Thermophysical and Mechanical Properties of SiC/SiC Composites (5/28/98 draft)

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The key thermophysical and mechanical properties for SiC/SiC composites are summarized in the following. It is anticipated that these data will be available in an upcoming version of the fusion Materials Properties Handbook (MPH) whose activities are coordinated by J.W. Davis (Boeing, St. Louis). The MPH is updated regularly, and should be used as the reference point for design calculations wherever possible.

The engineering database for SiC/SiC composites is very limited, since large quantities of high-quality fibers such as Hi-Nicalon type S (produced by Nippon Carbon) have not been available up to the present time. Much of the published data has been generated on composites fabricated with lower-quality fibers such as ceramic grade Nicalon (cg-Nicalon). The chemical composition, density, elastic constants, thermal conductivity, and neutron radiation resistance of cg-Nicalon (which contains 11.7 wt.% O and has a C/Si atomic ratio of 1.31) [1] is considerably different from that of bulk crystalline SiC which is present in the matrix. The Hi-Nicalon fibers (containing 0.5 wt.% O and a C/Si atomic ratio of 1.39) [1] are also considerably different from SiC. Recent fibers such as Hi-Nicalon Type S (0.2 wt.% O and a C/Si atomic ratio of 1.05) [1] and Dow Sylramic (0.8 wt.% O and a C/Si atomic ratio of 1.0) [2] are expected to produce improved composite properties in the unirradiated and irradiated condition compared to cg-Nicalon and Hi-Nicalon. Table 1 compares some properties of commercial SiC-based fibers and bulk SiC.

Table 1. Comparison of properties of commercial SiC-based fibers and bulk SiC [1-4].

	cg-Nicalon	Hi-Nicalon	Hi-Nicalon type S	Dow Sylramic	Bulk SiC
Diameter (μm)	14	12-14	12	10	----
Tensile strength (GPa)	2.0-3.0	2.8-3.4	2.6-2.7	2.8-3.4	~0.1
Elastic modulus (GPa)	170-220	270	420	390-400	460
Density (g/cm^3)	2.55	2.74	2.98-3.10	3.0-3.10	3.25
Coefficient of thermal expansion (10^{-6}/K)	3.2	3.5	---	5.4	4.0
Thermal conductivity at 20˚C (W/m-K)	1.5	4	18	40-45	100-350
Oxygen content (wt.%)	11.7	0.5	0.2	0.8	0.0
C/Si atomic ratio	1.31	1.39	1.05	1.0	1.0

1. Yield and ultimate tensile strength (unirradiated)

Most of the available data on ceramic matrix composites have been generated using flexural bend strength tests (3- or 4-point bending). Although bend tests are useful for qualitative screening in order to investigate variations in processing parameters, uniaxial tensile testing is preferred for the generation of an engineering data base. Ceramic matrix composites are engineered to produce a moderate amount of fiber pullout during deformation. Extensive fiber pullout produces low ultimate tensile strengths, whereas limited fiber pullout leads to brittle failure modes similar to monolithic ceramics. The optimum tensile toughness generally occurs in ceramic composites with tensile elongations on the order of ~0.2 to 0.5%. Therefore, the 0.2% "yield" strength, which is commonly used for tensile testing in metals, is comparable to the composite ultimate tensile strength. A more appropriate "yield" strength for ceramic matrix composites is the proportional stress limit (corresponding to the onset of matrix microcracking), although the location of the proportional limit is subject to relatively large experimental uncertainty.

The ultimate tensile strength of several different grades of SiC/SiC composites containing 40 vol.% fibers (0/90 weave) have been recently measured by tensile testing [5]. The UTS ranged from 200 to 240 MPa at room temperature and from 228 to 254 MPa at 1000˚C for two different types of SiC/SiC composites fabricated with cg-Nicalon fibers. A room temperature UTS of 217 MPa was measured for a composite fabricated using Hi-Nicalon fibers. The corresponding proportional stress limits were 55 to 70 MPa for room temperature tests of SiC/SiC composites fabricated with cg-Nicalon fibers. Tensile data are not yet available for SiC/SiC composites fabricated with Hi-Nicalon type S or comparable advanced SiC fibers, although composite strengths comparable to that of present-day SiC/SiC composites are expected from theoretical considerations. Specifically, the matrix microcracking stress would be expected to be slightly higher with Hi-Nicalon type S fibers (due to a better match with the elastic modulus of the matrix), whereas the ultimate tensile strength would be reduced due to the lower fiber strength of prototype versions of Hi-Nicalon type S (cf. Table 1).

