Comments Regarding
Silicon–Carbide Design Limits
for Fusion Applications*

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COMMENTS REGARDING SILICON-CARBIDE DESIGN LIMITS
FOR FUSION APPLICATIONS

SUMMARY

In a recent paper entitled "Nonmetallic Materials For Plasma Facing and Structural Applications in Fusion Reactors," potential design limits for candidate nonmetallic materials were discussed [1]. The effects of neutron irradiation on silicon carbide (SiC), titanium carbide (TiC), and boron carbide (B₄C) were addressed, and operating limits for fusion applications were suggested.

Because of the sparsity of data, particularly irradiation–damage responses of ceramic matrix composites such as SiC/SiC composites, extrapolation from bulk material data is necessary. However, matrix–reinforcement interactions, which are responsible for the characteristic properties of composites, are often neglected. Furthermore, the response of plasma–facing ceramic compounds is complex and subject to large uncertainties. Major issues regarding SiC raised in Ref. [1] are restated, followed directly by our comments. For more detailed descriptions of the comments, the reader is referred to the main body of the text. Following the restatements and comments, highlights of neutron irradiation effects on SiC are listed.

- ACTIVATION
  - The low–activation characteristic of SiC is questioned, based on the second–step aluminum reaction that forms long–lived $^{26}\text{Al}$.
  - The high–threshold–energy $^{26}\text{Al}$ production is limited to within a few centimeters of the first wall. The structural materials of an SiC/SiC–composite first–wall/blanket module, such as that of ARIES–I and ARIES–IV reactors, reaches the remote–handling surface–dose limit of 1 mR/h after only 2.5 days, while the hands–on limit of 2.5 mR/h is reached after 27 years of cooling (total exposure 20 MWy/m$^2$). The hands–on limit is desirable for recycling processes, which is not necessary for SiC because it does not have any resource limitations.
• PLASMA–FACING ISSUES

EVAPORATION–RATE OF SiC:
— The relatively high SiC vapor pressure compared to that of B₄C and TiC suggests much larger evaporation rates for SiC than for the other candidates.

○ For plasma–facing multicomponent materials, the evaporation rate will be determined by the component least likely to be sputtered preferentially. For prolonged exposure of TiC and SiC to scrape–off–layer plasmas, carbon depletion will result in the formation of, respectively, almost free Ti and Si surfaces. The evaporation rates of such surfaces is thus determined by those of the elemental vapor pressures. Because the vapor pressure values of Si and Ti are within a few factors, the pseudo or “net” evaporation rates for SiC and TiC will also be similar. However, impurity gettering processes will complicate sputtering and evaporation processes and will have to be considered in future experiments.

TRITIUM RETENTION:
— Based on deuterium retention measurements, a minimum operating temperature of 800°C for plasma–facing SiC components is suggested.

○ Chemical–vapor–deposited SiC has very small proton–diffusion coefficients. Consequently, plasma–driven permeation of tritium through the first wall may not be a major concern. First–wall evaporation and sputtering time scales are larger than tritium–diffusion time scales of SiC. Small diffusion coefficients of tritium, particularly at low temperatures, will not necessitate high temperature operation of an SiC first wall in order to ensure low tritium inventories (note: an SiC/SiC–composite first wall is coated with a few mm of sacrificial chemical–vapor–deposited SiC).

• DIMENSIONAL CHANGES

SiC SWELLING:
— Based on bulk swelling data, a narrow operating–temperature window between 800 and 950°C is suggested.

○ The swelling of most SiC compounds shows a tendency to saturate at low fluences of $2 \times 10^{24}$ m$^{-2}$ and to have minimum
linear expansion (< 0.05%) when irradiated to between 850 and 1100°C. However, the macro-structure of SiC/SiC composites will widen the minimum-swelling temperature window significantly, because of their ability to accommodate swelling internally.

SIC-FIBER SHRINKAGE:
— Presently available SiC fibers will undergo significant shrinkage under irradiation, which reduces the fracture strength of SiC/SiC composites significantly.

○ Present-generation SiC fibers with high oxygen content (16 wt%) experience significant fiber shrinkage when exposed to neutron irradiation. Newly developed SiC fibers with low oxygen content (0.3 wt%) not only show a significant improvement in high temperature strength, but will also experience smaller dimensional changes under irradiation.

• LIFETIME
— Mechanical property changes in neutron-irradiated SiC samples were reviewed. A lifetime limit of 1 to 2 MWy/m² based on recent fracture-strength data of irradiated bulk SiC is suggested.

○ Lifetime estimates for composite materials is possible only after complex analysis of an extensive data base. Such a data base does not exist for SiC/SiC composites generally, much less for neutron irradiated samples specifically. A limited data base for irradiated bulk SiC does exists. However, there is a vast scatter in the data which, for the most part, is due to differences in manufacturing processes and load history of the SiC samples. Therefore, extrapolation of present bulk-material data to composites is questionable.

The strength levels of ceramic composites are insensitive to matrix flaws (present-day high-fracture-strength composites may contain as much as 10% porosity). Consequently, composites exhibit tolerances to overstrains, such as severe thermal shock or impact, which would cause catastrophic failure of bulk ceramics. Radiation generated defects would, therefore, impact the strength levels of composites to a far lesser extent than they would of bulk ceramics or metallic alloys. Reasonable lifetime estimates are not feasible, given the present-day radiation data base of ceramic composite materials.
HELIUM GENERATION:

- Based on the fracture strength reduction of irradiated sintered SiC, a helium content of a few 1000 appm is suggested as an upper limit for SiC.

