Irradiation stability and thermo-mechanical properties of NITE-SiC irradiated to 10 dpa

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Five variants of nano-infiltration transient eutectic (NITE) SiC were prepared using nanopowder feedstock and sintering additive contents of <10 wt%. The dense monolithic materials were subsequently irradiated to 2 and 10 dpa in a mixed spectrum fission reactor at nominally 400 and 700 °C. The evolution in swelling, strength, and thermal conductivity of these materials were examined after irradiation, where in all cases properties saturated at <2 dpa, without appreciable change for further irradiation to 10 dpa. Swelling behavior appeared similar to high-purity chemical vapor deposition (CVD) SiC within measurement uncertainty. The strength roughly doubled after irradiation. Thermal resistivity increase as a result of irradiation was ~20% higher when compared to CVD-SiC.© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Among the myriad methods used to produce SiC, only a select few yield “radiation-stable” structures in this ceramic. Radiation stability for nuclear structural applications may be defined as the ability of the material to limit its dimensional change to an acceptable design envelope and to withstand degradation in mechanical properties as a function of irradiation dose up to high displacements per atom (>tens of dpa). Given the promise of SiC as structural material in a variety of fission and fusion energy systems [1,2] or as constituents of encapsulated fuel forms in the former [3], much effort has gone into understating irradiation stability and thermo-mechanical properties of SiC-based materials after neutron irradiation [4,5].

The most important criteria for radiation stability in SiC is the purity, crystallinity of the material, and the related state of the grain boundaries where the purest materials without secondary phases and impurities at the grain boundaries are the best performing. Therefore, the chemical vapor deposition (CVD) route is ideal since under the appropriate processing conditions it produces a highly pure and crystalline material. Swelling behavior of CVD-SiC in different temperature regimes [6], corresponding to different stages of point defect mobility, is well understood [5,7]. Also, CVD-SiC does not exhibit any degradation in strength after high dose irradiation in point defect saturation regime [7] or higher temperatures [8], while increased resistance to transgranular cleavage after irradiation has been reported [9].

On the other hand, lack of irradiation stability in less pure, less crystalline variants of SiC have been reported [10,11]. These include reaction-bonded, polymer-derived, or SiC-powder sintered materials. The first variant involves reaction sintering of Si and C and will inevitably result in residual Si, C, or both in the microstructure. Polymer-derived variants are based on pyrolysis of Si-bearing polymers (e.g. polycarbosilane) and often result in high density of microcracks as a result of enormous shrinkage during this process as well as amorphous pockets. Sintering of SiC powder may be aided by various additives (e.g. B, C, various oxides and their mixtures) to produce a dense material at temperatures well below what is needed if only SiC powder is used (~2200 °C). Not surprisingly, these additives will then decorate the SiC grains in the microstructure of the final material. In all these materials, it is expected that the differential swelling behavior between the SiC and
the secondary or amorphous phases will result in stress buildup in the microscopic scale that in turn degrades the strength of the bulk material.

The nano-infiltration transient eutectic (NITE) SiC variant is a special manifestation of liquid phase sintering (LPS) of SiC where nanopowder is used as feedstock. As the acronym suggests, this forming method is ideal for infiltrating the volume surrounding fibers or coated fuel particles to form a dense SiC matrix around them. The use of SiC nanopowder allows for reduction of sintering additives and processing temperature to achieve a dense SiC matrix. The additives used during sintering are often alumina-rare earth (RE) oxide mixtures, while other systems have been recently explored as well. After sintering, large SiC grains as compared to the starting powders (>10^3 increase) are observed with the oxide additives limited to secluded islands at the triple junctions and as thin (<2 nm) oxide films at the grain boundaries.

The NITE processing route of SiC yields a dense material in flexible geometries and is less costly and time consuming to produce than the CVD type. However, its applicability for nuclear applications needs to be assessed. The focus of this paper is to examine the irradiation stability and thermo-mechanical properties of five monolithic NITE-SiC variants irradiated up to 10 dpa.

