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Properties and radiation effects in high-temperature pyrolyzed PIP-SiC/SiC

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Abstract

Polymer-derived silicon carbide has been regarded to be susceptible to radiation damage, because of severe radiation damage associated with radiation-induced crystallization of amorphous structure. However, recent advancement of highly heat-resistant silicon carbide fiber allows pyrolysis of matrix precursors at higher temperatures and expectedly the production of polymer impregnation and pyrolysis (PIP)–SiC/SiC composites with improved radiation resistance. In this work, characterization of microstructure, mechanical properties, and radiation stability of a developmental high-temperature pyrolyzed PIP–SiC/SiC composite was carried out. Although mechanical properties of Tyranno™-SA-reinforced composite pyrolyzed at 2023–2073 K were not very encouraging due to insufficient matrix densification, Tyranno-SA fiber appeared to retain its strength after repeated pyrolysis at temperatures $\geqslant$ 2023 K. Carbon coating on the fiber fabric worked effectively as a fiber-matrix (F-M) interlayer in this system. Superior radiation stability was demonstrated by microstructural examination following dual-beam ion irradiation to 10 dpa at 873 K.

1. Introduction

Silicon carbide fiber-reinforced silicon carbide matrix composites (SiC/SiC composites) are attractive potential materials for nuclear and fusion energy systems, because of their inherent low activation characteristics, excellent thermo-physical properties, high-temperature strength, chemical stability, and pseudo-ductile fracture behavior [1–3]. The improvement in mechanical properties and neutron irradiation resistance, as a result of recent efforts in developing high performance SiC fibers and composites for fusion and advanced gas turbine applications, makes SiC/SiC composites even more attractive [4–6].

Baseline properties and irradiation response of SiC/SiC composites have been extensively studied. In the studies for nuclear and fusion applications, materials produced by chemical vapor infiltration (CVI) method are most frequently used, based on a consensus that, presently, CVI is the only method to produce a fully crystalline, stoichiometric and homogeneous SiC matrix. Therefore, CVI-produced composites are appropriate for the study of fundamental irradiation effects in SiC/SiC composites.

Among the alternative fabrication processes, polymer impregnation and pyrolysis (PIP) method is an attractive and widely studied technique for industrial production of SiC/SiC composites. The major advantage of PIP method lies in the potential drastic reduction in fabrication cost, to which a continuous impregnation and pyrolysis process is applicable for a large-scale production. On the other hand, several disadvantages of conventional PIP-produced SiC/SiC have been pointed out, such as low thermal conductivity, insufficient elastic modulus, poor radiation tolerence, and chemical incompatibility with liquid coolants and breeders. These undesirable properties are associated with amorphous structure and excess carbon (and oxygen) contents in the PIP-produced matrix after typical pyrolysis at temperatures of 1473–1673 K.

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In order to obtain a highly crystalline and stoichiometric matrix through a PIP process, it is essential to elevate the pyrolysis temperature and to use a pre-ceramic polymer that yields a stochiometric composition after a ceramization. New pre-ceramic polymers for stochiometric SiC production are under development and will be made available in the near future [4]. Pyrolysis temperature for conventional PIP process has been limited below 1673 K to maintain the strength of SiC fibers of older generations. Recent commercialization of highly heat-resistant advanced SiC fibers, represented by Tyranno™-SA (Ube Indstries, Ube, Japan), opened a potential applicability of pyrolysis at substantially higher temperatures to a PIP process [7,8].

The objective of this work is to determine the applicability of high-temperature (HT) pyrolysis to a Tyranno-SA/PIP-SiC system and to study the radiation response of HT-pyrolyzed matrix. For these purposes, a small-scale fabrication of Tyranno-SA-reinforced SiC matrix composites was performed using a polyvinylsilane (PVS) matrix precursor [9]. Microstructure, flexural property, and response to dual-beam ion irradiation will be reported in this paper.