○ Helium generation in SiC exposed to fusion neutrons is high (~1500 appm per MWy/m²). After generating about 2300–appm helium in Br-sintered SiC samples, a drastic reduction of strength was measured in some samples, while others showed a slight increase. It is important to note that even with ~2300–appm He generation, void formation in SiC is suppressed unless irradiation or anneals are performed at temperatures well above 1000°C. The term “helium embrittlement” cannot be applied to ceramic composite materials, because the ceramic matrix is not only brittle to begin with, but the primary failure mode of ceramic composites occurs under loads that cause fiber pullout or failure. Composite strength levels are primarily determined by fiber—matrix debonding—layer characteristics.

Many variables affect the response of ceramics to radiation (e.g., microstructure, manufacturing technique, dopants, additives, and load history). The response of ceramic composites is further complicated by fiber choice, fiber—matrix interface characteristics, matrix—reinforcement volume fractions, weave type, and matrix porosity. The existing data base for bulk ceramics is small. Thus, it may be somewhat premature to define operating limits for these materials, and particularly for composites. Research and development efforts are necessary to develop ceramic composites that are specifically tailored for fusion applications.
HIGHLIGHTS OF SiC NEUTRON–IRRADIATION DATA

Swelling:

- At temperatures below 1050°C, expansion saturates at a fluence level of about $2 \times 10^{24}$ m$^{-2}$ [2].
- Swelling of SiC is minimum when irradiated between 800 and 1000°C (< 0.1%) [2].

Effect of helium generation:

- Below 1000°C, void formation is suppressed even at high fluences and with significant helium (2300 appm) content [3], [4].
- Annealing of high-fluence irradiated samples above 1200°C produces voids and continuous expansion [3], [4], [5].
- Irradiated reaction–sintered SiC samples, with internally generated helium (~2300 appm), have shown an increase in bending strength [3], [6].
- Other tests have shown a significant (24%) reduction in flexural strength with comparable helium-generation rates (~2000 appm) [1], [7].

Fracture toughness:

- Fracture toughness of irradiated hot–pressed SiC containing 1% BeO increased by 10% after fluences of $6 \times 10^{24}$ m$^{-2}$ ($E_n > 1$ MeV) [6].
- Fracture toughness of proof–tested irradiated chemical–vapor–deposited SiC is virtually unchanged when irradiated to a fluence of $2 \times 10^{26}$ m$^{-2}$ [8].
- More recent data with higher fluences of $3 \times 10^{26}$ m$^{-2}$ of non–proof–tested chemical–vapor–deposited SiC show a 50% drop in fracture toughness [9].
- Fracture toughness of sintered and reaction–bonded SiC containing B, C, and free Si is reduced significantly (by up to 50%) after neutron irradiation [7].

SiC–fiber response:

- Heat–treated SiC fibers, have shown a gradual increase in tensile strength and density with neutron fluence ($1 \times 10^{25}$ m$^{-2}$) [10].
- Oxygen–rich SiC fibers (16 wt% [11]) experience significant shrinkage when exposed to neutron irradiation [12].
COMMENTS REGARDING SILICON CARBIDE–DESIGN LIMITS
FOR FUSION APPLICATIONS

ABSTRACT
At the 17th Symposium on Fusion Technology held in Rome, Italy, Sept. 1992, an invited paper, “Nonmetallic Materials for Plasma Facing and Structural Applications in Fusion Reactors,” was given by H. H. Bolt [1], in which several candidate ceramic materials (B₄C, TiC, and SiC) were compared. Each was examined from the perspective of radiation effects, activation, plasma-facing performance, and lifetime. Silicon carbide has been advocated as the primary low-activation-material candidate for fusion applications. This low activation characteristic of SiC was questioned by Bolt, and several design limits of SiC were suggested. As determined in the recent ARIES reactor study [13] [14], SiC can qualify as a low activation material with hands-on limits of 2.5 mR/h (after 20 MWy/m² exposure and 27 y of cooling); however, remote-handling surface dose rates are reached after only 2.5 d of cooling. Bolt cites high-temperature evaporation rates of SiC that are found to be orders of magnitude higher than those of TiC or B₄C. However, for plasma-facing components, sputtering processes will change compound evaporation rates to those of the surface’s main constituents (Si, Ti, or B). The issues of plasma-driven tritium permeation through a first wall and desirable tritium release-rate temperature ranges are addressed by Bolt. However, the low tritium-diffusion coefficient through SiC, coupled with erosion processes, will ensure a low first-wall tritium concentration. Therefore, first-wall operating temperatures are not restricted to the limits suggested by hydrogen-release experiments. Radiation induced swelling of SiC is generally small below 1200°C. Post-irradiation anneal experiments indicate that helium bubbles do not form in chemical–vapor–deposited SiC below 1200°C, even with internal helium generation of up to 2300 appm. The fracture toughness data of irradiated bulk-SiC samples shows a great scatter. Some chemical–vapor–deposited SiC samples have shown no decrease in fracture toughness, while others have shown a drastic reduction. Numerous sintered–SiC samples have shown a drastic reduction of toughness after neutron irradiation, while some have shown slight increases. Extrapolation from bulk SiC data to SiC/SiC composite behavior is discussed. Because of fundamental differences in load response between composites and bulk ceramics, actual SiC/SiC composite data are required in order to suggest more accurate design limits and guidelines.
1. \textbf{INTRODUCTION}

In a recent paper entitled "Nonmetallic Materials For Plasma Facing and Structural Applications in Fusion Reactors," potential design limits for candidate nonmetallic materials were discussed [1]. The effects of neutron irradiation on silicon carbide (SiC), titanium carbide (TiC), and boron carbide (B\textsubscript{4}C) were addressed, and operating limits for fusion applications were suggested. Among ceramic composite materials, SiC/SiC composites are currently the primary candidates for structural applications in fusion reactors. Because of this, only issues raised regarding SiC will be discussed here.

