame (a total of 12 bars, only 4 of which are shown in Fig. 4), the loss of strength following 150 hours of oxidation at 800°C was 65%; for exposures in the 0.2 Mach flame (two bars) the loss was 52%; and for two bars in the 0.1 Mach flame it was 51%. It appears the APBR degrades our Hi-Nicalon™/BN/SiC material more severely at 0.3 Mach than at the lower flame speeds; however, the 0.1 and 0.2 Mach results were obtained recently and a detailed explanation of the phenomenon is not yet available.

3.2 Micrography

The stress-strain response gave a reliable indication of degradation in these composites, as shown above. Visual inspection, even with the unaided eye, also provided a striking evidence of degradation as fracture changed from fibrous (with extensive fiber pull-out) in as-received samples to totally brittle and flat in degraded material. This is evident in Figure 5, which compares fracture surfaces of the Hi-Nicalon™/BN/SiC composite from: (a) as-received material, and (b) a sample exposed in the APBR for 150 hours at 800°C. The former was characterized by the pull out of nearly every fiber to lengths averaging a few millimeters. The latter was characterized by two features: flat fracture across fiber and matrix, indicating the absence of crack branching; and the fact that the BN interphase between every pair of adjoining fibers had been replaced by glassy borosilicate that is perforated by rounded pin-holes.

4. Discussion

Normal degradation is expected to initiate at the machined surface of a sample bar (where contact is made with the environment) and progress inward with time, resulting in two distinct fracture zones: a rim of flat and brittle fracture around a core of good material that is still characterized by fibrous fracture [11]. However, APBR pest degradation of our samples left no zone of fibrous failure, which is indication that degradation occurred simultaneously throughout the volume of material that was in the flame. The pin holes seen in Fig. 5(b) were present on all fracture surfaces of APBR-exposed samples and were recognized as tunnels through which volatile products of oxidative reactions were vented to the exterior. The connectivity of these pin holes and simultaneous (rather than progressive) nature of APBR pest degradation strongly hints at the existence of pathways for rapid and pervasive ingress of oxidants to the interior of this material.

A coating of adventitious carbon on the fibers was suspected and confirmed through EDS and XPS examination of the as-received fiber surfaces [10]. Since a carbon layer between fiber and interphase is not a design feature of SiC/BN/SiC composites, it probably arose inadvertently during processing. Hi-Nicalon fibers are highly hyper-stoichiometric with respect to carbon (containing ~40% excess carbon), and free carbon can easily migrate to the fiber surface under the thermodynamic conditions of matrix infiltration. In the case of Sylramic/BN/SiC composites it was determined that APBR degradation occurred only in those varieties distinguished by a certain type of fiber sizing, and it seems likely that the sizing had not burned off fully during processing but instead converted to a carbon film.

Figure 6 is a schematic illustration of the deleterious configuration in question: a layer of adventitious carbon forming a buffer between a fiber and its BN interphase coating. The oxidatively volatile carbon is preferentially consumed when the exposed fiber end comes in contact with the flame. The BN layer is oxidized more slowly [9]. Consequently, the carbon layer recedes to a greater depth (h) than the BN layer, exposing the BN layer to increased contact with oxidants. Without the carbon layer the BN is attacked only at the annular end, of area $2\pi rt$ (where r is radius of the coated fiber and t thickness of the BN layer). However, in the presence of a recessed carbon layer, the wall surface of the BN is also available for attack, its area being $2\pi rh$. Therefore, when a film of carbon coats the fiber, consumption of the BN interphase is increased by a factor, F, given by:

$$F = (2\pi rt + 2\pi rh)/2\pi rt = 1 + h/t \qquad (1)$$

And, for $h>>t$,
$$F \cong h/t \qquad (2)$$

Connectivity of the pin-holes indicate that carbon recession is continuous throughout the sample hot zone, a distance of ~0.5 inch (~1270 μm) while the BN thichness is ~0.5 μm. Using these values one can see that the value of F is considerable, ~ 25000. Hence, an adventitious carbon layer increases oxidative consumption of the interphase by several orders of magnitude, with a swift and severe degradation of composite properties as the consequence. The process by which interphase consumption embrittles and weakens the composite has been detailed elsewhere [9]. Briefly, it involves interphase conversion to boria, borosilicate (by oxidative and hydrolytic dissolution of the fiber), and eventually to SiO_2 (by loss of volatile boron hydroxides). The main effect is to stiffen the material with brittle silica welding the fibers down. That alone has been shown to cause pronounced local stress concentration at the weldments [14] and probably accounts for much of the degradation we observed in samples exposed for short times (15 hours), especially at the lower temperature end of the pest regime.

