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High-temperature mechanical and material design for SiC composites *

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Silicon carbide (SiC) fiber reinforced composites (FRCs) are strong potential candidate structural and high heat flux materials for fusion reactors. A concise discussion of the main material and design issues related to the use of SiC FRCs as structural materials in future fusion systems is given in this paper. The status of material processing of SiC/SiC composites is first reviewed. The advantages and shortcomings of the leading processing technology, known as chemical vapor infiltration are particularly highlighted. A brief outline of the design-relevant physical, mechanical, and radiation data base is then presented. SiC/SiC FRCs possess the advantage of increased apparent toughness under mechanical loading conditions. This increased toughness, however, is associated with the nucleation and propagation of small crack patterns in the structure. Design approaches and failure criteria under these conditions are discussed.

1. Introduction

An important feature of fusion reactions is that the resulting radioactive products are short-lived. However, the interaction of neutrons with structural materials in fusion systems can lead to long-lived radioactive decay chains. Proper selection of structural materials can therefore lead to significant reductions in the level and duration of environmentally hazardous radioactive products. Several neutronic and conceptual fusion reactor studies have concluded that the postshutdown radioactive inventories of FW/B structures made of pure SiC are dramatically lower than any metallic alloy considered for fusion so far [1–4]. The same assessments have shown conclusively that decay heat generated in the reactor, in case of a loss of coolant accident, can be safely and passively removed without the danger of radioactivity release to the environment. It is also realized that long-term radioactive inventories will mainly be controlled by the level of impurities in the structure. Therefore, processing technologies which offer the potential for significant reductions in the level of impurities should be attractive for the development of SiC structures. Another important feature of SiC structural materials is their high temperature capabilities. Operational temperatures approaching 1000°C are potentially attainable, which can lead to vastly improved thermal cycle efficiency. For these important reasons, the development of structural SiC components is perceived to be of paramount significance to the successful commercialization of fusion energy. In this article, we analyze and review the body of knowledge which is relevant to the application of SiC, as a structural material, in future fusion reactors.

2. Processing of SiC / SiC FRCs

Several methods have been developed for production of SiC fibers for use as reinforcements in high-temperature composites. Continuous yarns of 500 fibers are now in commercial production by Nippon Carbon Co. [1], under the trade name Nicalon. The process starts by dechlorinating dichlorodimethylsilane with molten metallic sodium to produce the solid polymer. Further processing steps are polymerization, and densification of amorphous Si and C at high temperatures (1200–1500°C). The final microstructure is crystalline β-SiC of density in the range 3.16 g/cmm^3, and of crystallite size of 20–50 μm.

SiC monofilaments can also be prepared by the chemical vapor deposition (CVD) process, as described in refs. [2,3]. SiC is deposited from vapor mixtures of alkyl silanes and H_2 onto a substrate formed by a resistance-heated W wire or C filament. The substrate has a diameter of 10–25 μm, and forms the fiber core. The final filament is commonly 100–150 μm in diameter.

Whiskers of SiC can be prepared either from rice hulls [4], or by a vapor–liquid–solid (VLS) process [5]. Whiskers produced from rice hulls are short; with lengths around 50 μm. Longer and smoother whiskers are prepared at Los Alamos [5], by the VLS process.

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Such whiskers possess superb mechanical properties, with an average strength of 8.4 GPa and an average elastic modulus of 580 GPa.

Multifilament fibers can be assembled into two- and three-dimensional structures by interlacing, intertwinning, or interlooping. Combining the high strength of fibers with proper matrix–fiber interface frictional properties, fiber architectures will expand the design options for tough and reliable fusion structural materials. Fiber architectures can be classified into six categories: discrete, continuous random, one-dimensional, two-dimensional, and fully integrated. Selection of one of these architectures will depend on a number of factors. These are: (1) the capability for in-plane multiaxial reinforcements, (2) through-thickness reinforcements, (3) the capability for final shape manufacturing, and (4) leak-tightness of the final components during high-temperature operation. Selection of a particular form of architecture for fusion may be premature at present, because matrix processing techniques are still evolving. While 3D architectures provide an orthotropically tougher composite, the CVD technology employed at present is limited to low fiber volume fractions, and the procedure is quite lengthy. On the other hand, 2D laminates can be produced at much greater speed, and can achieve higher fiber volume fractions, and the final component mechanical properties will be anisotropic. This feature will certainly lead to reduced capabilities of components to carry shear loads.

