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Thermal Expansion of High-Modulus Fibers[1]

N. J. Hillmer[2]

A resistance-heating technique was used to measure the axial thermal expansion of high-modulus boron and silicon carbide (SiC) fibers from room temperature to 700 and 1500°C, respectively. Both types of fibers investigated in this study were manufactured by a chemical vapor deposition (CVD) process. The boron fibers examined here are composed of boron and a tungsten boride core arising from reaction of deposited boron with a tungsten wire substrate. The composition of the SiC fibers consists of a SiC sheath with a carbon-rich outer coating surrounding an unreacted pyrolytic graphite coated carbon core. The thermal expansion of boron fibers was found to increase parabolically with temperature up to 700°C. Above this temperature the fiber contracted due to void migration and subsequent residual stress relaxation. For SiC fibers, a relatively small initial expansion from room temperature to 450°C was observed. Above 450°C the expansion was found to increase linearly with temperature up to 1300°C, where a hysteresis effect was observed involving a 50% reduction in expansion. Possible explanations for this hysteresis effect were considered and different theories presented. Volume percentage of carbon core was varied and found to have negligible effect on expansion. The conclusion was reached that expansion of these SiC fibers is controlled by the SiC sheath.

KEY WORDS: boron; fibers; silicon carbide; thermal expansion.

1. INTRODUCTION

High-modulus fibers have received much attention over the past 15–20 years as reinforcements for composite materials. One of the most widely used high-modulus fibers today is boron, which reinforces epoxy-based and aluminum matrices and is incorporated into jet aircraft and sporting equipment. The temperature limitations of boron filaments lead to development

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[2] Textron Specialty Materials, 2 Industrial Avenue, Lowell, Massachusetts 01851, U.S.A.

of silicon carbide fibers which have high-modulus, high-strength, thermal stability, and chemical compatibility. These attributes make them ideal for reinforcement of titanium and ceramic matrices.

The objectives of this study were to confirm previous thermal expansion measurements made on these fibers and to generate data over a larger temperature range than obtained in past experiments [1–3]. The approach used was similar to that used by DiCarlo [1]. It consisted of measuring the displacement of a constant axial load applied to a fiber as it was resistively heated in an inert gas environment.

An additional benefit of this study is the more complete characterization of these high-modulus fibers, which will assist development of new applications. Specifically, boron filament applications in the electronic packaging industry require an understanding of the thermal properties of this fiber as boron/Al is being considered as a heat-sink material. In the case of the silicon carbide fiber, the rapidly growing technology of metal matrix composites requires complete thermal expansion characterization, which is necessary for composite design and modeling. Also, to design properly ceramic composites incorporating SiC fibers, it is necessary to match the expansion characteristics of the fiber and matrix to minimize stresses between the two.

2. TEST SPECIMENS

2.1. Boron Fibers

The boron fibers examined in this study were produced by chemical vapor deposition (CVD), specifically, the hydrogen reduction of BCl_3 gas onto a heated tungsten substrate. During processing, deposited boron reacts completely with the tungsten substrate, creating a tungsten boride core. Two different-diameter fibers were examined: 102 and 142 μm, both manufactured by Textron Specialty Materials, Lowell, MA.

The atomic structure of the boron fibers is important in understanding the expansion results. Previous investigations [4, 5] have shown the boron atoms to be arranged in 12-atom icosahedra with regions of partial icosahedra and loosely bonded free boron atoms near the surface of the fiber.

2.2. Silicon Carbide Fibers

The silicon carbide fibers examined in this study were also produced by a chemical vapor deposition (CVD) process. In this case, the deposition occurs from the decomposition of an organo-silane-hydrogen gas mixture onto a pyrolytic graphite-coated carbon monofilament. The carbon core remains unreacted during processing.

The specific fibers examined here are the SCS-2, SCS-6, and SCS-9 fibers manufactured by Textron Specialty Materials, Lowell, MA. These fibers are differentiated by surface coatings and diameter. Figure 1 is a schematic representation of Auger plots indicating the ratio of Si/C within the surface coatings for these fibers. The diameter of both the SCS-2 and the SCS-6 fibers is nominally 142 μm, while the SCS-9 fiber has an outer diameter of 76 μm. The diameter of the carbon core is approximately 37 μm for all three fibers.