Reference [1] raises the following points:

- **ACTIVATION**
  - The low–activation characteristic of SiC is questioned, based on the second–step aluminum reaction that forms long–lived \textsuperscript{26}Al.

- **PLASMA–FACING ISSUES**
  - **EVAPORATION:**
    The relatively high SiC vapor pressure compared to that of B\textsubscript{4}C and TiC suggests much larger evaporation rates for SiC than for the other candidates.
  - **TRITIUM RETENTION:**
    Based on deuterium retention measurements, a minimum operating temperature of 800°C for plasma-facing SiC components is suggested.

- **DIMENSIONAL CHANGES**
  - **SiC–SWELLING:**
    Based on bulk swelling data, a narrow operating–temperature window between 800 and 950°C is suggested.
  - **SiC FIBER SHRINKAGE:**
    Presently available SiC fibers will undergo significant shrinkage under irradiation, which reduces the fracture strength of SiC/SiC composites significantly.

- **LIFETIME**
  - Mechanical property changes in neutron–irradiated SiC samples were reviewed. A lifetime limit of 1 to 2 MWy/m\textsuperscript{2} based on more recent fracture–strength data of irradiated chemical–vapor–deposited SiC is suggested.
  - **HELIUM GENERATION:**
    Based on doped and sintered SiC–irradiation experiments, helium contents of a few 1000 ppm are suggested as an upper limit for SiC.
The above topics are discussed in detail in the four sections that follow. Because of the sparsity of data, particularly irradiation–damage responses of ceramic matrix composites such as SiC/SiC composites, extrapolation from bulk material data is necessary. However, matrix—reinforcement interactions, which are responsible for the characteristic properties of composites, are often neglected. Fundamental differences between bulk ceramic and ceramic composite materials are discussed, and sample load responses are cited in Section 6.

2. ACTIVATION

The low–activation characterization of SiC is questioned [1]. Because the formation of $^{26}$Al, however, $^{26}$Al production would be restricted to a narrow region behind the first wall of an SiC/SiC–composite blanket module.

The silicon–aluminum transmutation reaction, $^{28}$Si(n,n’p)$^{27}$Al, has a threshold energy of about 2 MeV. Although $^{27}$Al is stable, a second–step reaction can form $^{26}$Al, which has a lifetime of $7.2 \times 10^6$ y. The threshold energy for the $^{27}$Al(n,2n)$^{26}$Al reaction is around 12 MeV [15]. This high–threshold energy restricts $^{26}$Al production to a narrow zone (a few centimeters) behind an SiC/SiC–composite first wall. Activity calculations for the ARIES–I [13] and ARIES–IV [14] tokamak reactors included the second–step reaction for aluminum. Figure 1 depicts the surface dose rate of several candidate blanket materials after 12.5 MWy/m$^2$ exposure [16]. Based on a total exposure of 2.5 y at 5 MW/m$^2$, the ARIES–I blanket–surface $\gamma$–dose rate is $7.03 \times 10^{-6}$ Sv/h after 100 years of cooling. The blanket dose rate calculations include the first–wall structural material. The surface dose rates of the ARIES–I first–wall structure alone are much higher and are estimated to be $2.19 \times 10^{-4}$ Sv/h after 100 years of cooling. Figure 2 shows the dose rates of several first–wall structures after a 12.5 MWy/m$^2$ exposure [17].

The required cooling time to achieve surface dose–rate limits for remote–handling and hands–on levels are shown in Fig. 3. SiC requires a cooling time of only about 0.5 d for the surface dose rate to drop below the remote handling limit of 1 R/h.

The dose rate for the ARIES–I blanket falls below the “hands–on level” limit of about $2.5 \times 10^{-5}$ Sv/h, while that of the first wall by itself does not. Although recycling of SiC is not reasonable [1], these calculations show that SiC can be classified as a low–activation material.

3. PLASMA–FACING ISSUES

3.1. Evaporation Rate of SiC

The vapor pressure of SiC is about one order of magnitude higher than that of B$_4$C, and about 3 orders of magnitude higher than that of TiC. Based on
Fig. 1. Averaged blanket plus first-wall surface γ-dose rate for various structural materials after exposure of 2.5 y to a neutron wall loading of 5 MW/m² [16].

compound vapor pressure alone, SiC evaporation would be significantly higher than that of the other candidates [1]. However, sputtering effects have to be considered in along with the evaporation rates for plasma-facing compound materials.

As pointed out by Bolt, sputtering of a binary compound causes preferential removal of the lighter component from the top surface layers. The surface layers of SiC that are exposed to low-energy plasmas (few eVs) would consequently undergo a depletion of carbon atoms. This leads to the formation of Si-rich surface layers. The combined effects of preferentially sputtered carbon and the evaporation of silicon would determine the net erosion rate of plasma-facing SiC materials. Research done on SiC single crystals at elevated temperatures shows
Fig. 2. First-wall surface γ-dose rate for various structural materials after exposure of 2.5 y to a neutron wall loading of 5 MW/m² (316 L—stainless steel [17], LAAS—low-activation austenitic steel (OPTSTAB2: 0.07C-0.3N-0.2Si-15Cr-16Mn-65Fe-1.2Ta-2W) [17], V-5Cr-5Ti [16], HT-9 [16], SiC [16]).