More damage can and does occur when the fibers themselves come under direct oxidative attack, as may be seen in Figures 7 (a) and (b). For the Hi-Nicalon^{TM} composite shown in Fig. 7(a), discontinuous attack on the fibers produced the notches at their periphery which arise from localized dissolution of fiber by borosilicate liquid derived from the interphase by oxidation. In the Sylramic^{TM} composite shown in Fig. 7(b), attack on the fibers is quite systematic. Oxidation has consumed most of the fiber in Fig. 7(b) as well as the cladding of SiC around the interphase, converting it all to silica (identified by EDS). Only a small core of the fiber remains unoxidized. In either case oxidation of the fibers causes very prominent flaws that degrade fiber strength, diminishing its ability to bear load when it spans a propagating matrix crack.

5. Summary and Conclusion

The advantages of SiC/BN/SiC composites (over metallic components and oxide CMCs) in turbine engine hot sections are many, but their full benefits cannot be realized until a few lingering issues are resolved. One such issue, pest degradation in an engine flame, is of major concern. However, it appears to be caused by the presence of a process-induced film of adventitious carbon between fiber and interphase hence, rather than by intrinsic inadequacy of the SiC/BN/SiC constituents. That calls for renewed emphasis on the need to optimize CMC processing steps.

References

1. P. Baldus, M. Jansen, and D. Sporn, "Ceramic Fibers for Matrix Composites in High-Temperature Engine Applications", *Science* (Energy Review), vol. 285 (1999) 699-703
2. J. Smialek, et al., "Design for Oxidation Resistance", ASM Handbook, vol. 20 (1997) pp. 589-602
3. L.U.J.T. Ogbuji & E.J. Opila, "A Comparison of the Oxidation Kinetics of SiC and Si_3N_4," J. Electrochem. Soc., vol. **142**, No. 3 (1995) 926-30
4. J. Aveston and A. Kelly, "Theory of Multiple Fracture of Fibrous Composites", J. Mater. Sci., **8** (1973) 352-62
5. H. Carpenter and J. Bohlen, pp. 238-56 in Ceramic Engineering & Science Proc. (ed. J. Wachtman), Am. Ceram. Soc., Westerville OH 1992
6. L.U.J.T. Ogbuji, "Evaluation of Porous Fiber Coating in SiC-Si_3N_4 Minicomposite", J. Mater. Res., vol. 12 No. 5 (1997) 1287-96
7. G.N. Morscher, D.R. Bryant, and R.E. Tressler, "Environemental Durability of BN-Based Interphases for SiC_f/SiC_m Composites in H_2O Containing Atmospheres at Intermediate Temperatures, Ceram. Eng. & Sci. Proc., vol. **18**, No. 3 (1997), J.P. Singh ed., Am. Ceram. Soc., Westerville OH

8. R. Bodet, X. Bourrat, J. lamont, and R. Naslain, "Tensile Creep Behaviour of a Silicon Carbide-Based Fibre with a Low Oxygen Content", J. Mater. Sci. **30** (1995) 661-677
9. L.U. Ogbuji, "A Pervasive Mode of Oxidative degradation in a SiC-SiC Composite", J. Am. Cer. Soc., 81 [11] (1998) 2777-84
10. L.U.J.T. Ogbuji, "Identification of Carbon Sublayer in a Hi-Nicalon/BN/SiC Composite", J. Mater. Sci. Lett. **18** (1999) 1825-1827
11. A.G. Evans, F.W. Zok, R.M. McMeeking, and Z.Z. Du, "Models of HighTemperature Environmentally-Assisted Embrittlement in Ceramic-Matrix Composites", J. Am. Cer. Soc., 79 [9] (1996) 2345-52
12. N.S. Jacobson, "Corrosion of Silicon-Based Ceramics in Combustion Environments", J. Am. Cer. Soc., **76** [1] (1993) 3-28
13. E.J. Opila: "Variation of the Oxidation Rate of Silicon Carbide with Water-Vapor Pressure" , J. Am. Ceram. Soc., **82** (1999) 625-36
14. W.H. Glime and J.D. Cawley, "Stress Concentration Due to Fiber-Matrix Fusion in Ceramic Matrix Composites," J. Am. Ceram. Soc. 81 [10] (1998) 2597-604