All three fibers also exhibit the same morphology, which has been characterized previously. In their study of crystal structure and grain growth patterns of the CVD SiC fibers, Wawner et al. [4, 6] have shown that at the typical deposition temperature of 1350°C, the deposit consists of beta-SiC columnar grains oriented perpendicular to the substrate. The preferred orientation of these cubic phase grains is $\langle 111 \rangle$. There is also

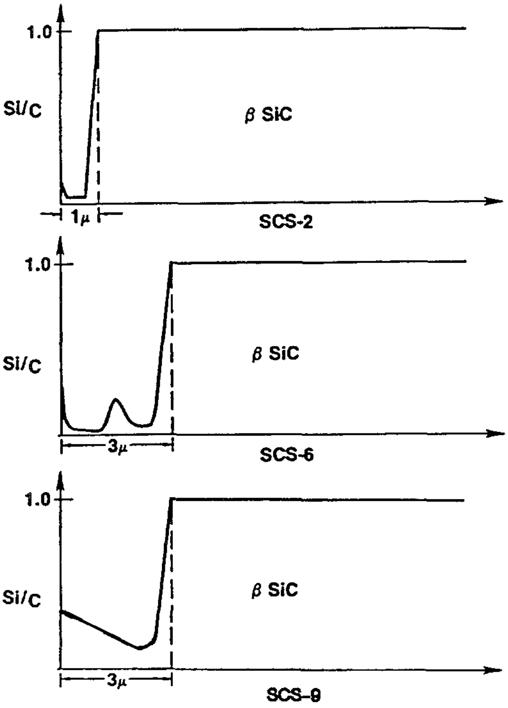

Fig. 1. Schematic representation of Auger plots for SCS fibers.

evidence of a hexagonal phase present with a ⟨001⟩ preferred orientation. The columnar grains of the beta-SiC are characterized by an extremely high density of (111) stacking faults and microtwins [4, 6].

3. TEST PROCEDURE

The general methodology adopted for this study involved suspending a fiber with a constant axial load applied to it in an argon-purged Pyrex reactor, resistively heating the fiber, monitoring temperature from 450 to 1500°C with a series of optical pyrometers, and measuring fiber displacement with a cathetometer. Electrical contact to the fiber was made by mercury pools at the top and bottom of the reactor. System qualification was performed using well-characterized molybdenum wire. Figure 2 shows a schematic of the apparatus.

In the study of silicon carbide, the temperature of the fiber was measured over the temperature range 450–1500°C using three Williamson dual-wavelength pyrometers, Model Nos. 8200, 8100, and 9100. Each pyrometer covered a different temperature range:

No. 8200, 450–850°C;
No. 8100, 800–1100°C; and
No. 9100, 1000–1500°C.

For boron fiber testing, only the Model 8200 was used because expansion measurements were made only to 700°C.

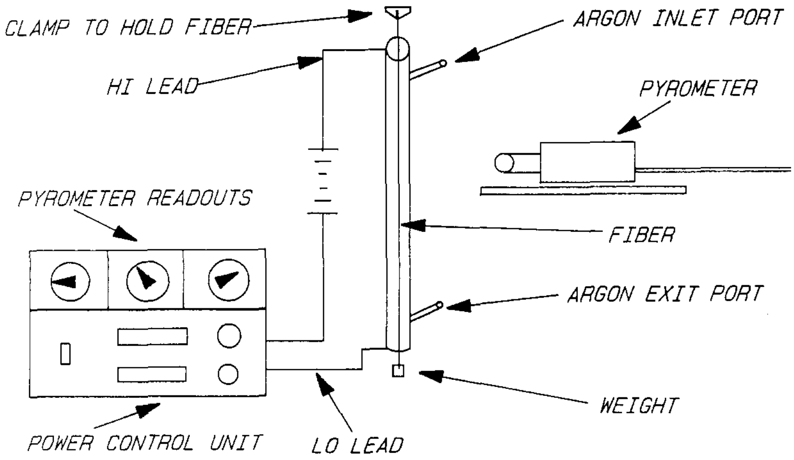

Fig. 2. Schematic of apparatus.

Resistive heating provided two important advantages over other heating methods attempted: (1) a well-defined hot zone and (2) a relatively uniform temperature profile. Temperature profile measurements were made along the length of the fiber. A cold spot observed at the gas inlet port was reduced to less than 6.3 mm in length by preheating the argon to over 100°C. During actual testing, temperature measurements were made 79 cm from the gas inlet port. Small temperature variations (less than 30 at 1500°C) were observed elsewhere along the length of the hot zone (164 cm) due to fiber diameter variations.

The other critical variable of this study, deflection, was measured using a Gaertner Scientific cathetometer. The deflection of an 11.6-g weight attached to the fiber was measured as a function of temperature to a precision of ±0.05 mm.