2. Experimental procedures

In this work, two batches of materials, namely Tyranno-SA(U/D)/SiC^{PVS} and Tyranno-SA-C(P/W)/PyC/SiC^{CVI}/SiC^{PCS}, were fabricated. Tyranno-SA was selected as the reinforcement due to its proven strength retention after heat treatment at over 2073 K [10].

The first material was fabricated using uncoated Tyranno-SA (lot# S1F08PX) in a uni-directional (U/D) architecture. The primary objective of this fabrication is to characterize the matrix microstructure and examine its response to an ion beam irradiation. Polyvinylsilane (PVS) was used as the matrix precursor. The major reason for the use of PVS was to determine if the in situ F-M interphase formation could work with Tyranno-SA fibers in a high-temperature pyrolyzing condition [11]. The pyrolyzing temperature was selected to be 2073 K, at which an almost complete crystallization of SiC matrix and a significant reduction in excess carbon in argon environment could be expected [12]. The number of impregnation and pyrolysis cycles was limited to 4, since the matrix porosity suppression was not essential for the purpose of this fabrication. SiC particles of nominal 270 nm diameter were incorporated during the first impregnation. The nominal fiber volume fraction (V_f), mass density and calculated porosity of the composite after final pyrolysis were 40%, 2.48 Mg/m^3 and 19.2%, respectively.

The second material was fabricated with a coated Tyranno-SA-C plain-woven (P/W) fabric (lot# PSA-S17F08NN-R). The suffix C indicates that the final heat-treatment to produce the SA fibers was applied after the weaving of green body fibers. The average tensile strength of Tyranno-SA-C fibers in this lot was 2.2 GPa instead of the nominal single-filament tensile strength of 2.8 GPa for the regular Tyranno-SA fibers [13]. An F-M interphase coating on the fabric was applied by an isothermal CVI method at the National Research Institute of Metals (Tsukuba, Japan) [14]. Pyrolytic carbon (PyC) was deposited to a nominal thickness of 200 nm, followed by a protective coating with SiC as thick as 500 nm. The objective of overcoating with SiC was to prevent a severe damage of the coated preform during the CVI fixture disassembly. This CVI-coating process will be replaced by a thermochemical surface carbonizing treatment in the near future. Impregnation to 30% polycarbosilane (PCS) solution and the following pyrolysis at 2023 K for 600 s were repeated 6 times. Particulate SiC loading was not applied. The fiber volume fraction, mass density, and calculated porosity of the final product were 34%, 2.29 Mg/m^3 and 25.4%, respectively. The increase in composites' mass density and the decrease in porosity with the increasing number of impregnation and pyrolysis cycles are plotted in Fig. 1. Additional PIP cycles will effectively reduce the porosity, since the closed porosity still remains at a low fraction.

For a comparative study on the ion irradiation effect, Tyranno-TE(P/W)/SiC^{PCS} composite was used as a reference PIP–SiC/SiC. The PIP condition was eight cycle pyrolysis at 1573 K for 3600 s in nitrogen. An F-M carbon interphase was produced by a thermochemical treatment.

Microstructural characterization was carried out by means of optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The SEM examination was performed on polished cross-section of the as-fabricated samples and the fracture surface of flexure-tested bend bars.

Mechanical properties were evaluated by a three-point flexural test, following the general guidelines of

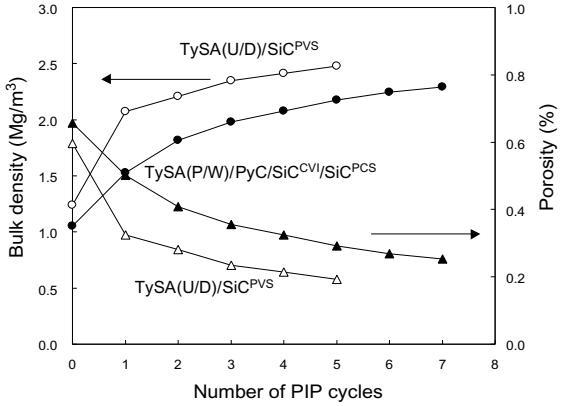

Fig. 1. Changes in apparent mass density and porosity with the increasing number of impregnation and high-temperature pyrolysis cycles.