2. Yield and ultimate strength (irradiated)

Neutron irradiation can produce a significant decrease in the flexural strength of SiC/SiC composites fabricated with cg-Nicalon fibers, due to neutron-induced densification of the fibers which causes debonding at the matrix/fiber interfaces [6,7]. Strength decreases up to a factor of two have been observed in some cases. Improved irradiated behavior is predicted for composites containing SiC-based fibers which have demonstrated better resistance to neutron irradiation, such as Hi-Nicalon, MER-999, and Dow Corning Sylramic fibers [3,8-10]. Experimental studies on composites fabricated with advanced fibers are need to determine whether there is any significant degradation of mechanical strength in these materials.

3. Elastic constants

The elastic constants for SiC/SiC composites depend on the details of the fabrication procedure. Fibers such as cg-Nicalon have elastic constants which are considerably different from crystalline SiC, and therefore strongly influence the measured elastic constants of the composite. In addition, matrix porosity (typically ~8 to 10%) also affects the elastic constants of the composite. The room temperature Young's moduli of SiC-based fibers range from ~200 GPa for cg-Nicalon to 270 GPa for Hi-Nicalon, and 420 GPa and 400 GPa for Hi-Nicalon Type S and Dow Sylramic [1,2,8]. The corresponding Young's modulus for bulk crystalline SiC varies from 460 GPa at room temperature to 435 GPa at 1000˚C [11]. Somewhat lower values of 415 GPa (20˚C) to 392 GPa (1000˚C) have been reported for sintered alpha-SiC [12]. According to measurements obtained during tensile testing, the Young's modulus for a given SiC/SiC composite shows a very slight (5%) increase as the temperature is increased from 20 to 1000˚C [5]. The quantitative values are strongly dependent on the fabrication process, with values for cg-Nicalon fiber-based composites (40 vol.% fibers) ranging from 141 to 215 GPa at room temperature [5]. The corresponding Young's modulus for a SiC/SiC composite fabricated with Hi-Nicalon fibers was 270 GPa. Values approaching 400 GPa would be expected for high-quality, low-porosity SiC/SiC composites fabricated with Sylramic or Hi-Nicalon type S fibers. Matrix microcracking (in composites subjected to stress above the proportional limit of ~70 MPa) will cause a reduction in the elastic modulus [13]. The shear modulus for bulk (sintered) alpha-SiC is 179 GPa at room temperature and 169 GPa at 1000˚C [12]. Poisson's ratio for bulk SiC is ~0.18 between 20 and 1000˚C [11,12].

4. Thermal expansion, specific heat and thermal conductivity

The themophysical properties of SiC/SiC composites (particularly thermal conductivity) are also dependent on the fabrication procedure. The measured instantaneous coefficient of thermal expansion (α_{th}) for SiC/SiC composites fabricated with cg-Nicalon fibers (40 vol.% fibers) are 2.5-3 ppm/˚C, with no pronounced dependence on temperature between 20 and 1000˚C [5,14]. The lower value refers to through-thickness measurements on 2-D composites, and the higher value refers to in-plane measurements. The bulk SiC value is 2.2 ppm/˚C at room temperature and 5.0 ppm/˚C at 1000˚C, with an average value between 20 and 1000˚C of 4.0 ppm/˚C [11,12]. The specific heat at constant pressure (C_P) varies from 620-640 J/kg-K at 20˚C to 1200-1250 J/kg-K at 1000˚C for both monolithic SiC and SiC/SiC composites, where the higher values refer to bulk SiC [5,11,12,15]. The most rapid changes in the specific heat occur at temperatures below 200˚C, which corresponds to about one-half of the Debye temperature for SiC (~900 K). The specific heat for bulk SiC is 1134 J/kg-K at 500˚C and 1189 J/kg-K at 700˚C [11,15]. A slightly less pronounced variation in the temperature-dependent specific heat has been recently presented for sintered alpha-SiC [12]. The source of the specific heat discrepancy between ref. [12] and refs. [11,15] is uncertain.