System calibration was accomplished using a 36-μm-diameter molybdenum wire. Measured expansion values were within ±7% of literature values at temperatures of 1000 and 1250°C [7]. The extremely small wire diameter precluded temperature measurements below 1000°C, and calibration at higher temperatures, above 1250°C, was prohibited by creep of the specimen.

4. RESULTS

4.1. Boron Fibers

The thermal expansion behavior of 102 (4 mil)- and 142 (5.6 mil)-μm boron fibers is shown in Fig. 3. It is evident from the data that there is virtually no difference in expansion between the different-diameter fibers. The curve fit to this data is parabolic, indicating that the coefficient of thermal expansion (CTE) increases linearly with temperature. CTE values taken from the curve are in good agreement with previous measurements made on boron fibers [3, 8].

The upper temperature of the expansion measurements was limited by a severe contraction of the fiber above 750°C. Above 750°C the fiber gradually begins to contract. This contraction is more pronounced at 800°C. Figure 4 shows the contraction of 142-μm (5.6 mil) boron versus time as the fiber was held at a constant temperature of 800°C. This curve is indicative of the contraction observed on 102-μm boron filament also. The causes for this contraction are elaborated upon in Section 5.

4.2. Silicon Carbide Fibers

Figures 5–7 depict thermal expansion behavior of SCS-2, SCS-6, and SCS-9 fibers, respectively. Figure 6 compares expansion results of SCS-6

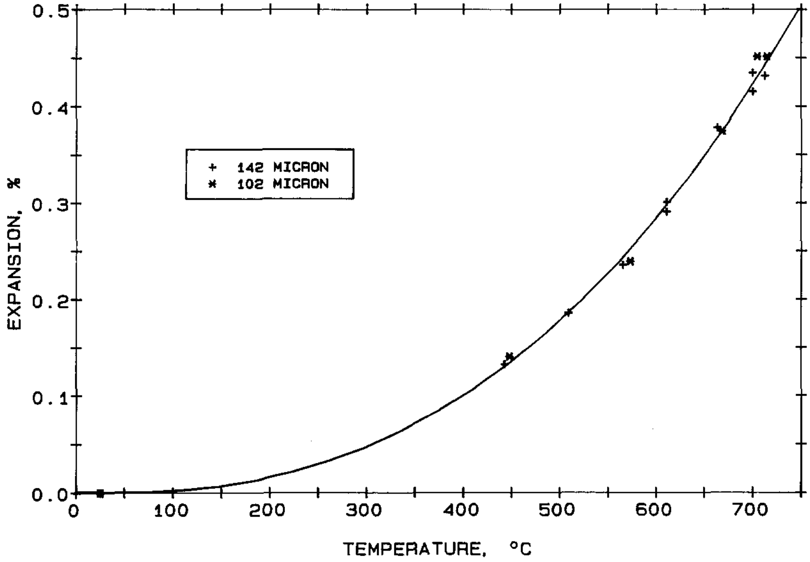

Fig. 3. Linear thermal expansion of 102- and 142-μm boron fibers.

fiber and bulk beta-SiC data from Taylor and Jones [9]. As can be seen from these curves there is relatively small initial expansion from room temperature to 450°C. Further studies are under way to investigate the deviation from linearity over this temperature range.

Above 450°C, the fibers expand linearly until 1300–1350°C (depending

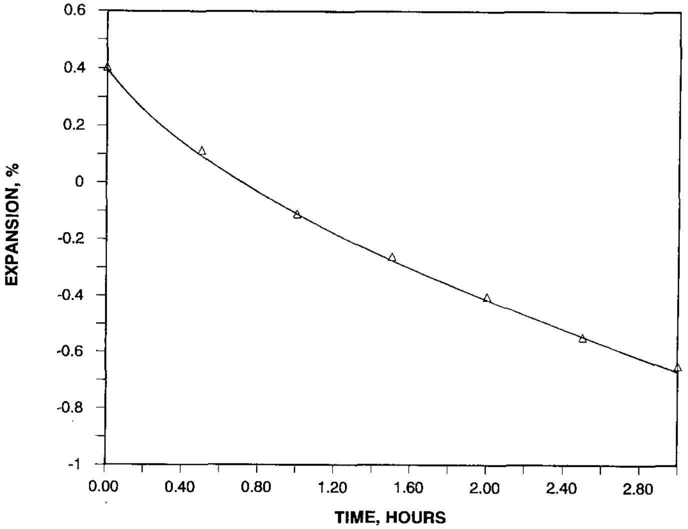

Fig. 4. Contraction of 142-μm boron fiber vs time at 800°C.