Figure Captions

1. Arrhenius plot comparing oxidation kinetics of superalloy constituents with those of siliceous ceramics

2. Schematic illustration of two viable schemes for achieving a shear-weak interphase in a ceramic-matrix composite

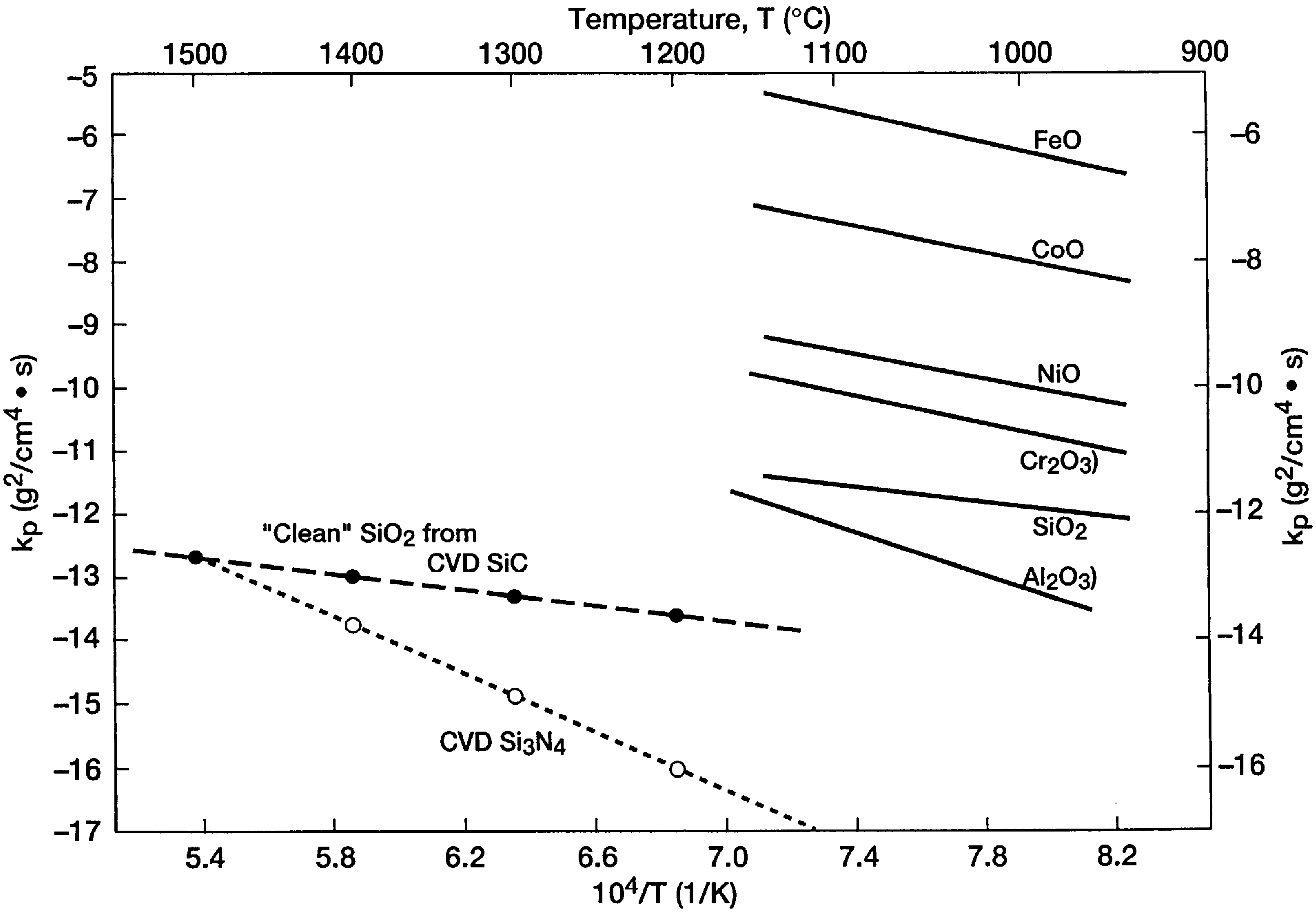
3. Tensile behavior of a Hi-Nicalon^{TM}/BN/SiC composite as received, and after exposure in the atmospheric-pressure burner (APBR) rig for 150 hours at 800°C