ASTM C1341-97, using an Instron Model 5581 load frame. A set of miniature bend bars, that measure 25 mm(l) × 4 mm(w) × 1.5 mm(t) as a standard size for three-point bending tests in Japanese SiC/SiC development program for fusion applications, was tested at a support span of 18 mm and a crosshead displacement rate of 0.5 mm/s.

The materials used for the ion-irradiation study were the Tyranno-SA(U/D)/SiC^{PVS} and the Tyranno-TE(P/W)/SiC^{PCS} composites. The ion irradiation was carried out at the dual-beam irradiation target at the High-fluence Irradiation Facility, University of Tokyo (HIT Facility) [15] with 4 MeV Ni^{3+} and energy distributed He^{+} ions. The irradiation temperature, displacement damage rate, and total dose were 873 K, 1×10^{-3} dpa/s, and 10 dpa, respectively. Following the ion bombardment, cross-sectional thin foils were prepared in a focused ion beam (FIB) microprocessing device. The irradiated surface was protected by a physically deposited tungsten layer during the FIB-thinning. Microstructural investigation was performed with a JEOL JEM-2010 conventional TEM operating at 200 kV. Details of the dual-ion irradiation set-up, thin foil processing, and TEM examination procedure have been reported elsewhere [5].

3. Results and discussion

3.1. Baseline property characterization

A set of SEM secondary electron images of a cross-section of Tyranno-SA-C(P/W)/PyC/SiC^{CVI}/SiC^{PCS} is presented in Fig. 2. The composite exhibited a significant amount of large inter-bundle and inter-laminar pores corresponding to the porosity of 25% calculated from densitometry. An appropriate particulate loading should have been required to reduce these large pores to a sufficient level within a reasonable number of PIP cycles, as suggested in the previous work [11]. However, the higher magnification micrograph shows that the HT-PIP technique is still applicable to fill intra-bundle pores effectively.

The load – crosshead displacement curves during three-point bending tests on the three kinds of composites are presented in Fig. 3. The absolute flexural strength is rather small, as compared to those of typical commercial SiC/SiC composites. This is a general tendency observed in SiC/SiC bearing large pores, in which a compressive failure precedes during a flexural deformation and consequently a shift of effective mid-plane to the tension side results in a reduced apparent strength. Average tensile strength of the Tyranno-TE(P/W)/SiC^{PCS} was 203 MPa in contrast to the average three-point flexural strength of 143 MPa. In addition to the porosity effect, the specimen thickness is contributing to the measured reduced flexural strength, as seen in Fig. 3.

An encouraging part of the result is that the composite with coated fibers exhibited a pseudo-ductile fracture behavior. The apparent strengths of Tyranno-SA(U/D)/SiC^{PVS} and Tyranno-SA-C(P/W)/PyC/SiC^{CVI}/SiC^{PCS} were comparable. Considering the difference of reinforcing architecture and a situation in which the very porous matrix has a very small load carrying capacity, it can be concluded that the latter composite exhibits substantially superior mechanical property. The sound