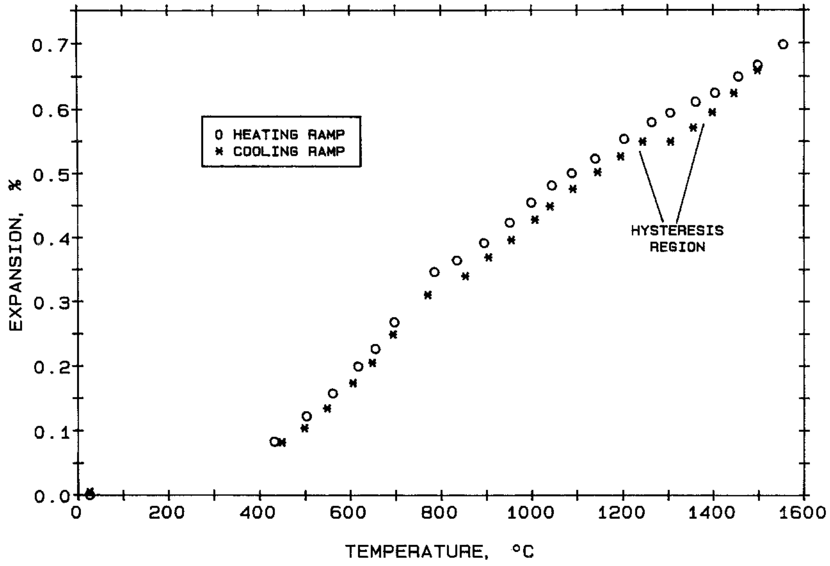

Fig. 5. Linear thermal expansion of SCS-2 SiC fiber.

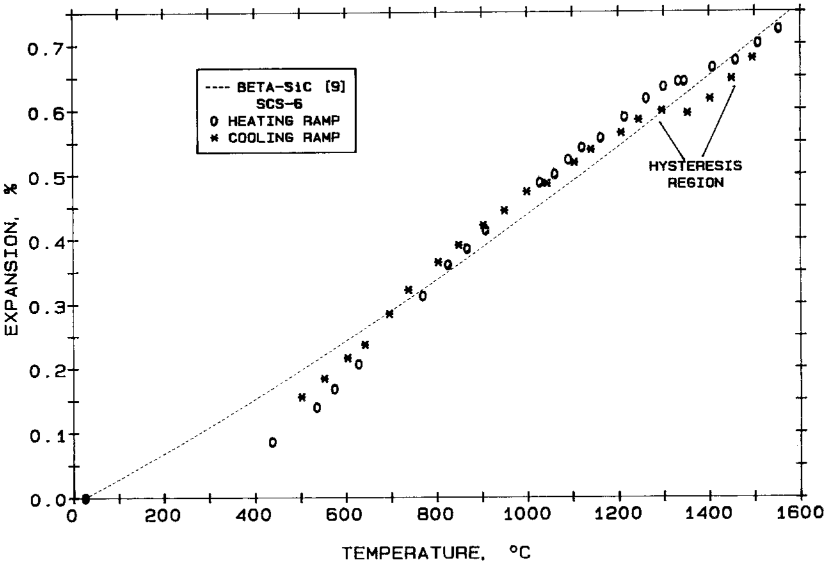

Fig. 6. Linear thermal expansion of SCS-6 fiber and beta-SiC.

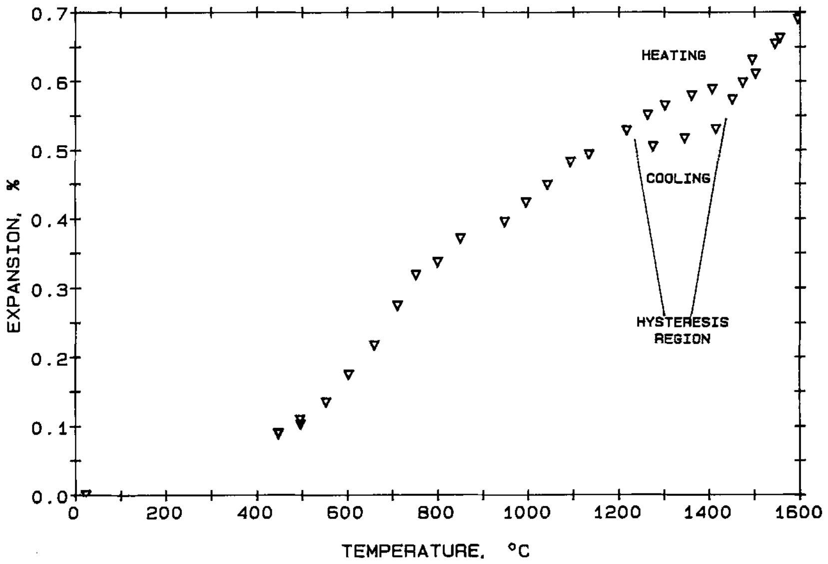

Fig. 7. Linear thermal expansion of SCS-9 SiC fiber.

on the specific SCS fiber). In this temperature range, a dramatic reduction in expansion is observed, with a gradual return to linear expansion at 1470°C.