4. Residual tensile strength of Hi-Nicalon^{TM}/BN/SiC composite following 150-hour exposure in the burner rig, or steam furnace of various moisture contents

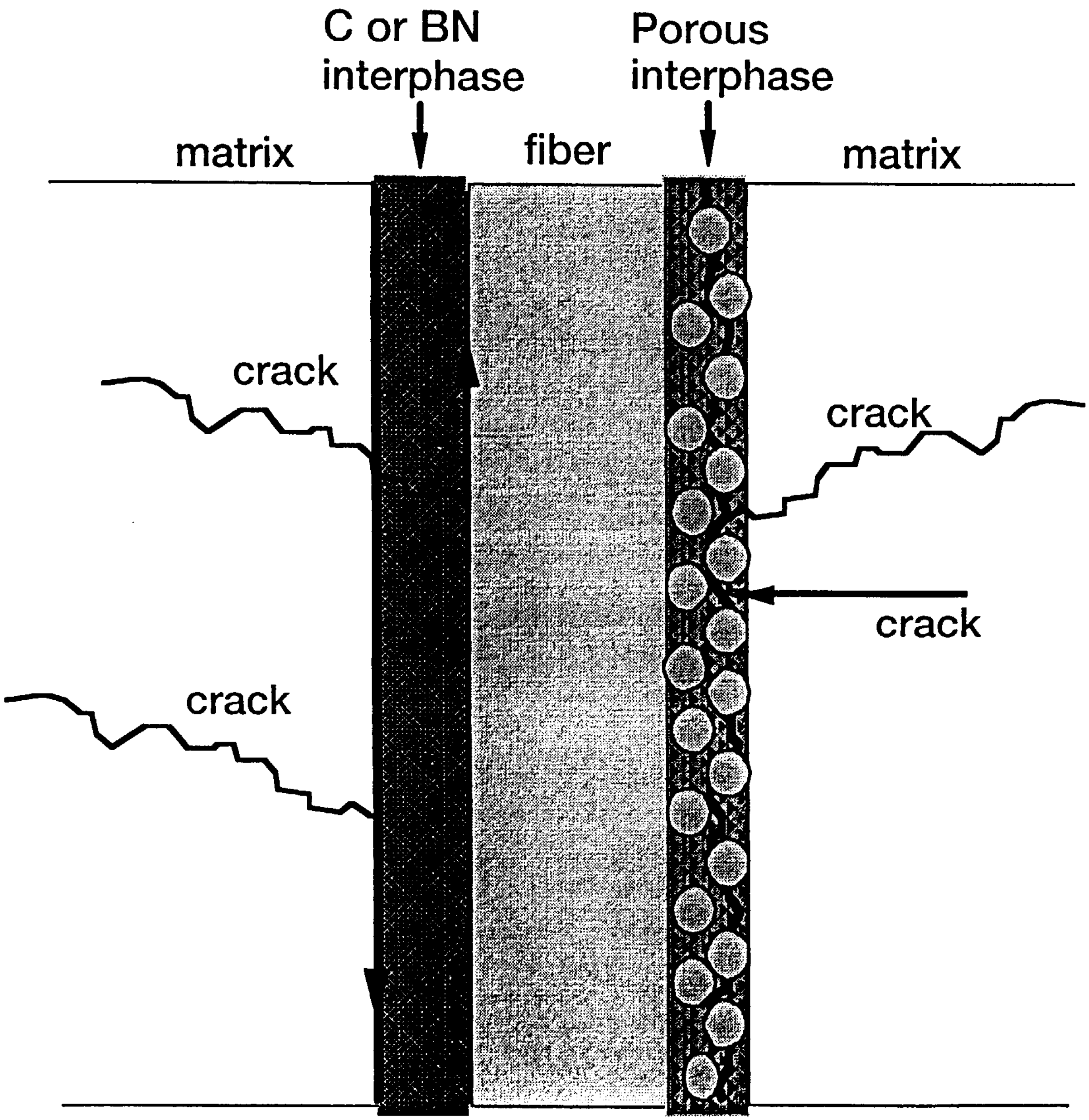
5. SEM fractographs from Hi-Nicalon^{TM}/BN/SiC composite: (a) fibrous fracture of the composite as received, and (b) flat/brittle fracture after 150 hours APBR at 800°C