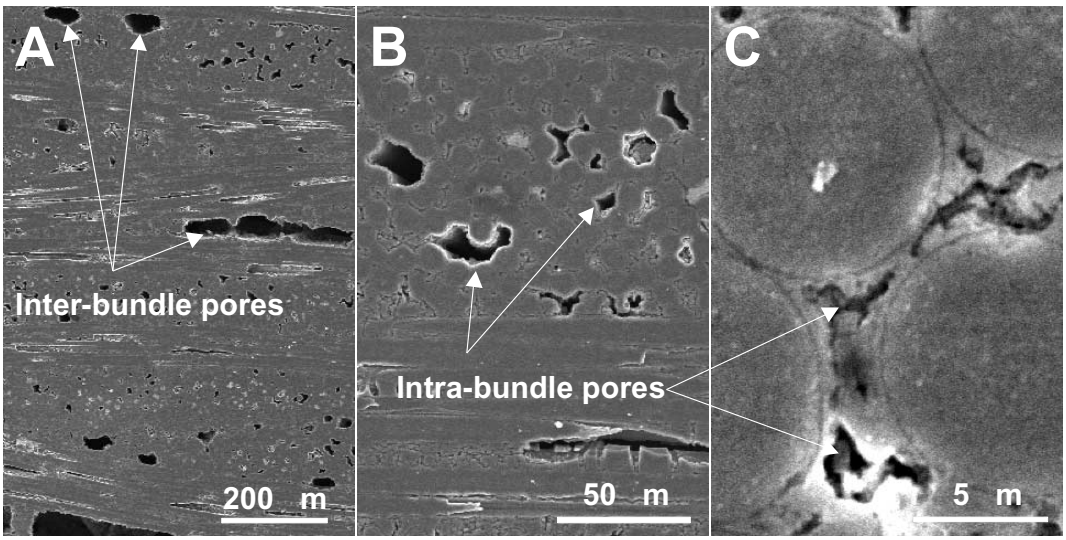

Fig. 2. Scanning electron micrographs of the cross-section of Tyranno-SA-C(P/W)/PyC/SiC^{CVI}/SiC^{PCS} composite at low (A), medium (B) and high (C) magnifications.

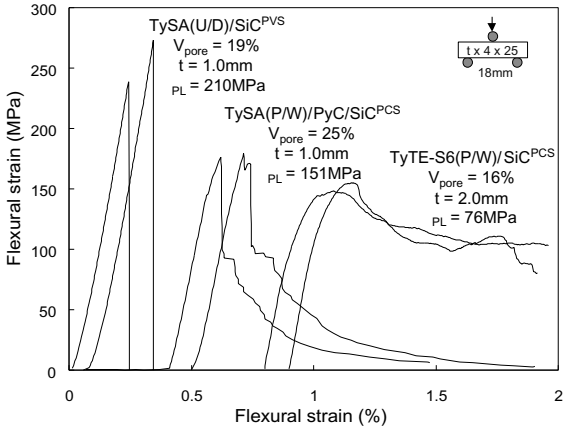

Fig. 3. Stress–strain relationship during three-point flexure tests on the HT- and conventional PIP–SiC/SiC composites. V_{pore} = calculated porosity, t = specimen thickness, and σ_{PL} = average proportional limit stress.

fiber pull-outs observed in the tensile fracture surface (Fig. 4) confirm the effectiveness of carbon interphase and the strength retension of Tyranno-SA fibers throughout the HT-PIP processing. Mechanical properties, such as reasonably achievable flexural strength and elastic modulus, will be assessed in the future, after fabricating composites with a nearly saturated matrix density.

3.2. TEM examination and irradiation effects

A low magnification bright field TEM image of cross-sectional thin foil specimen from the dual-beam ion irradiated Tyranno-TE(P/W)/SiC$^{\text{PCS}}$ composite is shown in Fig. 5. According to an ion transport calculation by the TRIM-98 code [16], the ranges of 4 MeV Ni and energy-distributed He in the matrix are approximately 2700 and 800–1300 nm, respectively. The He-deposited range can be regarded as a dual-beam irradiated area. The rest of the Ni-induced damage range, that is splitted by the dual-beam irradiated area, is regarded as single-beam irradiated areas. The region beyond the Ni deposition range is free from irradiation effects and labeled unirradiated area. The irradiated area can easily be distinguished by its slightly reduced brightness in the bright field image. The irradiated volume in both fiber and matrix also decreased significantly, as clearly demonstrated by morphological changes in the fiber-interphase boundary and the matrix-interphase boundary in Fig. 5. The surface step between fiber and matrix is not necessarily representing a differential densification, because of potential polishability difference during a specimen preparation.