The thermal conductivity of SiC/SiC composites is strongly dependent on the processing conditions, type of fiber, and fiber architecture. The upper limit for thermal conductivity corresponds to that obtained in single crystal and high-purity CVD SiC, with maximum values of ~320 W/m-K at room temperature and 78 W/m-K at 1000˚C (Fig. 1). The thermal conductivity of most of the currently-available commercial fibers is significantly lower than that of bulk high-purity SiC, and therefore the fibers typically do not make a large contribution to the conductivity of the composite. The thermal conductivity of SiC-based fibers at 20-500˚C varies from ~1.5 W/m-K for cg-Nicalon and ~4 W/m-K for Hi-Nicalon to 18 W/m-K for Hi-Nicalon type S [16]. Room temperature thermal conductivities for recently developed Sylramic and Tyranno-SA fibers are ~40-45 and 64 W/m-K, respectively [2,17]. The in-plane thermal conductivity for a 2-D (0/90) plain weave SiC/SiC composite fabricated from cg-Nicalon fibers (40 vol.%) and a CVI matrix (10% porosity) varies from ~19 W/m-K at 20˚C to 8 W/m-K at 1000˚C [5]. The corresponding through-thickness conductivities are 9 and 3 W/m-K, respectively. The through-thickness thermal conductivity for a 2-D (0/90) plain weave SiC/SiC composite fabricated from Hi-Nicalon fibers (40 vol.%) and a CVI matrix (10% porosity) is ~15 W/m-K at 20˚C [5]. SiC/SiC composites with transverse thermal conductivities of ~75 W/m-K at room temperature and 30-35 W/m-K at 1000˚C have recently been fabricated using CVR and reaction sintering techniques [18,19].

Unlike the case for metals (where the thermal conductivity is dominated by electron transport), irradiation can cause a significant reduction in the thermal conductivity of SiC/SiC composites. The degradation is particularly large at low irradiation temperatures, as shown in Fig. 2. An approach to saturation occurs at low damage levels during low temperature (<300˚C) irradiation. The fluence dependence of the conductivity degradation has not yet been studied at high temperatures. The limited existing data base indicates the irradiated thermal conductivity at high irradiation temperatures (~1000˚C) is about 25 to 50% of the unirradiated value for bulk SiC irradiated to damage levels greater than 20 dpa [6,20]. The largest relative degradation in thermal conductivity is observed in materials with the highest initial thermal conductivity, i.e., the irradiated thermal conductivity in bulk tends to approach a similar value irrespective of the unirradiated thermal conductivity.

The values shown in Fig. 2 represent the upper limit of expected thermal conductivities for irradiated SiC/SiC composites, since impurities and porosity introduced during fabrication of composites (as well as fiber-matrix phonon scattering and the lower conductivity of existing fibers compared to bulk SiC) would cause a degradation in the conductivity of SiC/SiC composites compared to monolithic SiC. Due to the poor radiation stability of cg-Nicalon, very low irradiated thermal conductivity data are obtained in composites fabricated with this type of fiber [20]. A more realistic estimate of the irradiated thermal conductivity of composites with advanced (radiation resistant) fibers is obtained by using data obtained on composites fabricated with SiC whiskers (SiC_W). The thermal conductivity of a SiC/SiC_W composite irradiated to 43 dpa at 1000˚C ranged from ~12.5 W/m-K at 400˚C to ~10 W/m-K at 1000˚C [20]. The effects of fusion-relevant helium generation rates on the thermal conductivity of irradiated SiC has not been investigated.