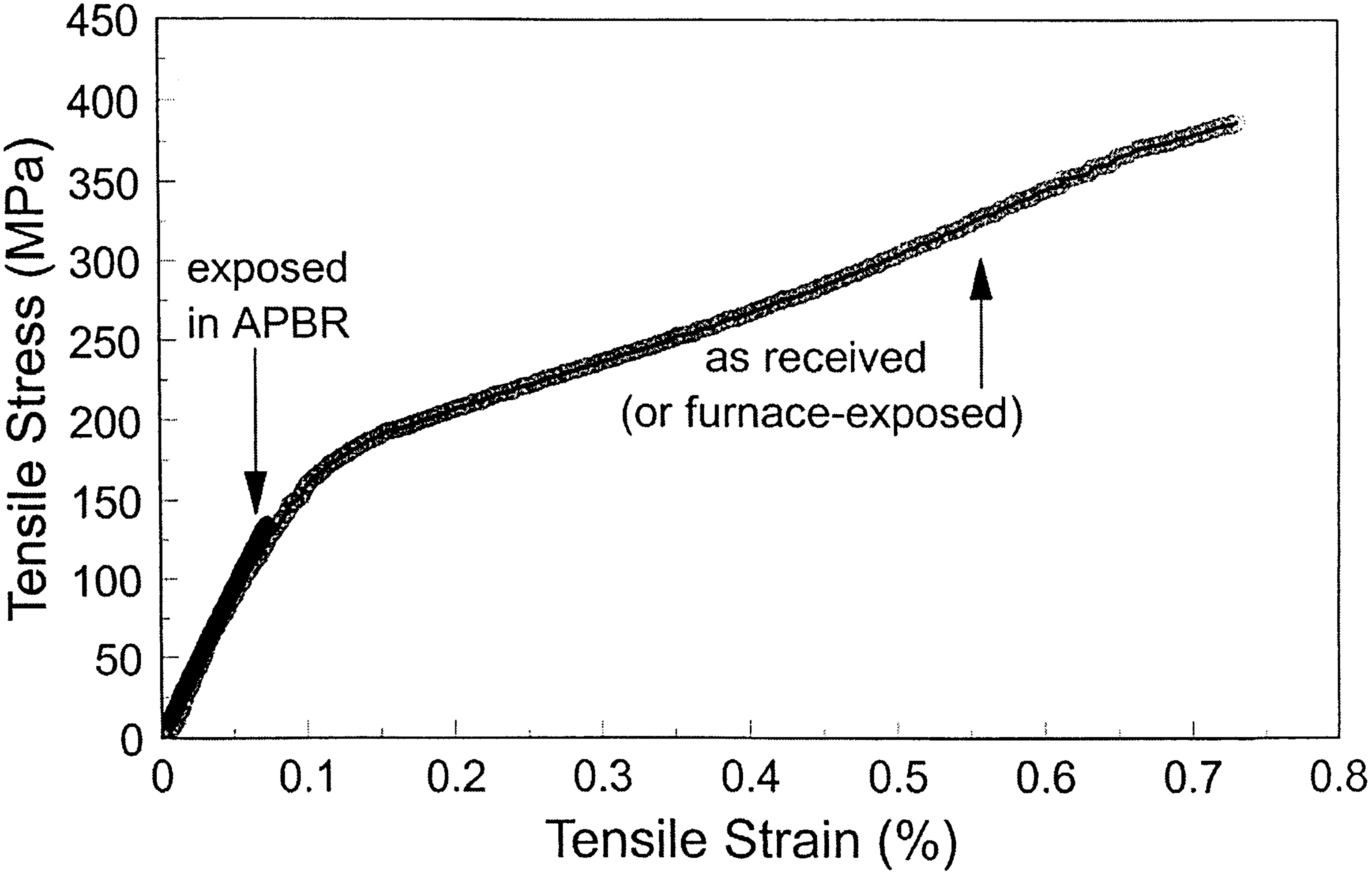
6. A sketch illustrating adventitious carbon film beneath BN interphase layer in a SiC/BN/SiC composite, and the faster oxidation (recession) of the carbon film