2. Experimental details

2.1. Materials processing

Five variants of NITE-SiC were examined in this study. Table 1 specifies the mixture of various powders and additives prior to hot-pressing. One difference between the four specimens in the I-series of samples and the sample K was the SiC nanopowder feedstock itself. For the I-series specimens, nanopowder of <40 nm with 99% purity (Nanostructured & Amorphous Materials, Inc., China) was used whereas the K specimen was made using nanopowder of <100 nm with >99% purity (Nanomakers, France). Alumina was present in all the mixtures and except for one specimen, yttria was used as the RE oxide additive. For the I-3 specimen yttria was replaced with a mixture of gadolinia-erbilia. While Y has a very small neutron absorption cross sections, Er and Gd are potent neutron poisons (ratio of thermal neutron absorption cross section for Y: Er: Gd is 1: 100: 40,000). Gd, Er, or other RE elements that are neutron poisons may be intentionally added into NITE-SiC to for fission reactor core reactivity control. Therefore, it was important to investigate the impact of their presence on irradiation stability of these materials. While all the SiC nanopowders have some extent of oxide species present on their surface prior to consolidation, additional silica was added to the K specimen. The mixture of alumina, silica, and rear earth oxides ultimately result in nucleation of the eutectic phase at ~1400 °C during the densification process.

Also included in some of the powder feedstocks were polyethylenimine (PEI) and polyethylene glycol (PEG) as dispersants and binders. Since both of these organic polymers dissociate and leave very little residual C in the material, their incorporation was deemed inconsequential for irradiation stability of NITE-SiC. Nonetheless, their effect was investigated as well.

All the powder blends were thoroughly milled in ethanol (using Si3N4 milling media) and the dried feedstock was hot-pressed in graphite at 1850–1875 °C under Ar for 1 h at an applied pressure of 15–20 MPa to produce disks of 65 mm diameter and ~8 mm thick. Additional processing details are available in our previous publications. After hot-pressing, the density of NITE-SiC samples was measured via Archimedes method using ethanol and is

![Fig. 1. HAADF images of RE elements in the oxide distributed at the triple junctions and grain boundaries after NITE-SiC densification (courtesy of Ritesh Sachan).](image)
reported in Table 2. Also shown in this table is the concentration of select elements in the sintered materials that was determined using inductively coupled plasma optical emission spectroscopy (ICP-OE). Some of the discrepancy between Tables 1 and 2 is attributed to the small amount of oxide volatilization that is expected during hot-pressing [22], while the rest may be associated with measurement errors during mixing and ICP-OE analysis. Fig. 3 shows the microstructure of the various specimens. Note that the K variant consists of significantly larger SiC grains and less porosity compared to the I variants.

### 2.2. Irradiation and post irradiation examination

The specimens were machined (PremaTech Advanced Ceramics, Worcester, MA) to produce square slabs of 6 × 6 × 0.5 mm that were subsequently assembled into an irradiation vehicle and irradiated in the flux trap region of the High Flux Isotope Reactor. In most cases two specimens from each NITE-SiC variant were irradiated. Details of irradiation capsule design and parameters are available in Ref. [23]. Briefly, four different capsules were partially utilized to irradiate the five NITE-SiC variants in this study along-side CVD-SiC at 400 and 700 °C to 2 and 10 dpa (10^{25} n/m²). E > 0.1 MeV, is ~1 dpa in SiC. The irradiation temperatures were determined via passive SiC thermometry [24] and a variation of ±50 °C should be taken into account for the irradiation temperatures in this study given the uncertainty and distribution of temperatures in between and within various irradiation capsules.

A Keyence IM-6120 instrument was used to determine the width and length of the disks before and after irradiation. Specifically, this task was done by measuring the distance edge-to-edge on the square disks since no other fiducial marks were available. The average change in width and length (ΔW and ΔL) along with their errors (in this case calculated as the difference between the maximum and average change) were used to calculate the volumetric swelling, S, as

\[
S = \frac{3}{2} \left( \frac{\Delta W}{W} + \frac{\Delta L}{L} \right) \tag{1}
\]

where W and L are the average width and length for each specimen before irradiation. This method of determination in the absence of reliable fiducial markers resulted in a large error. Inherent assumption in Eq. (1) is that swelling is isotropic.