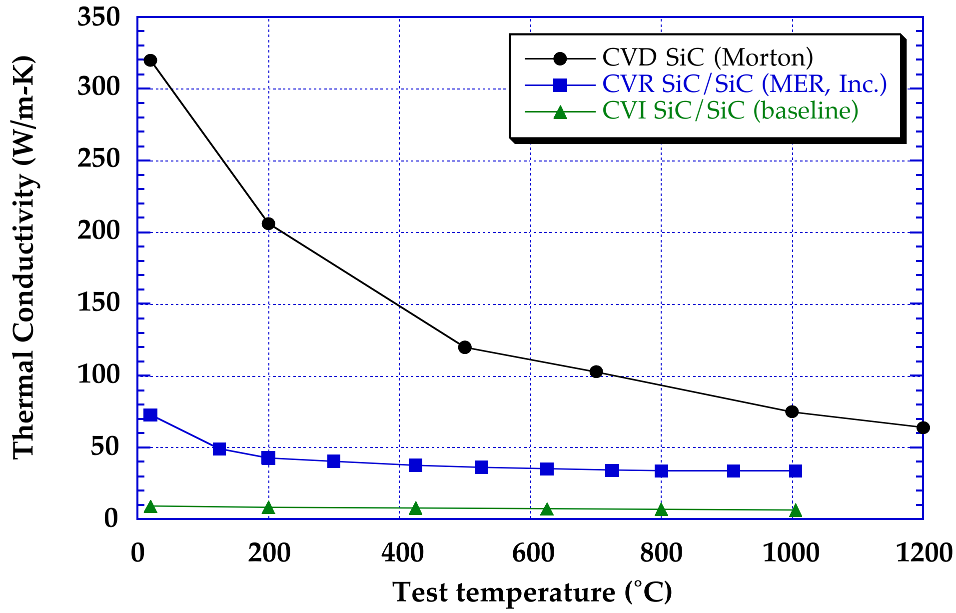

Fig. 1. Comparison of the transverse thermal conductivity of monolithic CVD SiC and two grades of SiC/SiC composites [11,19].

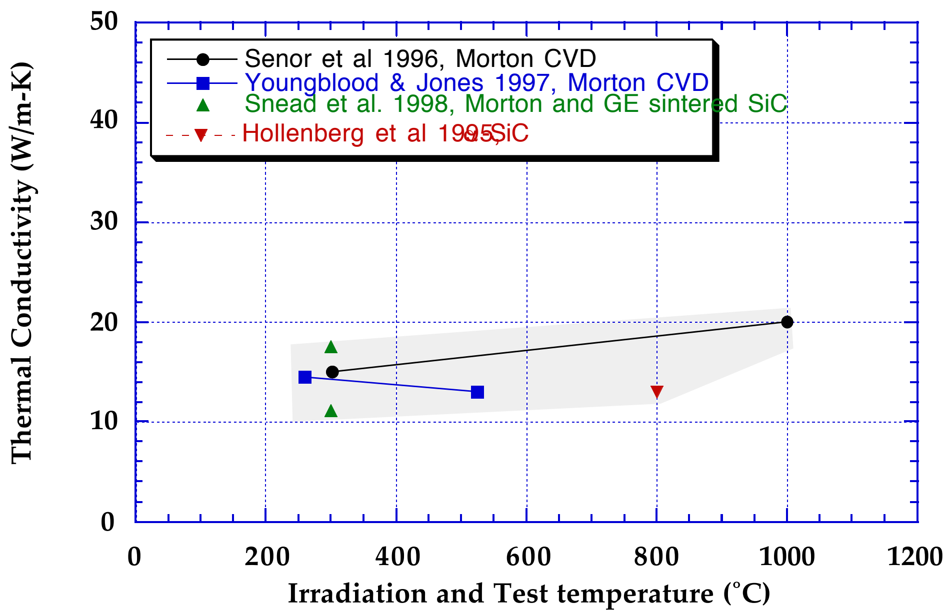

Fig. 2. Effect of neutron irradiation on the thermal conductivity of bulk SiC [9,20-22]. The studies in refs. [20-22] were performed on samples irradiated to 25-43 dpa, whereas the data by Snead et al. were obtained on samples irradiated to 0.1 dpa.