7. SEM fractographs showing effects of interphase oxidation in SiC/BN/SiC systems: (a) in the Hi-Nicalon^{TM}/BN/SiC composite, fiber flaws from localized attack; (b) in the Sylramic^{TM}/BN/SiC composite, destruction of the fiber by oxidation

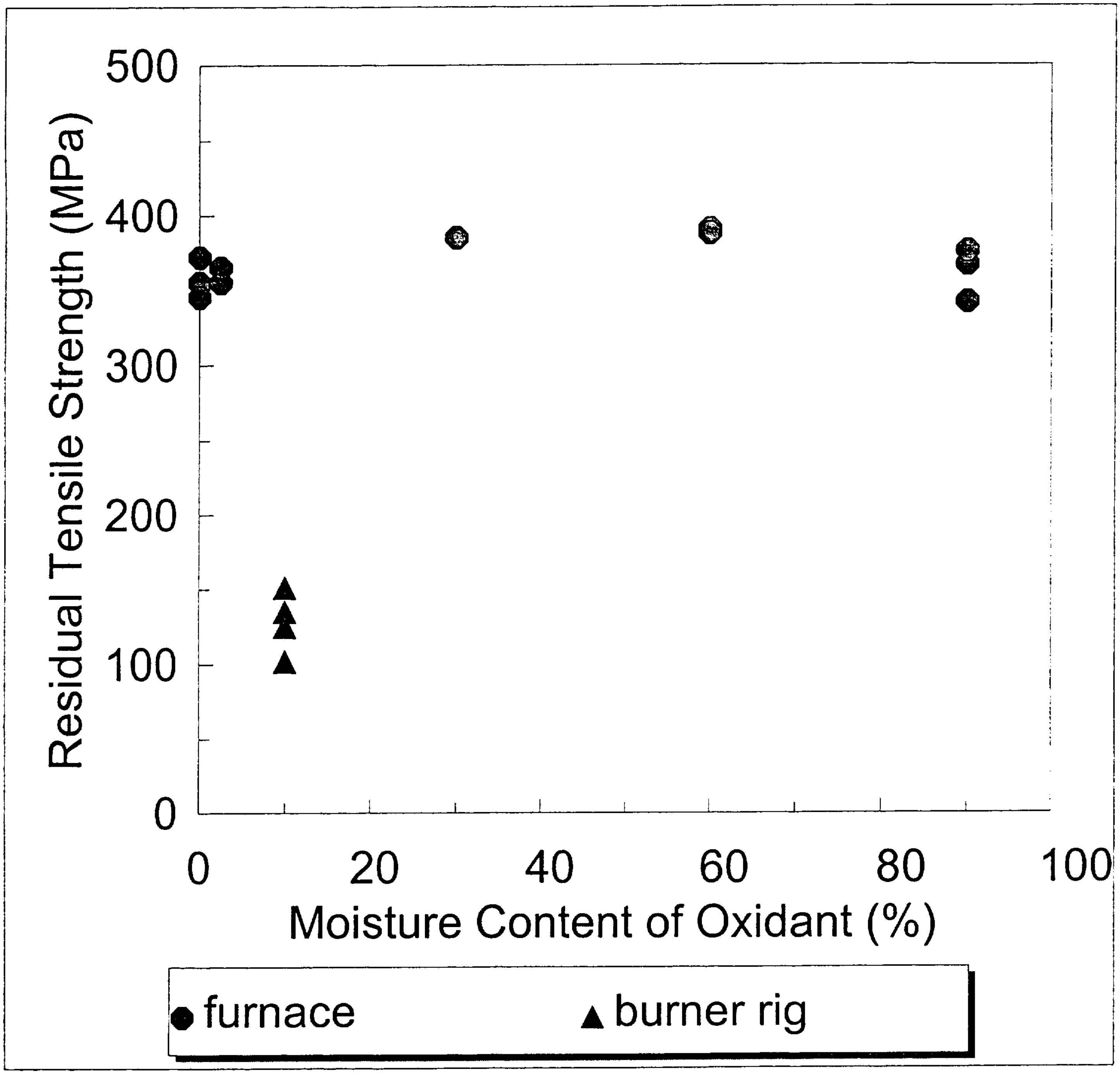

Temperature, T (°C)
1500
1400
1300
1200
1100
1000
900
kp (g²/cm⁴ • s)
−5
−6
−7
−8
−9
−10
−11
−12
−13
−14
−15
−16
−17
FeO
CoO
NiO
Cr₂O₃)
SiO₂
Al₂O₃)
"Clean" SiO₂ from CVD SiC
CVD Si₃N₄
5.4
5.8
6.2
6.6
7.0
7.4
7.8
8.2
10⁴/T (1/K)
kp (g²/cm⁴ • s)
−6
−8
−10
−12
−14
−16