A set of selected area diffraction (SAD) patterns, shown as a subset of Fig. 5, was taken from single-beam irradiated, dual-beam irradiated, and unirradiated areas with small thickness variations. A projected diameter of the selected area aparture on the focal plane was

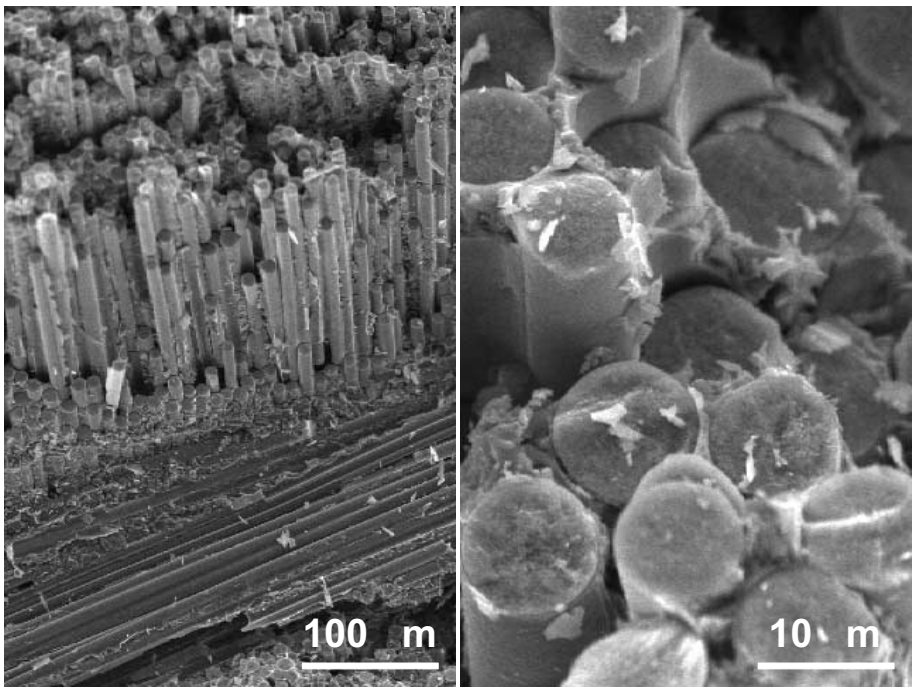

Fig. 4. Fracture surface on the tension side of flexural tested Tyranno-SA-C(P/W)/PyC/SiC$^{\text{CVI}}$/SiC$^{\text{PCS}}$ composite.

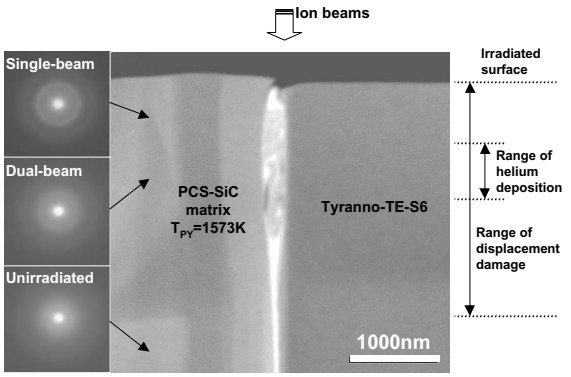

Fig. 5. A TEM image of cross-sectional thin foil specimen from dual-beam ion irradiated Tyranno-TE(P/W)/SiCPCS composite. The selected area diffraction patterns are taken from single-beam irradiated (top), dual-beam irradiated (middle) and unirradiated (bottom) regions.

approximately 175 nm. The fact that the three diffraction rings from the single-beam irradiated area correspond to SiC $\langle 111 \rangle$, $\langle 022 \rangle$ and $\langle 113 \rangle$ reflections confirms that the ion irradiation at this temperature apparently induced an amorphous to nanocrystalline transition, or simply crystallization, of SiC. It should be noted that the dual-beam irradiation substantially decelerated the irradiation-induced crystallization. Dark field imaging from a part of SiC $\langle 111 \rangle$ diffraction ring confirmed the existence of SiC crystallites as large as 5 nm in diameter in the single-beam irradiated area, while no crystallites were identifed in unirradiated and dual-beam irradiated areas by a conventional TEM.