an increase in surface carbon concentration above 1000°C to a complete graphite-type carbon-atom coverage at 1500°C [18]. The increase in surface carbon concentration was attributed to silicon vaporization. Chemical sputtering accelerates carbon removal from plasma-facing surfaces. Therefore, evaporation and sputtering of silicon would represent removal rates of SiC surfaces more closely than compound vapor pressures alone. Similar arguments hold for other ceramic compounds. Figure 4 shows ceramic compounds and their elemental vapor pressures. While TiC and SiC have vapor pressures that differ by several orders of magnitude, those between Si and Ti are within a factor of 2 – 3 at specific temperatures. Based on the elemental vapor pressures coupled with sputtering processes, the net evaporation rates of SiC and TiC should fall within the same
Fig. 3. Required cooling times to reach surface $\gamma$-dose rates of 2.5 mR/h (hands-on) and 1 R/h (remote) for candidate blankets after exposure of 2.5 y to a neutron wall loading of 5 MW/m$^2$ [16]).

order of magnitude. Table 1 lists elemental vapor pressures as a function of temperature for candidate ceramic constituents Si, Ti, and B.
Fig. 4. SiC, TiC, B₄C [1], and their elemental (Si, Ti, and B [19]) vapor pressures.

Table 1
Vapor Pressure of B, Si, and Ti.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>B</th>
<th>Si</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻¹⁰</td>
<td>1450</td>
<td>1071</td>
<td>1124</td>
</tr>
<tr>
<td>10⁻⁸</td>
<td>1620</td>
<td>1244</td>
<td>1310</td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>1900</td>
<td>1476</td>
<td>1554</td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>2076</td>
<td>1636</td>
<td>1709</td>
</tr>
<tr>
<td>1</td>
<td>3802</td>
<td>3276</td>
<td>3289</td>
</tr>
</tbody>
</table>
3.2. Hydrogen Retention

Hydrogen retention of TiC, SiC, and B₄C were compared in Ref. [1]. For SiC, a minimum operating temperature of 800°C is implied to ensure the release of trapped tritium. However, extremely low hydrogen–diffusion rates, coupled with sputtering effects, will ensure low tritium content for plasma–facing SiC components.

Hydrogen-to-atom ratios cited in Ref. [1], are 0.26, 0.4, and 0.5 H per host atom, for respectively, TiC, B₄C, and SiC. Based on annealing experiments, TiC and B₄C release hydrogen readily at temperatures between 150 and 700°C, while SiC has to be heated well above 800°C for significant release to occur. This implies that an SiC first wall could retain a significant amount of tritium during operation. However, hydrogen diffusion coefficients in SiC have to be considered also. Chemical–vapor–deposited SiC has a low hydrogen–diffusion coefficient. At 1000°C, tritium diffusion coefficients range from $10^{-14}$ cm²/s to $10^{-9}$ cm²/s, for respectively, chemical–vapor–deposited SiC and HIP (hot, isostatic pressurized) SiC) [20].

The low gas permeability of SiC has made it the primary candidate for coating fission fuel pellets [21]. Because SiC retains fission gases “completely,” it provides the ultimate barrier to volatile fission products for spherical TRISO fuel particles for future HTR plants [22]. One of four coatings surrounding the 500–μm–diameter kernel of UO₂ in TRISO is a 20–40 μm–thick SiC shell. Earlier R&D efforts to develop nuclear–fuel cladding for UK gas–cooled reactors resulted in fabrication of reaction–sintered SiC with exceptional physical and mechanical properties [23]. The SiC coatings were fully dense, impermeable to gases, and resistant to oxidation up to 1400°C. The strength remained at about 500 MPa up to 1400°C and thermal conductivity was measured to be 50 W/mK at 1000°C.

Hydrogen retention data referenced in Bolt’s paper were measured using a 13–keV deuteron–implantation beam at room temperature [24]. These conditions can be misleading when applied to plasma–facing conditions. The penetration depth of 13–keV deuterons (up to 0.2 μm in SiC) is several orders of magnitude larger than that of low energy (few eVs) scrape–off–layer plasmas (1 to 2 nm). Extrapolation from ion–beam–implanted hydrogen experiments to fusion–reactor operating conditions is difficult, given the much smaller penetration depths and surface topology changes of SiC (due to carbon depletion).

Furthermore, the hydrogen implantation experiments on SiC were conducted at room temperature [24]. Two phenomena are responsible for gas entrapment: (1) trapping at irradiation–produced defects, and (2) chemical bonding to free compound constituents. Target surface temperatures play a significant role in these processes. High–temperature hydrogen–implantation data have not been published. However, high–temperature helium implantation in SiC is available [25]. Helium ion beams (0.5–20 keV) produced surface porosities at room temperatures, while at 600°C such porosities were not observed. Thermal
annealing is responsible for the lack of surface porosity at elevated temperatures [25]. High irradiation temperatures alter the microstructure and, thus, will affect trapped gas concentrations.

Temperature gradients through the solid play an important role in gas content. Whether gases migrate up or down a temperature gradient in solids is generally expressed by a term called heat-of-transport [26]. A preliminary literature search has not found published heat-of-transport measurements for hydrogen in SiC. In order to determine the behavior of surface-implanted hydrogen, the heat-of-proton transport in SiC has to be known.

