

CHARACTERIZATION OF SILICON CARBIDE COMPOSITES PRODUCED BY POLYMER-IMPREGNATION AND HIGH TEMPERATURE PYROLYSIS PROCESS—Y. Katoh and T. Nozawa (Oak Ridge National Laboratory), K. Ozawa and A. Kohyama (Kyoto University)

OBJECTIVE

The objective of this task is preliminary assessment of polymer-impregnation and pyrolysis (PIP) process that incorporates near-stoichiometric SiC matrix and/or very high temperature treatment as a potential processing technique for SiC/SiC structural ceramic composite for fusion blanket applications. The present work focuses on characterization of microstructures and flexural properties of high temperature-treated PIP SiC/SiC composites with near-stoichiometric SiC fiber reinforcement and pyrolytic carbon / SiC bi-layered interphase.

SUMMARY

Near-stoichiometric SiC fiber composites with polymer-derived high-crystallinity SiC matrices were produced and were characterized their microstructures and mechanical properties. The material was produced through repeated polymer-impregnation and pyrolysis (PIP) cycles of Tyranno™-SA sintered SiC fibers, following pyrolytic carbon and SiC bi-layer interphase deposition. Co-polymer of polycarbosilane (PCS) and polymethylsilane (PMS) was used as the precursor for near-stoichiometric SiC matrix. The final heat treatment was performed at 1100 – 1800°C in flowing commercial-purity argon. The produced composites were dense in general with small macro-porosity. Transmission electron microscopy revealed that the matrix microstructures after heat treatment at >1500°C consisted of fine layers of SiC crystallites in amorphous SiC and carbon matrix. High temperature heat treatment promoted crystallization at the expense of porosity. No degradation of Tyranno-SA fiber was identified after heat treatment at 1800°C. PIP-composites with well-crystallized SiC matrices exhibited flexural fracture behavior very similar to that of chemically vapor infiltrated composites. The composites maintained ambient temperature strength up to 1000°C in air and to 1300°C in argon.

PROGRESS AND STATUS

Introduction

SiC continuous fiber-reinforced SiC-matrix composites (SiC/SiC composites) are an advanced option for structural materials in nuclear fusion and gas-cooled fission systems [1,2]. Nuclear applications of SiC/SiC composites require crystallinity and stoichiometry to both fibers and matrices in order for achieving acceptable tolerance against neutron-induced damage [3]. Among several industrially available matrix densification techniques, chemical vapor infiltration (CVI) best meets such requirements. On the other hand, CVI composites generally contain macroscopic inter-fiber bundle pores which hamper several important properties related with composite rigidity and transport properties [4]. Incorporating polymer impregnation and pyrolysis (PIP) process for the purpose of filling the macropores is one of the potential concepts of process hybridization oriented for complementing the known drawbacks of CVI products. PIP-produced matrices are generally carbon-rich, oxygen containing, and amorphous to nano-crystalline and therefore extremely susceptible to neutron damage [5]. However, it has been demonstrated that the irradiation resistance of PIP-matrices would be improved through pyrolysis and/or heat treatment in

conditions where enhanced crystallization occurs [6]. In this work, near-stoichiometric SiC fiber composites with pyrolytic carbon (PyC) / SiC bi-layered interphase were produced by pyrolysis and/or heat-treatment at temperatures of <1800°C and characterized for microstructures and mechanical properties.

Experimental Procedure

The fabricated composites and their processing conditions are summarized in Table 1. SiC fiber used was Tyranno™-SA near-stoichiometric sintered SiC fiber except for the case of TyTE-S6/PCS-1100°C, which was studied as a commercial standard PIP composite. For the interphase between fibers and matrices, bi-layers of 200nm-thick PyC and 500nm-thick SiC were deposited on the fiber fabric by CVI. The inner PyC layer provides compliant interlayer that easily debonds, while the outer SiC layer helps filling fine inter-fiber openings, adds rigidity to composites, and provides protection to the PyC layer. The preceramic polymers used were polycarbosilane (PCS), polyvinylsilane (PVS) [7], and co-polymer of polymethylsilane and PCS (PMS/PCS) [8]. The PMS/PCS co-polymer was designed so that near-stoichiometric SiC to be produced by setting a mixing ratio of PMS/(PMS+PCS) = 0.7. The PIP cycles were repeated typically for 10 times until composite mass density of >2.2g/cm³ was achieved.