CD-98-79921

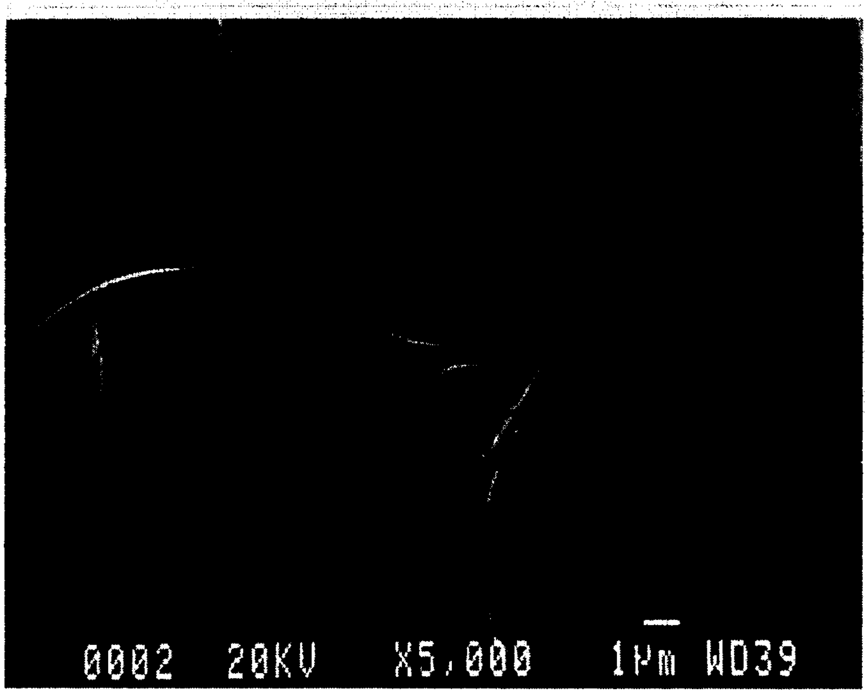

C or BN interphase
Porous interphase
matrix
fiber
matrix
crack
crack
crack
crack


Tensile Stress (MPa)
450
400
350
300
250
200
150
100
50
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Tensile Strain (%)
exposed
in APBR
as received
(or furnace-exposed)