Monotonic equibiaxial testing was carried out at RT in conformance to ASTM C1499 prior to and after irradiation. Five specimens from each variant were tested in the unirradiated state while only one or two specimens were tested in the irradiated condition.

Finally, thermal diffusivity of the specimens before and after irradiation was determined using the laser flash methodology (ASTM E1461) via a Netzsch LFA 457 instrument. Thermal diffusivity was measured at RT and incrementally higher values but never exceeded the irradiation temperature for the specimens to avoid any annealing of the irradiation induced defect in the microstructure. Only one disks from each variant and irradiation condition was used for the laser flash studies.

### 3. Results

#### 3.1. Swelling

The swelling data from the NITE-SiC variants in this study and prior reports are plotted alongside the recommended correlations of CVD-SiC (see Ref. [5]) in Fig. 4. Significant scatter is observed in the data from this study given the relatively large uncertainty in the measurements. However, the swelling profile for NITE-SiC appears to follow the basic trends observed from CVD-SiC: i) swelling saturates at ~1 dpa in the temperature regime of this study (point defect saturation regime: 150–800 °C), and ii) the magnitude of swelling decreases with an increase in temperature in this regime. No discernable trends were observed regarding swelling behavior of different NITE-SiC variants. Essentially, within the limited accuracy of these measurements, different additives did not result in quantifiable differences in the swelling behavior.

#### 3.2. Strength

Fig. 5 shows the strength determined from equibiaxial tests on the specimens before and after irradiation. The unirradiated strength of the various NITE-SiC specimens agrees well with our previous study using the same testing setup and geometry [22]. That figure also shows the characteristic strength for unirradiated CVD-SiC from another study that used a similar testing geometry [8]. After irradiation at 400 and 700 °C at 2 dpa, a significant increase in strength of NITE-SiC variants was observed where it nearly doubled. Upon extending the dose to 10 dpa, the strength values appeared to slightly decrease and increase (~20% change) for 400 and 700 °C irradiations, respectively.

#### 3.3. Thermal properties

Fig. 6 shows the thermal conductivity of the NITE-SiC variants before and after irradiation. Thermal conductivity was calculated using the product of experimentally determined thermal diffusivity with the heat capacity from Ref. [4] and density of the various specimens (with ~1% swelling accounted for). As shown clearly in this figure, although the thermal conductivity degradation in NITE-
SiC is significant (similar to CVD-SiC [28] or CVI SiC/SiC [5]), it saturates at or below 2 dpa and no notable change is observed up to 10 dpa. The K variant, consisting of large grains and minimal porosity, exhibited the highest unirradiated thermal conductivity amongst the different NITE-SiC specimens examined in this study. After irradiation, it also exhibited the highest thermal conductivity.

4. Discussion

4.1. Strength evolution after irradiation

A large increase in strength was observed for the 400 and 700 °C irradiated specimens after 2 dpa (Fig. 4). This result is inconsistent with the general notion that sintered SiC degrades in strength after irradiation [4]. Also, Koyanagi et al. [29] reported degradation in monolithic NITE-SiC (with 12 wt% oxide additives) strength after irradiation at 830–1270 °C to ~6dpa (NITE SiC/SiC specimens in that
study did not experience notable strength degradation after irradiation). The mechanism for this strength degradation is often explained by differential swelling between the SiC grains and the secondary phases at the grain boundaries that results in stress buildup and microcracking.

Although a limited number of specimens (only one or two) were tested from each NITE-SiC variant in this study, the collective dataset from all five variants shows a uniform increase in strength after irradiation. The absence of irradiation-induced strength degradation may be explained by the reduced amount of secondary phase (mostly oxides) in these NITE-SiC variants as the additive content was limited to below 9 wt%. However, the significant increase in strength after irradiation still merits an explanation. This increase may be a result of two separate phenomena. The first is the increased fracture toughness [30] of the NITE-SiC at a 400 °C irradiation temperature for each variant and the results are compared to the correlation for CVD-SiC based on a complete set of experimental data in Ref. [4]. Given the large uncertainty in swelling measurements (see Sect. 3.1), Fig. 7(a) was generated by assuming that swelling in NITE-SiC is identical to that of CVD-SiC.