The ARIES-I reactor study addressed plasma-driven tritium permeation through the SiC/SiC-composite first wall [13]. The first-wall surface temperature ranges from 550°C to a maximum of 1030°C. Maximum proton-implantation rates were assumed. Diffusion coefficients for tritium in SiC specimens have been measured [20]. Tritium diffusion coefficients at 1000°C are low, $10^{-14}$ to $10^{-9}$ cm$^2$/s depending on the manufacturing process. The plasma-facing side of an SiC/SiC-composite first wall has a 2-mm-thick chemical-vapor-deposited SiC layer. Erosion rates of SiC first-wall surface layers are comparable to tritium diffusion rates (0.01 mm/y). The SiC erosion rate was estimated to be 0.01 mm/y for plasma energies below 20 eV. Erosion of the surface layers recycles protons back into the scrape-off layer, before any significant permeation into the bulk material takes place. Although sections of the first wall are well below the minimum hydrogen-release temperature limit of 800°C, surface layer erosion coupled with slow diffusion rates can prevent any significant buildup of tritium in the first wall.

4. RADIATION EFFECTS

4.1. Swelling of SiC

In Ref. [1], an operating temperature window of between 850 and 950°C was suggested. The temperature range was based on ~0% swelling of bulk SiC. However, the effects of composite micro- and macrostructure will cause different swelling behavior in SiC/SiC composite than in bulk SiC. Minimum swelling will probably occur over a wider temperature range for SiC/SiC composites.

Neutron-irradiated bulk SiC shows two distinct features:

1. Saturation of expansion at low fluences of about $2 \times 10^{24}$ m$^{-2}$ ($E_n > 0.18$ MeV) [2], and

2. A fluence-independent linear-expansion minimum (< 0.05%) when irradiated between 850 and 1100°C [2].
Presently, three-dimensional (3-D) SiC/SiC composites have 5% to 10% porosity. The matrix is formed by a chemical-vapor-infiltration (CVI) process. The microstructure of a chemical-vapor-infiltrated matrix does not contain any residual silicon and is free from sintering-aid additives. Chemical-vapor-infiltrated SiC is similar to pyrolytic SiC, which shows low linear expansion of $< 0.2\%$ at 625°C after exposure to $1.2 \times 10^{25} \text{ m}^{-2} \ (E_n > 0.18 \text{ MeV})$ [5]. Swelling saturates with fluences of around $3 \times 10^{24} \text{ m}^{-2}$ at levels that decrease with increasing temperatures [2].

Composites have two features that will alleviate some of the neutron-induced macroscopic expansion: (1) matrix porosity can "absorb," in principle, some expansion internally; and (2) the fibers are only "loosely" interfaced with the matrix and, as such, there is some allowance for fiber—matrix interaction. These characteristics may result in a lower net expansion of composites compared with bulk matrix materials. The temperature range over which minimum swelling occurs will probably be between 500 and 1100°C for net design swelling of $< 0.5\%$. SiC/SiC–composite swelling data are necessary to establish swelling–temperature design windows.

Future SiC/SiC composites will most likely be tailored to fusion applications. Alloying additives and dopants may be present in matrix and fiber. Such additives can greatly vary the swelling response of SiC exposed to neutron environments.

The effects of sintering aids on bulk SiC swelling have been reported for low fluences of up to $6 \times 10^{24} \text{ m}^{-2} \ (E_n > 1 \text{ MeV})$ at irradiation temperatures between 280 and 640°C [27]. Sintering–aid additives such as B, C, and BeO were used to study expansion of post irradiation anneals up to 2000°C. Macroscopic length changes were very sensitive to the type of sintering aid used. Free Si containing SiC showed continued decrease in length change up to 2000°C of about $-1\%$. Samples containing B and C showed large increases in length changes up to 10% when annealed to 2100°C. SiC containing 1% BeO showed a decrease of up to about 0.7% in length change. These samples were the only ones that exhibited a saturation level in length change occurring around 1400°C. Further annealing to higher temperatures did not affect length changes significantly. These examples demonstrate that alloying can affect the swelling behavior of SiC significantly.

Although the data base for swelling behavior of SiC is small and practically non–existent for composites, general trends indicate a resistance to bubble formation associated with small dimensional changes below 1200°C. The morphology of composites suggests a swelling behavior that is different from that of bulk materials. The temperature range for negligible swelling of SiC/SiC composites may be as large as 500 to 1100°C.

4.2. Shrinkage of SiC fibers

Recently SiC/SiC–composite neutron–irradiated samples have been examined [12]. Neutron irradiation resulted in fiber shrinkage, which caused
separation between matrix and fibers, a decreased modulus, and reduced fracture strengths. These changes are attributed to the dissociation and crystallization of oxygen–rich SiC fibers (oxygen content up to 16 wt% [11]). Newly developed fiber–manufacturing techniques show oxygen contents around 0.3 wt% [28]. These fibers promise a significant improvement in resistance to irradiation–induced decomposition and shrinkage. Neutron–irradiated SiC/SiC composites made with the newly developed fibers will most likely not show significant fiber shrinkage.

The debonding layer between fibers and matrix has a strong bearing on ceramic composite properties. Matrix–fiber interfaces are of the order of a few microns. Presently the most common interface materials are C and BN. Matrix–fiber interface thermal stability and neutron irradiation resistance constitute the greatest challenge in developing fusion–environment–tolerant ceramic composites. Non–fusion related efforts are currently underway to improve SiC thermophysical properties by alloying and improving manufacturing processes, but fusion–specific tailoring efforts have not yet been initiated.