5. Irradiation-induced dimensional changes

A summary of the radiation-induced swelling in monolithic SiC as a function of irradiation temperature is shown in Fig. 3 [9,10,22-25]. Three distinct temperature regimes can be identified. At low temperatures (<150˚C), a crystalline to amorphous phase transition is induced at relatively low doses (0.1-1 dpa). The amorphous phase has a much lower density compared to the crystalline phase, which results in ~11% swelling [25]. Bulk SiC exhibits moderate swelling due to neutron irradiation at temperatures between 150 and 900˚C. The swelling in this temperature range is attributable to small point defect clusters, and is commonly referred to as "point defect swelling". The swelling decreases with increasing irradiation temperature, and reaches an apparent saturation level after relatively low doses. For example, the swelling observed at 500˚C after 25 dpa [22] lies within the data scatter band obtained for ~1 dpa irradiations. At high irradiation temperatures, void swelling occurs in SiC. The minimum temperature for significant void swelling in SiC is somewhat uncertain. Early work by Price [24] indicated that significant void swelling did not occur for irradiation temperatures below ~1100˚C. However, two recent studies have observed high volumetric swelling in SiC irradiated at ~1000˚C [9,10]. Further work is needed to determine the minimum temperature for void swelling in SiC. The effects of fusion-relevant helium generation on the dimensional stability of SiC has not been adequately studied.

One important consequence of the large chemical differences between currently available SiC-based fibers and pure SiC (Table 1) is that that the fibers and stoichiometric SiC matrix in the composite will respond differently to irradiation. Figure 4 shows the effect of neutron irradiation on the density of SiC and SiC-based fibers at 500-650˚C [3,9,22,26]. A moderate amount of swelling (~1.2%) occurs in pure SiC during irradiation, with an apparent saturation in swelling observed at doses above ~0.1 displacements per atom (dpa). In contrast, both ceramic grade Nicalon and Hi-Nicalon experience significant densification, with the largest densification observed in the lower-grade cg-Nicalon fibers. The data in Fig. 4 and other studies [3,22,27,28] indicate that amount of densification in cg-Nicalon increases with increasing irradiation temperature between 150 and 810˚C. The shrinkage of the fibers during irradiation causes debonding with the matrix, and produces low strength in irradiated composites fabricated using current grades of SiC-based fibers. The typical decrease in strength observed in irradiated composites is $\geq$20%, depending on the irradiation conditions.[6,9,22] Smaller strength changes would be expected in irradiated composites containing advanced fibers (due to a better match with the SiC matrix behavior), but experimental data are not yet available.