Microstructural examination was performed by scanning electron microscopy (SEM) on polished cross-sections for all the materials and by transmission electron microscopy (TEM) on thin films produced by focused ion-beam micro-processing for selected samples. Mechanical property was evaluated primarily by three-point flexural testing at ambient temperature in air and at 1300°C and 1500°C in a flow of commercial purity argon.

Table 1. Summary of processing conditions and properties of composites studied

Material ID	TyTE-S6 /PCS-1100C	TySA /PVS-1800C	TySA/(PyC/SiC) /PCS-1750C	TySA/(PyC/SiC) /PCS-1700C	TySA/(PyC/SiC) /(PMS/PCS)- 1200C	TySA/(PyC/SiC) /(PMS/PCS)- 1500C	TySA/(PyC/SiC) /(PMS/PCS)- 1700C
Fiber	Tyranno-TE-S6	Tyranno-SA	Tyranno-SA	Tyranno-SA	Tyranno-SA	Tyranno-SA	Tyranno-SA
Architecture	2D-PW	Unidirectional	2D-PW	2D-PW	3D(1:1:0.2)	3D(1:1:0.2)	3D(1:1:0.2)
Interphase(s)	Carbonized	(none)	PyC ^{200nm} /SiC ^{500nm}				
Precursor	PCS	PVS	PCS	PCS	PMS/PCS	PMS/PCS	PMS/PCS
Pyrolysis/HT temperature	1100C	1800C	1750C	1700C	1200C	1500C	1700C
Particulate loading	None	First cycle	None	None	None	None	None
V _f	~40%	~40%	34%	32%	~35%	~35%	~35%
Mass density	2.10g/cm ³	2.48g/cm ³	2.29g/cm ³	2.58g/cm ³	2.24g/cm ³	2.29g/cm ³	2.27g/cm ³
Porosity	15.7%	19.2%	25.4%	17.1%	Not measured		
Flexural properties							
Modulus	76GPa	128GPa	98GPa	132GPa	63GPa	60GPa	55GPa
Prop. Limit	76MPa	216MPa	153MPa	252MPa	153MPa	154MPa	148MPa
Ultimate	124MPa	237MPa	170MPa	258MPa	302MPa	282MPa	198MPa
ε at Load Max	1.17%	0.19%	0.19%	0.24%	0.96%	0.74%	0.42%

Results and Discussion

The SEM microstructures of polished fiber bundle cross-sections are presented in Fig. 1. It was confirmed that the bi-layered interphases were deposited as designed in all the composites. Appearance of the matrices were similar in TyTE-S6/PCS-1100°C and TySA/(PyC/SiC)/(PMS/PCS)- 1200°C, both with very small microporosity within their fiber-bundle regions. Neither deformation of Tyranno-SA fibers nor structural instability of the bi-layered interphase was noticed after heat treatment at 1500 – 1750°C. Heat treatment at 1500°C slightly added micropores in the PMS/PCS-derived matrix, and that at 1700 and 1750°C resulted in rather severe microporosity in the PCS and PMS/PCS matrices due probably to volume shrinkage associated with crystallization and carbothermal reduction. There was a significant difference in appearance of heat-treated matrices; the PCS- and PVS-derived matrices shrunk into blocky grains leaving intergranular openings, while the PMS/PCS-derived matrix shrunk toward the fiber surfaces leaving pores amid inter-fibers.

Figure 2 shows TEM images of the matrix regions in selected materials. The PCS-1100°C matrix comprises nanocrystallites of cubic SiC (crystallites imaged by reflection at partial $\langle 111 \rangle$ ring as the tiny bright spots are indicated by arrows in Fig. 2-a) embedded in amorphous siliconoxycarbide, which is typical for conventional PCS-derived products [9]. The PCS-1700°C and -1750°C matrices were polycrystalline cubic SiC of typical grain size of 100 – 500nm with small amount of graphitic pockets located at multi-grain boundaries. The PVS-1800°C matrix was very similar to the lower temperature matrices with slightly larger grain sizes of SiC. Therefore, microstructural evolution in the PCS-derived matrices during heat treatment is probably isotropic growth of SiC crystallites accompanied by emission of gaseous oxides and