3. Data base

SiC is known to have high intrinsic strength and stiffness ($E = 450$ GPa at RT), high-temperature stability (decomposition temperature = 2830°C), and excellent oxidation resistance. Its relatively high conductivity ($k = 0.25$ W cm^{-1}°C^{-1} at 200°C) and low coefficient of thermal expansion ($\alpha = 3.8 \times 10^{-6}$°C^{-1} at 200°C) result in favorable thermal shock resistance when compared to other ceramic materials. The thermal conductivity of CVD SiC, k(W cm^{-1}°C^{-1}), and the specific heat, C_p (J kg^{-1}°C^{-1}) are given by empirical equations of the form:

$$\text{property} = \sum_{i=1}^{4} M_i T^1$$

where T is temperature in °C. Values of the polynomial fit coefficients are shown in table 1.

3.1. Mechanical properties

The tensile strength of Nicalon fibers is statistical because of the existence of defects (e.g. voids and cracks) during the manufacturing process. It is also strongly influenced by heat treatment, test atmosphere and test temperature. Commercial Nicalon fibers in various atmospheres show degradation in strength at or above 1000°C [6]. Strength deterioration is attributed to: (1) chemical reaction between SiO_2 and free C, leading to surface damage; (2) crystallization of the amorphous structure; (3) oxidation in gaseous atmospheres. The tensile strength of CVD-prepared SiC fibers on C cores is retained only up to 800°C. The 100 h rupture strength of CVD fibers was shown to degrade greatly above 1100°C [7]. While the average tensile strength of unirradiated monofilaments is 2.8 GPa et temperatures below 900°C, preform wires have an average flexural strength of only 1.3 GPa. The uniform elongation at fracture is 1.5–2.0%.

For CVD fibers, it was observed that fiber creep is anelastic (i.e. recoverable), and is a result of grain boundary sliding [8], controlled mainly by a small amount of free Si in the grain boundary. Fiber creep activation energy of 480 kJ mole^{-1} was concluded to be similar to sintered SiC material, and the resulting creep rate is about an order of magnitude greater than the Nicalon fibers [8]. The lower creep resistance of the more commercial Nicalon fibers was attributed to the lower grain boundary (GB) viscosity of free Si. Diffusional creep by GB sliding has an activation energy estimated at 611 kJ mole^{-1}, and a preexponential of 3.1×10^{-7} m^2 s^{-1} [9].

These observations indicate that high-temperature creep properties of the composite may be life-limiting

Table 1
Coefficients of polynomial fits to selected properties of SiC, property = $\Sigma_{i=1}^{4} M_i T^i$

Property / Coefficient	Thermal conductivity [W m^{-1} K^{-1}]		Specific heat [J kg^{-1} K^{-1}]	Fracture stress, σ_f [MPa]	Young's modulus [GPa]	Swelling $\delta V/V$	
	Unirradiated	Irradiated				< 1000°C	> 1000°C
M_0	209.3	22.62	435.53	−993.9	605.632	1.43	−71.19
M_1	−0.319	−0.0282	3.08	7.42	−1.407	0.0059	0.15
M_2	2.6×10^{-4}	1.389×10^{-5}	−0.0047	−0.013	0.003	-1.56×10^{-9}	1.09×10^{-4}
M_3	-1.3×10^{-7}	8.3×10^{-9}	3.31×10^{-6}	9.54×10^{-6}	-2.087×10^{-6}	8.58×10^{-9}	2.56×10^{-8}
M_4	2.6×10^{-11}	-2.28×10^{-12}	-8.41×10^{-10}	-2.42×10^{-9}	0	0	0

in fusion. In particular, the crack bridging mechanism, which is the main feature for enhancement of the composite's thoughness, will have to be critically examined.

The high-temperature deformation characteristics of hot-pressed SiC have been experimentally investigated, and may be taken as indicative of the matrix in a composite [8,9]. The activation energies for power law as well as lattice diffusion creep were found to be about 912 kJ mole^{-1} [9]. Transition from power law creep at high stresses to diffusional creep at low stresses was also observed [10]. However, the diffusional matrix creep rates were found to be very small. A power law index of 5 was found to be similar to that of pure Si. The mechanical properties of unirradiated reaction sintered SiC (i.e. Young's modulus, E (GPa), and bend strength, σ_f (MPa)) as functions of temperature, T (°C), are also given by polynomial fits, with coefficients defined in table 1. Graphical representation is shown in fig. 1.