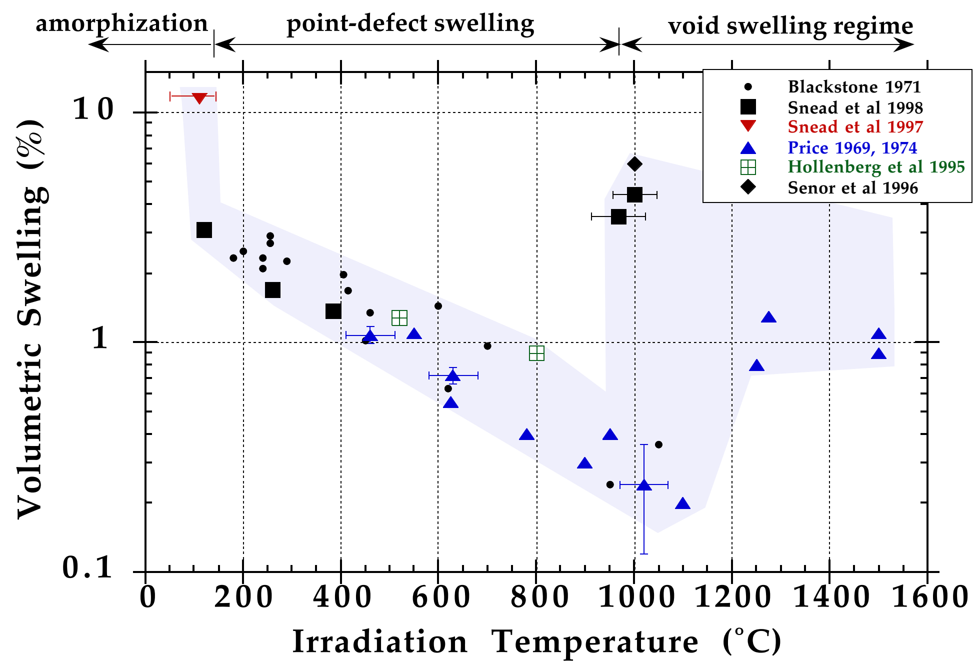

Fig. 3. Radiation induced swelling in bulk SiC as a function of irradiation temperature [9,10,22-25].

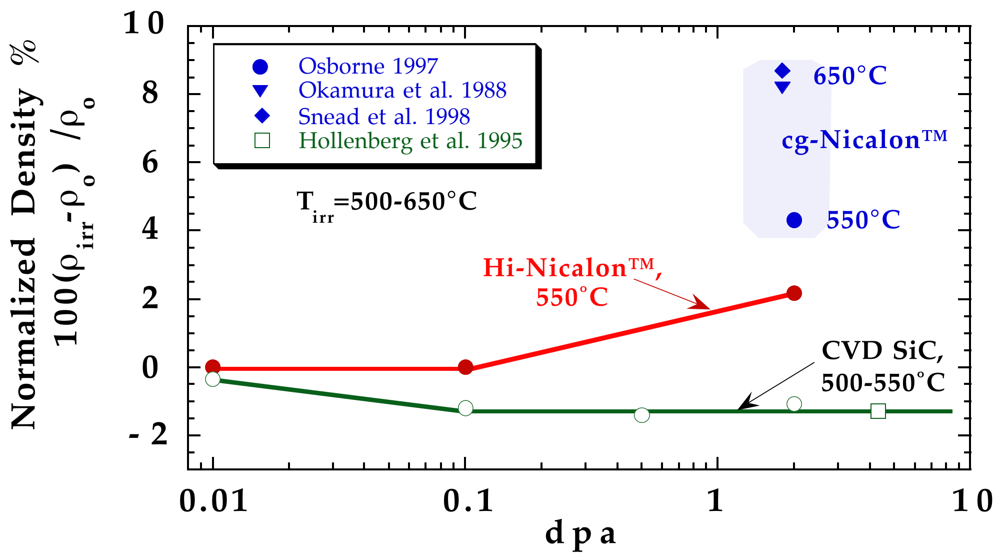

Fig. 4. Comparison of the effect of low-dose neutron irradiation at 500-650˚C on the density of SiC and SiC-based fibers [3,9,22,26].

6. Irradiation creep

The magnitude of irradiation creep has not been accurately determined for either monolithic SiC or SiC/SiC composites. Rough estimates obtained for monolithic SiC suggest that the irradiation creep constant may be $K \sim 10^{-12}$ $(Pa\text{-}dpa)^{-1}$ at 500-1100˚C [29], which is lower than the value observed for some other ceramics [30].

7. Recommended reference operating temperature limits

The minimum operating temperature limit will be determined by either the crystalline to amorphous transition temperature (~120˚C for fusion reactor damage rates) [25], or else radiation-induced degradation in the thermal conductivity. The thermal conductivity degradation is very severe even at low doses for low temperature ($\leq$300˚C) irradiations (cf. Fig. 2). The thermal conductivity degradation becomes less pronounced with increasing irradiation temperature up to ~1000˚C, due to a decrease in the saturation concentration of point defect clusters. Additional experimental data at temperatures between 400 and 1000˚C are needed to quantify the thermal conductivity degradation as a function of dose and temperature. The maximum temperature limit will likely be determined by void swelling considerations, although there are not sufficient data at elevated temperatures (900-1400˚C) to make a clear determination. The tentative reference minimum and maximum operating temperature limits for the purposes of the APEX design study are 400˚C (due to thermal conductivity degradation concerns) and 1000˚C (due to void swelling concerns).

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