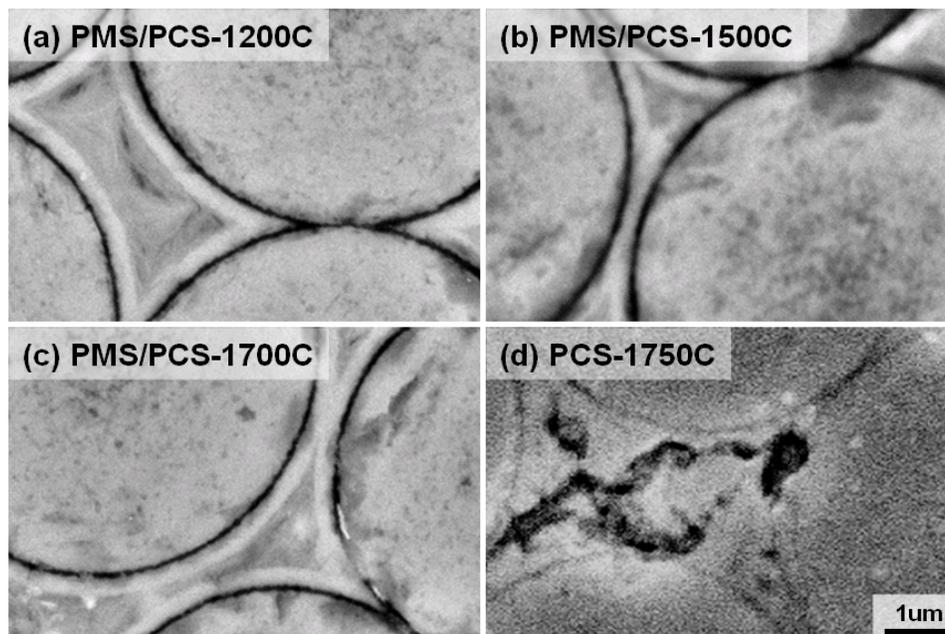


Fig. 1. Scanning electron micrographs of polished cross-sections of PCS- and PMS/PCS-derived matrix composites. Note that only micrograph (d) is a secondary electron image while the others are backscattered electron images.