The critical stress intensity factor of the SiC matrix is expected to be low, as compared to metallic alloys. However, the bridging of cracks with the strong fibers will possibly allow for higher values of an effective K_{IC}, especially when one is concerned about catastrophic through cracks. Room temperature values of K_{IC} for an unbridged hot pressed SiC range from 2.6 to 5.7 MN.M$^{-3/2}$, and is independent of temperature, up to 1000°C. Sintered SiC shows temperature-independent K_{IC} of about 3 MN.M$^{-3/2}$, up to 1500°C.

An allowable design stress for SiC FRCs will depend on a wide range of manufacturing and operational factors. For example, recent fracture test results at PNL at 800°C on SiC FRCs from several vendors showed them to have strengths in the range 300–600 MPa in the unirradiated condition. Neutron irradiation at the same temperature, and up to approximately 10 dpa, showed that the fracture strength declined by about a factor of 2–2.5 [11]. It is possible then, with modest technology extrapolation, that low pressure FW/B components would be designed to operate reliably in a fusion environment.

3.2. Coolant compatibility

SiC has excellent resistance to oxidation up to 1000°C, because of the formation of a protective stable SiO_2 layer. The stability of the SiO_2 layer is dependent on the O_2 partial pressure, being unstable at pressures lower than 10^{-10} to 10^{-8} atm [12]. In a primary helium loop, the partial pressure of O_2 is expected to exceed these values. However, the reaction of the interfacial layer between the fibers and the matrix with oxygen will ultimately determine the upper usable temperature of the composite. At present, this layer is either C, BC_4, or BN. While carbon oxidation will severely limit the upper temperature, the production of He and H from nuclear reactions in B compounds is expected to degrade the strength of SiC FRCs. An important factor which needs yet to be studied is the possible reduction of the passive SiO_2 layer by tritium or hydrogen.

Compatibility studies of SiC in molten Li indicated that intergranular penetration degrades its fracture strength [13]. Reaction with the glassy phase at the GB

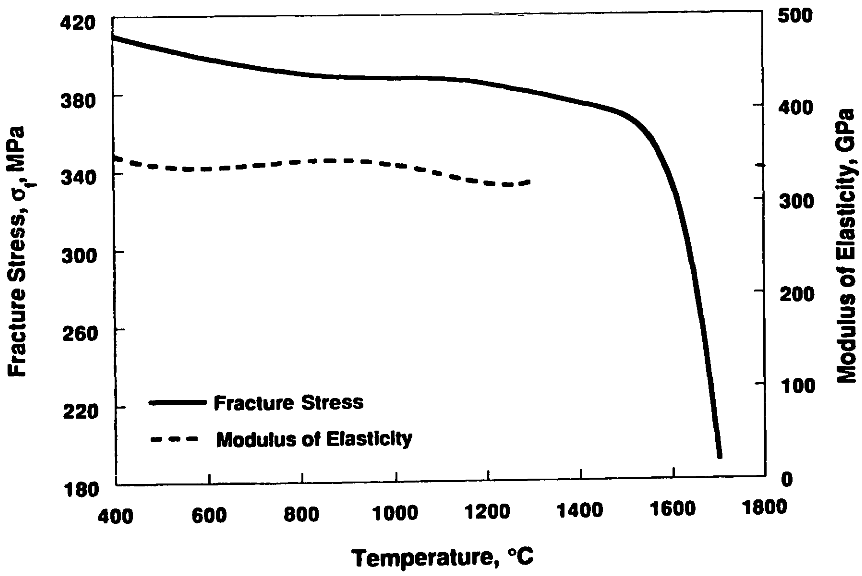

Fig. 1. Temperature dependence of the fracture stress and Young's modulus of SiC.

is thought to be the cause of this rapid penetration. In a molten lithium environment, the uniform corrosion rate was reported to be extensive [13].

3.3. Radiation effects

The strong directional bonding and the mass difference between Si and C atoms render the crystalline form of β-SiC exceptional radiation resistance characteristics. Recent molecular dynamics (MD) studies [14] show that replacement collision sequences (RCSs) are improbable, and that the displacement of C atoms is much easier than Si. MD computer simulations [14] show that while the average threshold displacement energy (E_d) is 16 eV for C, it is about 93 eV for Si. This indicates that the stoichiometry of the displacement cascade will differ substantially from that of the matrix. It is also observed that energetic Si PKAs displace multiple C atoms which end up on ⟨111⟩ planes. Thus, C-rich interstitial dislocation loops will tend to form on ⟨111⟩ planes. Experimental observations at temperatures below 1000°C corroborate this conclusion [15]. Vacancies and He atoms exhibit considerable mobility above 1000°C. These fundamental considerations may explain some of the observed features of SiC dimensional changes, as function of temperature and fluence [15–18].