As shown in this figure, the evolution of irradiation defect resistivity is similar between CVD and NITE-SiC variants and the magnitude of this parameter is ~20% higher for the latter. This significantly less than our previous ad-hoc and conservative recommendation in Ref. [22] and supportive of similar findings in Ref. [27]. Also, note that the NITE-SiC matrix has a significantly smaller irradiation induced thermal resistivity (roughly half) when compared to SiC fibers or SiC/SiC composites (see Fig. 13 in Ref. [5]).

4.2. Thermal resistivity increase due to irradiation

As explained in detail elsewhere [34,35], scattering of phonons by themselves (Umklapp) and defects (of various dimensions) in ceramic solids is the main source of resistance to thermal transport processes. This is the case, including for SiC, because the electrical resistivity is high and the electrons are ineffective for heat transfer. "Irradiation defect (thermal) resistivity" is the term that is routinely used [4,5] to quantify the increase in thermal resistivity of the material before and after irradiation. Fortuitously, in the irradiation defect saturation regime of SiC (150–800 °C), the number density, and therefore the thermal resistivity of these defects is directly proportional to the macroscopic swelling in the material; at least for high purity CVD-SiC [4]. Essentially these same defects that are responsible for increased thermal resistivity by scattering phonons are the ones that contribute to the observed macroscopic swelling (see Figs. 25 and 13 in Refs. [4] and [5], respectively).

The irradiation defect (thermal) resistivity, \( R_d \) (m-K/W), for NITE-SiC variants was quantified as the difference between the unirradiated and irradiated thermal resistivity near the irradiation temperature. Fig. 7 shows \( R_d \) as a function of swelling and irradiation temperature for each variant and the results are compared to the correlation for CVD-SiC based on a complete set of experimental data in Ref. [4]. Given the large uncertainty in swelling measurements (see Sect. 3.1), Fig. 7(a) was generated by assuming that swelling in NITE-SiC is identical to that of CVD-SiC.

As shown in this figure, the evolution of irradiation defect resistivity is similar between CVD and NITE-SiC variants and the magnitude of this parameter is ~20% higher for the latter. This is
data resolution and with irradiation to higher doses or at different temperature regimes. This overall behavior may be explained by the microstructure that consists predominantly of crystalline SiC grains. The seclusion of the secondary phases, mostly oxide sintering aides, at the triple junctions and very thin grain boundary films appears to render their presence largely inconsequential to the performance of the bulk material.

5. Summary

NITE-SiC variants with additive content <10 wt% exhibited excellent radiation stability when irradiated at 400–700 °C up to 10 dpa. The type and amount of sintering additives used for production of NITE-SiC variants in this study did not result in any obvious differences in the swelling behavior, strength, and thermal properties after irradiation. Irradiation induced swelling in the point defect saturation regime appeared to be similar with CVD-SiC within the envelope of measurement uncertainty. The strength of NITE-SiC variants in the unirradiated state was similar to that of CVD-SiC and improved substantially (roughly doubled) after irradiation. Detailed microstructure evolution analysis and nanoscale mechanical testing is required to understand the phenomena contributing to this increase. The contribution of irradiation defects to the overall thermal resistivity of NITE-SiC after irradiation appeared to be similar (only ~20% higher) to what has been quantified for CVD-SiC. As expected, NITE-SiC materials with higher unirradiated thermal conductivity exhibited better thermal conductivity after irradiation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jnucmat.2017.11.040.

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[4] L.L. Snead. Sintering is required to fully understand the microstructure contributing to this increase. The contribution of irradiation defects to the overall thermal resistivity of NITE-SiC after irradiation appeared to be similar (only ~20% higher) to what has been quantified for CVD-SiC. As expected, NITE-SiC materials with higher unirradiated thermal conductivity exhibited better thermal conductivity after irradiation.

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