4.3. Thermal Conductivity

Data on the thermal conductivity of 3–D SiC/SiC composites have not been published widely [29]. As indicated in the review article [1], further developments should result in higher thermally conductive SiC/SiC composites. Effects of additives to SiC on thermal and electrical conductivities are the subject of various non–fusion R&D efforts. The addition of 1.6–wt% BeO to sintered SiC has been shown to raise the thermal conductivity to 270 W/mK at room temperature [30]. Electrical resistivity of SiC can vary from $3 \times 10^{13}$ to 0.8 Ω·cm by adding, respectively, Be (1 wt%) and Al (1 wt%) [31]. No such R&D efforts have been reported for SiC/SiC composites. However, improvements in bulk SiC conductivities should, in principle, be transferable to composites.

5. LIFETIME

5.1. Mechanical Properties

Reference [1] suggests a fluence lifetime for SiC/SiC composites based on the response of chemical–vapor–deposited SiC to neutron irradiation. In Ref. [9], similar guidelines were put forward. Ceramic composite behavior will undoubtedly be different from that of its individual constituents. Matrix–reinforcement interactions determine key properties of composites (see Sec. 6). Since bulk ceramics and composites respond differently to loads, operating limits should not be based on bulk–ceramic data only.
Fig. 5. Flexural strength of SiC containing excess silicon [7]: (▲) 1200°C, (●) room, (●) room, (■) 1200°C, (◆) 1200°C, (●) 1300°C.

Furthermore, a large scatter in SiC post-neutron-irradiation measurement data exists. Reference [7] summarizes flexural strength measurements of data published before 1985. Neutron fluence data as high as $2 \times 10^{26} \text{ m}^{-2}$ are quoted. Reaction-bonded silicon-infiltrated SiC irradiated at temperatures between 540 and 1400°C showed a decrease in strength of about 30% (this is a three-phase material: α-SiC, β-SiC, and free Si). Figure 5 depicts the scatter in post-irradiation flexural-strength measurement data of reaction-bonded SiC samples. Pressureless sintered SiC also experienced a drastic reduction in strength, as shown in Fig. 6. However, some chemical-vapor-deposited SiC showed no significant change after high neutron fluence ($2 \times 10^{26} \text{ m}^{-2}$) exposure at 740°C [8].
In contrast to the strength retention data given in Ref. [8], more recent data [9] show a drastic reduction in bending strength for irradiated chemical–vapor–deposited SiC (Fig. 7). The two experiments that produced the data are different. The older data were generated using proof tested samples to eliminate ‘weak’ ones; the SiC samples were manufactured by the chemical–vapor deposition (CVD) process on graphite substrates with thickness ranging from 0.6 to 1.1 mm (the term ‘weak’ refers to samples that contain flaws of critical size). The recent experiment chose thicker samples cut from an SiC bar (3.5×4.5×45 mm) and no pre-irradiation proof-testing was reported. Furthermore, the newer data are based on somewhat higher fluences of $3 \times 10^{26}$ m$^{-2}$ ($E_n > 0.1$ MeV) [9] compared to $2 \times 10^{26}$ m$^{-2}$ ($E_n > 0.05$ MeV) in Ref. [8]. Bulk-ceramic failure
Chemical–Vapor–Deposited SiC

![Graph showing flexural strength vs. neutron fluence for different irradiation temperatures: 500°C, 740°C, and 1150°C.](graph.png)

**Irradiation Temp.**
- ▲ 500°C
- ● 740°C
- □ 1150°C

**NEUTRON FLUENCE (n/m²)**

Fig. 7. Flexural strength of SiC as a function of neutron fluence (room-temperature bending tests: (●) 0.6– to 1.1-mm thick deposited on graphite and proof tested before irradiation [8], (▲ and □) cut from a 3.5 × 4.5 × 45-mm thick SiC bar and not proof tested before irradiation [9]).

Distributions are statistical and depend on manufacturing technique, size, shape, and load history. A much more extensive data base for irradiated SiC samples is necessary to eliminate uncertainties.

Section 6 discusses some differences between the response of bulk and composite materials to loads. Tests show that the thermal shock resistance of composites is superior to that of the bulk materials, although bulk ceramics have higher thermal conductivities. Catastrophic crack propagation is inhibited in composites because of matrix—fiber debonding layers, which also affects the flexural strength behavior. Unless neutron irradiation destroys matrix—fiber interface layers significantly, composite crack—evolution mechanisms will be retained. Bulk—ceramic strength
measurements can not reflect composite behavior and, as such, should be used very cautiously to define operating limits for composites.

5.2. Helium Generation

Published data of irradiated SiC are all based on samples exposed to fission spectrum neutrons, which do not reflect helium generation rates of SiC when exposed to fusion neutrons. Based on helium embrittlement experience in metallic alloys, the high helium-generation rate in SiC implies a very low lifetime for SiC. Reference [1] suggests a lifetime limit of 1 to 2 MWy/m². This lifetime is based on a 24% decrease in fracture strength of reaction-sintered bulk SiC, in which a helium content of a few 1000 appm was generated during irradiation [4]. Extrapolation of sintered SiC irradiation data to SiC/SiC composite response is not considered a viable approach, given the fundamental differences between these materials.

The sintered SiC samples contained 0.5 wt% ¹⁰B and ¹¹B, which generated approximately 2000–appm helium during irradiation (1.2×10²⁵ m⁻²; Eₙ > 1 MeV; ¹⁰B(n,α)He) [4]. The B was added as a sintering aid in the form of B₂O₃ and B₄C. Section 5.1. outlined the impact of manufacturing techniques, in particular those of sintered SiC on neutron irradiation response. Sintering generally causes a multiphase, multicomponent material with sintering aid additives dispersed either inside the grains or near the grain boundaries. Some of the samples cited in Ref. [4] showed a uniform dispersion of B in the grains, while others exhibited “clumping” of chlorides and possible boron at fracture surfaces. Post-irradiation annealing to 1200°C resulted in fracture strength reduction of 24% and 70%, depending on the manufacturing process. Samples were irradiated at low temperatures (∼140°C) and then annealed at high temperatures (1200°C).