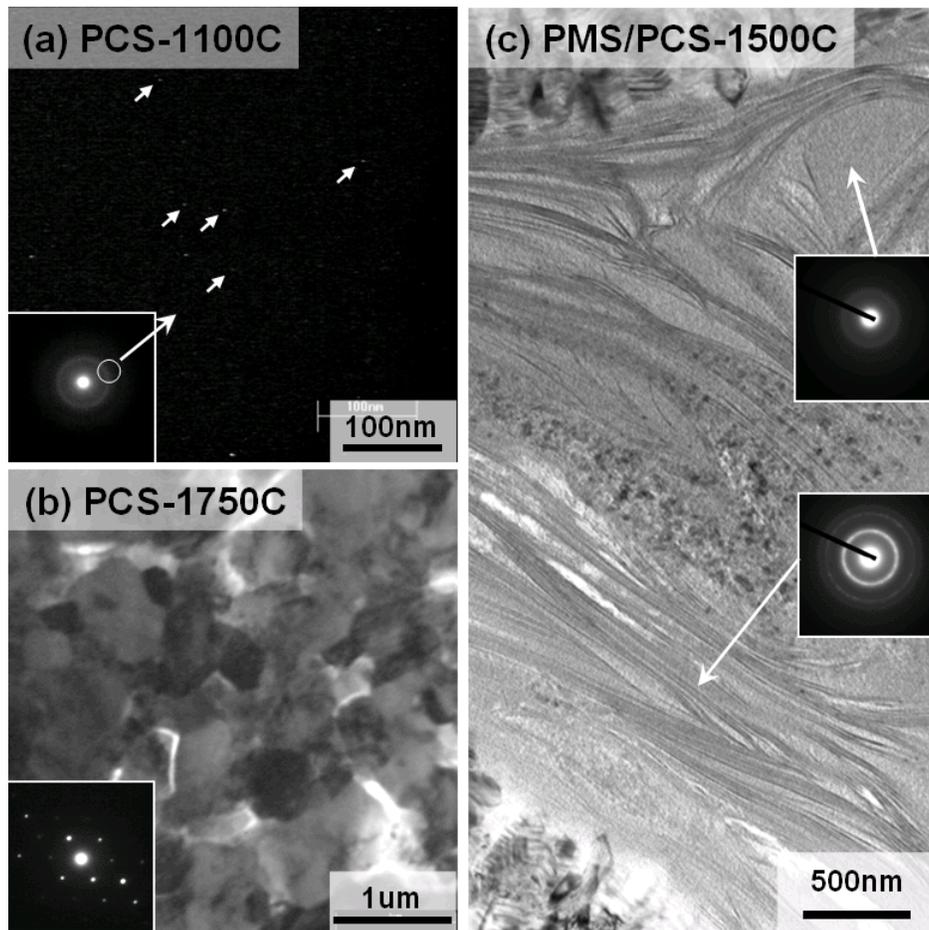


Fig. 2. Transmission electron images of polymer-derived matrices; (a) PCS-derived matrix pyrolyzed at 1100°C, (b) PCS-derived matrix heat-treated at 1750°C, and (c) PMS/PCS-derived matrix heat-treated at 1500°C.

graphitization of the residual carbon.

The microstructures of PMS/PCS-derived matrices were unique. They consisted of numerous numbers of very thin layers (~10nm in thickness) of polycrystalline SiC in an amorphous 'matrix', as shown in Fig. 2-c. The appearance in TEM did not undergo noticeable change by heat treatment at 1500°C. This suggests superior thermal stability of the near-stoichiometric PIP matrix over that of conventional PCS-derived matrices. However, heat treatment at 1700°C caused significant coarsening of the laminar structures of SiC, thin (10 – 100nm) planar openings between SiC layers, and a loss of amorphous phase. The lack of mass loss by the heat treatment (Table 1) suggests that significant outgassing did not take place during the enhanced crystallization.

It is worth noting that Tyranno™-SA Grade-3 fibers used in this study did not undergo significant change by the heat treatment at <1800°C. As shown in Fig. 3, the carbon-rich core region and the more stoichiometric near surface region were both microstructurally stable without noticeable grain growth during the heat treatment. Fiber deformation did not take place, no change in the fiber fracture surfaces

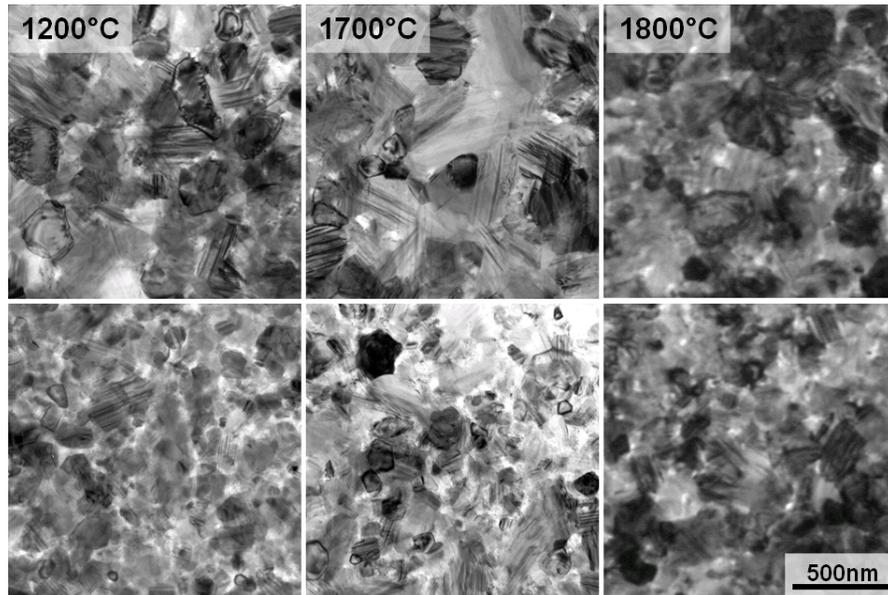


Fig. 3. Transmission electron micrographs showing microstructural stability of near-surface (upper) and core (lower) regions in Tyranno-SA fibers. Heat treatment temperature is indicated at the top left corners.

was noticed after heat treatment at $<1800^{\circ}\text{C}$, either [10]. This is in contrast to the reported slight grain growth in the same fiber after pressure sintering at 1780°C [11], where it is believed that the pressure of 20MPa was playing a major role.