Fig. 6 shows a TEM micrograph of Tyranno-SA(U/D)/SiC^{PVS} irradiated in the same condition. No noticeable effect of repeated pyrolysis at 2073 K on microstructure in Tyranno-SA fiber was observed in comparison with the as-fabricated microstructure [17]. However, solid bonding between the pyrolyzed matrix and the fiber surface is likely to be primarily responsible for the brittle fracture behavior of the composite. The result of flexural test on the Tyranno-SA-C(P/W)/PyC/SiC^{CVI}/SiC^{PCS} indicates that the introduction of carbon layer as an F-M interphase is essential to secure a crack deflection at the F-M boundary. Lowering the pyrolyzing temperature might have been helpful, since a sinterability of SiC drastically changes with temperature in this range [18]. The in situ F-M interphase formation via the use of PVS as a matrix precursor appeared not to work in the current system.

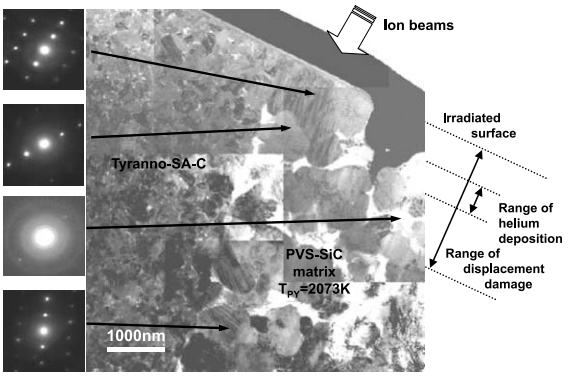

Fig. 6. A TEM image of cross-sectional thin foil specimen from dual-beam ion irradiated Tyranno-SA(U/D)/SiCPVS composite. The selected area diffraction patterns are taken from single-beam irradiated (top), dual-beam irradiated (middle) and unirradiated (bottom) SiC crystallites.

The matrix pyrolyzed at 2073 K consisted of beta-SiC grains with diameters up to about 1000 nm and a small fraction of excess carbon. The volume fraction of crystalline SiC was measured to be 81%. The excess carbon was present, mixed with matrix pores, within the intergrain openings. The structure of carbon phase was mostly amorphous, while a small amount of graphitic carbon was detected by an SAD analysis.

Effect of ion beam irradiation was apparent neither in the matrix nor in the fibers. Irradiation-produced defects were not observed by TEM in SiC grains and/or on grain boundaries in the matrix and the fibers. The carbon phase was not apparently affected, either, probably because irradiation at 873 K only promotes amorphization of graphitic carbon [19]. In this sense, small amount of excess carbon in amorphous phase may be allowed for SiC/SiC for nuclear applications, since the anticipated dimensional instability will not be serious unless the irradiation condition allows graphitization. A very smooth irradiated surface across the F-M boundary confirms that no significant differential volume change had been induced by irradiation.

4. Conclusions

SiC/SiC composites were fabricated by a PIP method that incorporated polymer pyrolysis at temperatures of 2023–2073 K using Tyranno-SA fibers. Characterization of the composites led to the following conclusions.

1. Tyranno-SA fiber retained its strength after repeated pyrolysis at temperatures of 2023 K or higher.
2. Carbon coating on the fiber fabrix worked effectively as an F-M interlayer in this system.
3. The HT–PIP matrix was demonstrated to be highly radiation-resistant at 873 K, as compared to a conventional PIP–SiC matrix.
4. Mechanical properties of a sufficiently densified composite and irradiation effects at high temperatures need to be further assessed.

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