Price [15] observed Frank-type loops on [111] planes which may be C-rich. Below 1000°C, point defects tend to form loops on [111] planes and swelling is therefore expected to saturate. For example, Harrison and Correli [19] observed large loops (10–200 nm) in β-SiC, after neutron irradiation to a fluence of 1.8×10^{23} cm^{-2}. At temperatures above 1000°C, cavities form, and swelling does not saturate. The presence of helium results in further increases in the swelling rate by the known gas-driven swelling mechanism. Swelling of β-SiC in the temperature range 625–1500°C, and at a neutron fluence ($E > 0.18$ MeV) of 1.2×10^{22} [15] is represented by two separate polynomials, with two different sets of coefficients below and above 1000°C, respectively. The coefficients, and the general swelling behavior as a function of temperature is shown in fig. 2. Additional helium will drive swelling to higher values, particularly at temperatures above 1200°C [20]. The limited accumulated evidence from radiation effects data indicate that the upper temperature limit for use of SiC in structural design is in the range of 900–1000°C.

4. Design with SiC / SiC composites

Design rules for SiC/SiC composites in the high-temperature and radiation environment of fusion reactors are obviously not established, mainly because the test data base is not complete. This data base for mechanical properties must also be made on full-size components. Failure stresses will have to be determined for particular applications (e.g. load bearing but not leak-tight components, leak-tight components, components which resist thermal stresses, etc.). A promising failure approach would be to use an interactive theory, such as the Tsa-Wu criterion. In such an

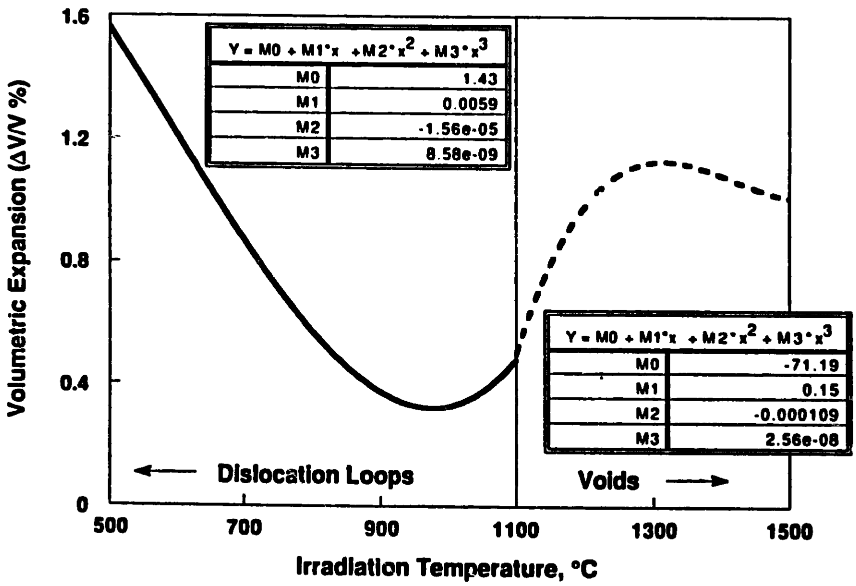

Fig. 2. Volumetric swelling of SiC as a function of temperature at a neutron fluence of 1.2×10^{22} n cm^{-2} ($E > 0.18$ MeV).

approach, the failure stress tensor is measured. This would give failure stress components in tension, compression, shear, for both in-plane and out-of-plane components. Structural analysis would be fairly complete, and would result in the definition of safety factors in each direction. This approach would take into account the probabilistic variability of properties, as determined by experimental measurements. There will be no need to use Weibull statistical analysis, because safety factors and the experimental failure tensor would guarantee safe operation, as desired from a particular component.

5. Conclusions

SiC/SiC FRCs are excellent, low-activation and safe structural materials for the high-temperature and radiation environment in commercial fusion reactors. Their superior mechanical and physical properties would allow for operational temperatures approaching 900–1000°C, thus achieving high thermal cycle efficiencies. The strong covalent bond between Si and C results in promising resistance to the damaging effects of neutron irradiation. Increased toughness because of the reinforcement with strong fibers will make deterministic design approaches possible. However, considerable research and development will be needed before the material will be able to meet its promise.

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