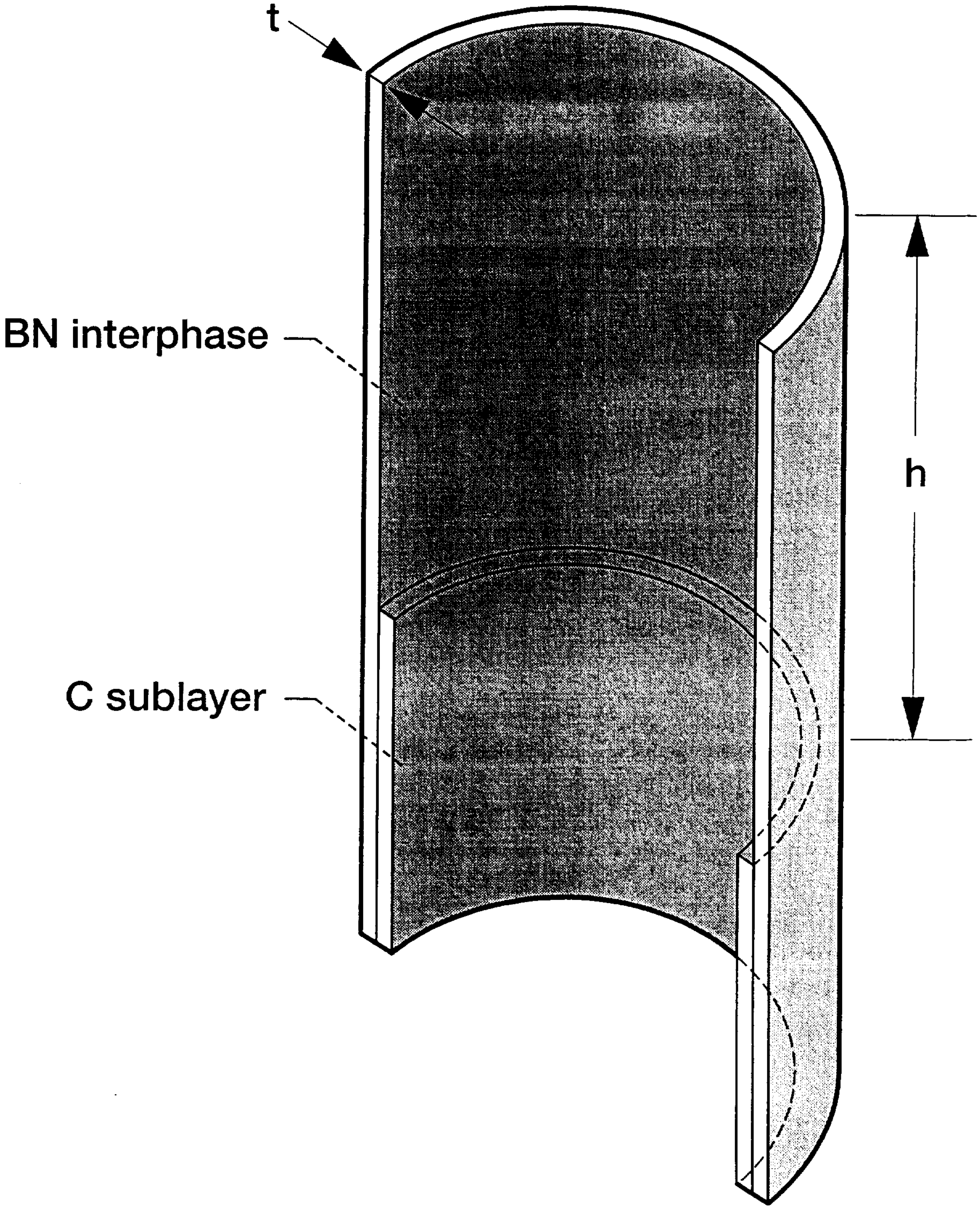
CD-99-79919


Residual Tensile Strength (MPa)
500
400
300
200
100
0
0
20
40
60
80
100
Moisture Content of Oxidant (%)
● furnace
▲ burner rig

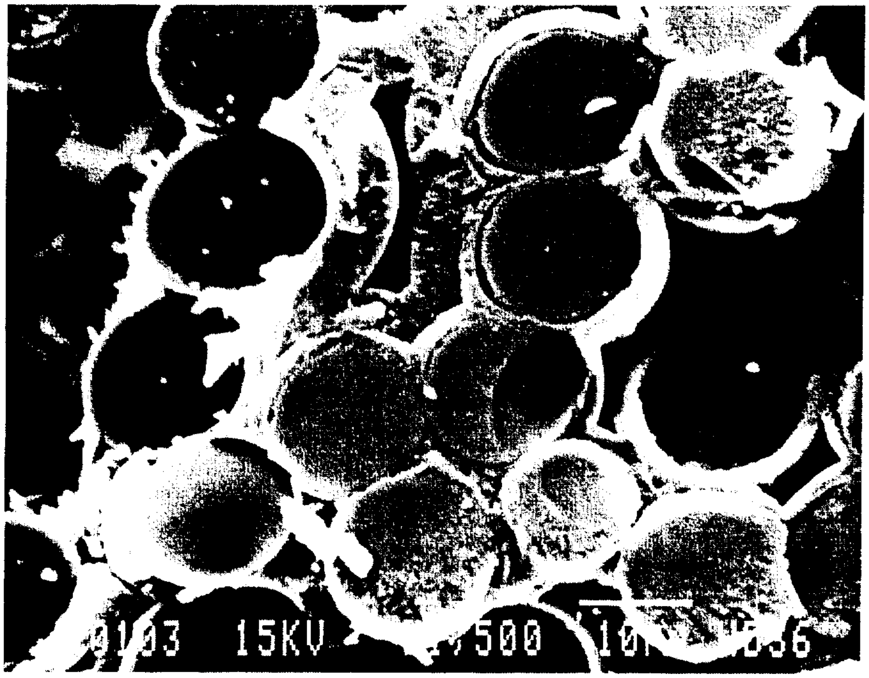
(a)



(b)



CD-99-79920



(a)

(b)