Low temperature irradiation followed by high temperature anneals will change the microstructure of irradiated samples to a degree that conclusive extrapolations can no longer be made.

1. Expansion measurements of bulk SiC showed that at low temperatures (280°C), length changes were about twice as large as those at higher temperature (640°C) [6].

2. Indentation crack lengths remain unchanged during annealing at temperatures up to the irradiation temperature, but increased with increasing annealing temperature, which indicates that irradiated SiC loses toughness by annealing [6].

3. Irradiated SiC samples, containing about 2300 appm helium, did not show a decrease, but rather an increase, in bending strength [6], [3].

Helium generation can result in an increase in bending strength, which is attributed to crack—pore interactions [6]. The effect of helium generation in SiC is
clearly subject to large uncertainties. The fracture strength response of SiC/SiC composites to internal helium generation will be more complex and, therefore, extrapolations from bulk material response to that of composites is highly questionable.

5.3. Absence of Void Formation in SiC

In general, helium atoms stabilize irradiation-produced defect clusters, which can serve as trapping sites for additionally generated helium atoms. As temperatures increase, the number density of stabilized defects decreases resulting in larger mean diameters and consequently greater swelling [5]. Post-irradiation annealing of irradiated SiC at elevated temperatures has shown an increase in swelling due to growth of such defect clusters [3]. Suzuki [3] notes that SiC samples containing B and C had a helium concentration of about 2300 appm helium after exposure to $6 \times 10^{24}$ m$^{-2}$ ($E_n > 1$ MeV) [3]. However, at the irradiation temperature of 640°C, there is no evidence for the formation of helium bubbles. Only after annealing above 1300°C did bubbles start to form, which was accompanied by an increase in swelling. Carey also finds no bubbles in neutron irradiated SiC that contains B even after annealing to 1200°C ($1.2 \times 10^{25}$ m$^{-2}$; $E_n > 1$ MeV) [4]. The appearance of helium bubbles above 1200°C is attributed to the generation of thermal vacancies, which are necessary for bubble growth [3]. Maximum first-wall temperatures would be around 1000°C [13] [14], which is below the helium–bubble growth limit of 1200°C. However, the effects of an order of magnitude higher helium generation on defect clustering has to be determined before any conclusive statements can be made.

5.4. Discussion on Lifetime Estimates

Factors affecting the lifetime of SiC/SiC composites in a fusion environment include:

- Radiation effects
  - defect production (dislocations, vacancies, amorphatization/recrystallization),
  - gaseous transmutation products (hydrogen; high helium–generation rate),
  - solid transmutation products (Al, Na, Mg),
  - matrix and fiber property changes;
- Non–nuclear effects
  - manufacturing process (CVD, DIMOX, sintering, reaction bonding),
  - matrix–fiber interface interaction,
  - load history (thermal, chemical, cyclic, creep).

Present data bases for all of the listed effects is small at best and, therefore, lifetime estimates can not be adequately made. However, radiation damage behavior of SiC shows promising characteristics (see the list of radiation highlights in the Summary).
Also, the failure mode of composites is one of fiber pullout and failure, rather than catastrophic crack propagation associated with isotropic ceramics. Whereas, bulk ceramics may exhibit a superior initial cracking strength, the failure strain at peak load is substantially smaller than that of ceramic composites. Ceramic composites show tolerances to overstrains, such as thermal shock or impact, which would cause catastrophic failure of bulk ceramics (see Section 6). An optimal ceramic composite is insensitive to component size because the matrix cracking stress and the ultimate tensile strength are both insensitive to matrix flaws. While bulk ceramic components are highly size dependent, attributable to the weakest-link mode of failure, ceramic composites are not (note: present-day high-strength ceramic composites contain between 5% and 10% porosity). Generally, cumulative radiation damage precipitates into localized defects. However, because composite strength levels are not very sensitive to matrix flaws, the consequences of radiation produced defects will be different in ceramic composites compared to bulk ceramics and metallic alloys. Only after compiling a composite–materials data base, can radiation damage effects on the strength and, thus, lifetime of ceramic composite materials be estimated.

Some of the non–nuclear issues are being addressed by major aerospace projects to develop and fabricate ceramic composites for the High Speed Civil Transport engines [32]. This program is a five–year, 88–M$ contract awarded by NASA to GE and Pratt & Whitney. The team has also been joined by NASA—Lewis and is currently concentrating on the primary and secondary processes to make SiC fibers for combustor ceramic–matrix composites; it is narrowing the field of fibers for ceramic composite nozzles.

Concurrent with national and international ceramic–composite development efforts, a fusion-directed research program is necessary to probe the questions relating to the lifetime of ceramic composites in fusion environments.

6. COMPOSITES VERSUS BULK CERAMICS

In discussing properties of SiC/SiC composite, a clear distinction between bulk ceramic materials and ceramic composites must be kept in mind (see Section 5.4).