Upon cooling the fiber, linear contraction occurs until 1300–1350°C (again depending on the fiber), at which time the fiber does not change length while cooling. Below 1200°C the fiber contracts linearly. This hysteresis was observed on all three SCS fibers and was also observed in previous studies [1, 2] performed on SCS fibers. Kern et al. [10] observed a similar hysteresis effect on bulk CVD SiC. They attributed this phenomenon to the contraction of free silicon when going from the solid to the liquid phase at 1412°C. Further discussion concerning the existence of free silicon in these fibers is presented in the following section.

5. DISCUSSION

The observed contraction of the boron fibers at 800°C may be attributed to residual stress relaxation. Microanalysis of the core–sheath interface indicated massive void formation, which is consistent with previous studies [4, 11]. This was attributed to loosely bonded boron atoms reacting with oxygen at the fiber surface, creating voids. These voids migrate toward the core, while boron atoms migrate to the surface. Void coalescense at the core–sheath interface results in relaxation of residual stresses created by boridization of the tungsten core [4, 11].

The exact cause of the hysteresis effect on the SCS fibers is still unclear. The theory presented by Kern et al. [10], attributing the hysteresis to melting of free silicon, could account for the dramatic reduction in expansion with increasing temperature near 1300°C observed in this study. This is based on the fact that silicon contracts in going from the solid to the liquid phase. The presence of free silicon in SCS fibers, however, has not been conclusively proven.

The existence of free silicon is supported by the creep measurements of SCS fibers conducted by DiCarlo [13], who attributed the observed creep in these fibers to grain boundary sliding (GBS) of beta-SiC grains. It is generally accepted that the activation energy for GBS should agree with the lattice self-diffusion energy, the grain-boundary self-diffusion energy of the particular material, or the lattice self-diffusion energy of the impurity phases in grain boundaries [12]. The creep activation energy measured by DiCarlo agreed favorably with the lattice self-diffusion energy of free silicon [13].

While DiCarlo's work suggests the presence of free silicon, previous Auger and TEM examinations have not shown any unreacted silicon [6]. In addition, the presence of free silicon seems unlikely since an excess of carbon is maintained during manufacture of the fiber through the addition of excess amounts of propane gas.

In consideration of the absence of direct proof of free silicon in the fibers, other mechanisms might be causing the hysteresis. Analysis of the microstructure of the fiber reveals an extremely high density of stacking faults and microtwins [6]. It is possible that a temperature-controlled morphological change occurs near 1300°C, which could result in a reconfiguration of these stacking faults. Further investigation is necessary to substantiate this hypothesis and is beyond the scope of this report.

Another possible explanation may be related to the processing temperature of approximately 1350°C, which is near the hysteresis region. CVD processes generate residual stresses which may be relaxing at the hysteresis region. Of course the reversible nature of the hysteresis is not easily explained by residual stress relaxation but the dynamics of the core and sheath interface are not completely understood, so possible mechanical interaction between the two causing the hysteresis is still plausible. Again, further investigation is necessary to validate this possibility. An interesting experiment would be to remove the carbon core and measure the expansion of the sheath independent of core–sheath interaction.

The hysteresis effect observed for all three grades of SCS fibers presents difficulties when incorporating the fibers in brittle matrices such as ceramics for high-temperature applications. No hysteresis is observed in ceramic matrices which are compatible with SCS fiber. Therefore, this thermal expansion mismatch between matrix and fiber will produce residual stress in the composites.

6. CONCLUSION

The resistance heating technique developed in this study proved to be a viable test method for measuring thermal expansion of conductive fibers. Also proven in this study was that thermal expansion of SCS fibers is controlled by the SiC sheath and does not depend on the fiber coatings or the carbon core.

It is apparent from Figs. 4–6 that the thermal expansion behavior of SCS fibers is linear from 450 to 1300°C. Above this temperature all three fibers exhibited a hysteresis effect. Different theories explaining this phenomenon exist, such as the free silicon theory, which is discussed. The absence of collaborating evidence of free silicon by powerful microstructural techniques such as Auger analysis and TEM allows for further speculation of possible causes of the hysteresis in SCS fibers.

The results of this study confirmed previous investigations on boron fibers.

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