Ambient temperature stress-strain behavior during flexural testing is compared in Fig. 4. Although the enhanced matrix crystallization makes composites' fracture behavior apparently more brittle, it actually accompanies a major transition of fracture mode from primarily interlaminar failure, often initiated by compressive failure, to trans-thickness fracture initiated on the tension side. The high temperature heat-treated composites still exhibit load increase beyond their proportional limit stresses. CVI composites with TyrannoTM-SA or Hi-NicalonTM Type-S exhibit similar flexural fracture behavior [12]. All the TyrannoTM-SA composites except the one pyrolyzed at 1800°C exhibited fiber pull-out with pull-out lengths comparable to those for CVI composites with the same fiber. Therefore, the apparently more brittle fracture observed does not actually mean problematic nature of the high temperature PIP composites. Interestingly, the initial flexural modulus was not significantly altered by the heat treatment. This is probably because the enhanced matrix crystallization compensated the effect of porosity increase on the composite modulus. At 1000°C and 1300°C in argon, ultimate flexural strength for all of the TySA/(PyC/SiC)/(PMS/PCS)- 1200°C , 1500°C and 1700°C composites were almost the same as that obtained at ambient temperature. Proportional limit stresses at elevated temperatures were by 10 – 20% higher than at ambient, possibly due to reduction of residual stress. Apparent flexural moduli at elevated temperatures decreased to 50 – 70% of the values at ambient temperature for all the composites [13]. The reason for this modulus reduction is uncertain.

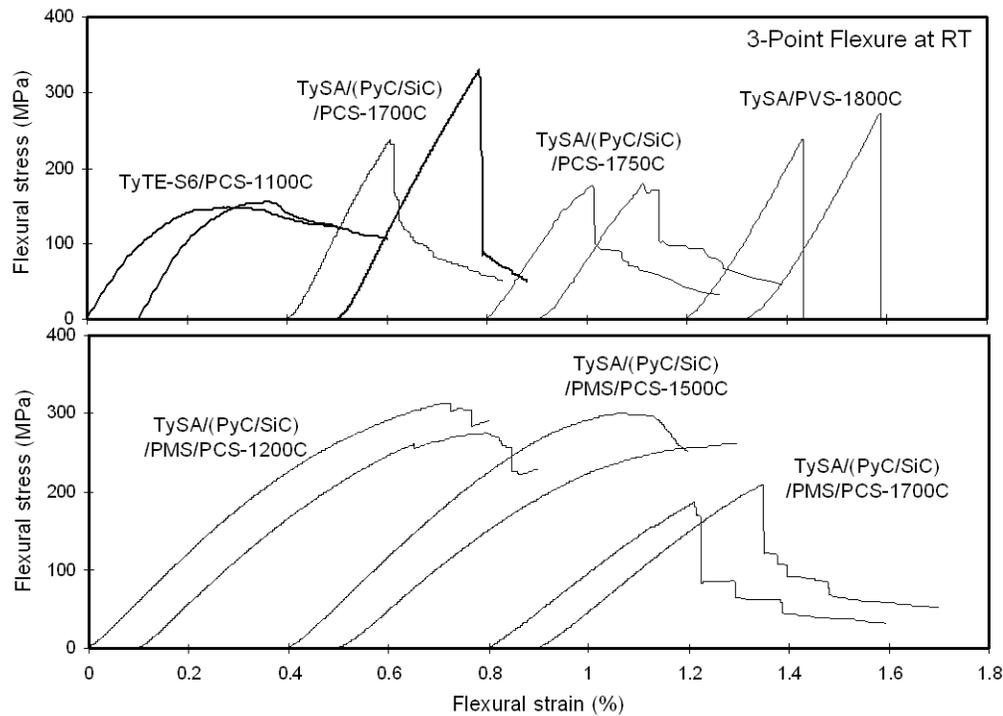


Fig. 4. Apparent stress – strain relationships of the composites during three-point flexural testing at ambient temperature.

Future Work

SiC/SiC composites made with Tyranno™-SA SiC fibers, PyC/SiC bi-layered interphase, and SiC-based matrices derived from PMS/PCS near-stoichiometric SiC precursor will be examined after neutron irradiation at 1,000°C for two HFIR cycles in a static rabbit irradiation capsule. Determination of irradiated tensile strength, proportional limit stress and tangential modulus, and microstructural examination are planned.

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