Ceramic–composite R&D efforts aim at eliminating the catastrophic failure modes inherent in bulk ceramic materials, and many advances have been made in achieving this goal. Exceptionally high Weibull–modulus and high fracture–tough ceramic composites have been manufactured recently using a newly developed process [33]. A Weibull modulus of 65, fracture toughness of 29 MPa–m$^{1/2}$, and flexural strength of 1050 MPa have been reported for some of these ceramics composites. Present–day ceramic–composite technology is capable of manufacturing various reliable commercial components for missiles, aircraft structures, integral hub–and–blade marine propellers, and liquid–propulsion thrust chambers [34] [35] [36] [37].
Generally, the fracture toughness of ceramic composites is about 2 to 4 times that of the bulk host matrix. Fracture toughness increases are attributed to crack—fiber interactions (crack growth is stifled). Furthermore, catastrophic failures can be minimized because critical-sized flaws can no longer uninhibitedly grow to traverse an entire component.

For example, the thermal shock resistance of a ceramic is generally represented by a figure of merit that depends strongly on its thermal conductivity. Although thermal conductivities of SiC/SiC composites are significantly less than those of bulk SiC, the thermal shock resistance of these composites far surpasses that of the bulk material. Thermal shock testing on a chemical–vapor–deposited SiC–composite tube (20–cm diam., 185–cm long) was done by combustion heating the tube to 1100°C from the inside, while at the same time exposing the outside to a stream of cold water [38]. Repeated tests with the same tube did not cause any damage, while comparable tests of monolithic tubes immediately resulted in complete shattering of the tube. Incorporating SiC whiskers into an alumina matrix has been shown to significantly improve the thermal shock resistance as compared with monolithic alumina. Thermal shock testing of an alumina–20 vol% SiC–whisker composite showed no decrease in flexural strength with temperature differences up to 900°C [39]. Alumina on the other hand normally shows a significant decrease in flexural strength with a temperature change of more than 400°C. Improvements in thermal shock resistance of ceramic composites is the result of the interaction between the fibers and microcracks in the matrix, which prevents coalescence of the cracks into critical flaws and uninhibited crack growth.

Because of fundamental differences between the behavior of bulk ceramic material and composites, experimental irradiation data for bulk ceramics can not serve as the sole basis for extrapolating the response of composites.

7. CONCLUSIONS

The high–threshold–energy 26Al production is limited to within a few centimeters of the first wall. An SiC/SiC–composite blanket, such as is used in the ARIES–I and ARIES–IV reactors, has surface γ–dose rates that fall below the hands–on limit of 2.5 mR/h after fluences of 20 MWy/m² and a cooling time of 27 y [16]. Remote–handling surface–dose limits are reached after 2.5 d of cooling.

For plasma–facing multicomponent materials, the evaporation rate will be determined by the component least likely to be sputtered preferentially. For TiC and SiC, carbon depletion of surface layers will cause free Ti and Si to evaporate after prolonged exposure. The vapor pressures for Si and Ti are very similar and, as such, evaporation rates for SiC and TiC should be similar. However, impurity gettering processes will complicate the net removal rates in that they affect sputtering rates drastically.
Chemical–vapor–deposited SiC has very small proton–diffusion coefficients. Consequently, plasma–driven permeation of tritium through the first wall may not be a concern. First–wall evaporation and sputtering time scales are larger than bulk–diffusion time scales for protons in SiC [13]. Small diffusion coefficients of tritium, particularly at low temperatures, will not necessitate high temperature operation of an SiC first wall in order to ensure low tritium inventories.

The swelling of most SiC compounds shows a tendency to saturate at low fluences 2×10^{24} m^{-2} [2], and to have minimum linear expansion ( < 0.05%) when irradiated between 850 and 1100°C. However, the macro–structure of SiC/SiC composites will most likely widen the minimum–swelling temperature window, because of its ability to accommodate some of the swelling internally.

Old–generation SiC fibers with high oxygen content (16 wt% [11]) experience significant fiber shrinkage when exposed to neutron irradiation. Newly developed SiC with low oxygen content (0.3 wt% [28]) not only show a significant improvement in high temperature strength, but will most likely experience much smaller dimensional changes under irradiation.

Lifetime estimates for composite materials would involve very complex analyses based on an extensive data base. Neither of these exist for SiC/SiC composites, especially for neutron irradiated components. Therefore, extrapolation of bulk material data for composites is highly questionable. Furthermore, complications arise from the vast scatter in irradiation data for bulk SiC materials which, for the most part, is due to differences in manufacturing processes and load history of samples. The strength levels of ceramic composites are insensitive to matrix flaws (present–day high–fracture–strength composites may contain as much as 10% porosity). Consequently, composites exhibit tolerances to overstrains, such as severe thermal shock or impact, which would cause catastrophic failure of bulk ceramics. Radiation generated defects would, therefore, impact the strength levels of composites to a far lesser extent than of bulk ceramics or metallic alloys. Reasonable lifetime estimates are not feasible, given the present–day radiation data base of ceramic composite materials.

Helium generation in SiC exposed to fusion neutrons is high (1500 appm per MWy/m²). After generating about 2300–appm helium, some B–sintered SiC samples show a drastic reduction of strength, while others show a slight increase. It should be noted that metallic alloys can be very susceptible to small helium–generation rates (He embrittlement), while SiC/SiC composites do not rely on ductility and, thus, He embrittlement in itself is most likely not the primary failure concern. The stability of the intricate matrix–fiber interface layer will probably be a more critical issue in developing fusion–specific SiC/SiC composites.

Many variables affect the response of ceramics to radiation (e.g., microstructure, manufacturing technique, dopants, additives, and load history). The response of ceramic composites is further complicated because of fiber choice, matrix–fiber interface characteristics, matrix–reinforcement volume fractions,
weave type, and matrix porosity. The existing data base for bulk ceramics is small. Thus, it may be somewhat premature to define operating limits for these materials, especially for composites. Research and development efforts are necessary to develop ceramic composites that are specifically tailored for fusion applications.
References


