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Development of SiC/SiC composites by PIP in combination with RS

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Abstract

In order to improve the mechanical performances of SiC/SiC composite, process improvement and modification of polymer impregnation and pyrolysis (PIP) and reaction sintering (RS) process were investigated. The fibrous prepregs were prepared by a polymeric intra-bundle densification technique using Tyranno-SA™ fiber. For inter-bundle matrix, four kinds of process options utilizing polymer pyrolysis and reaction sintering were studied. The process conditions were systematically optimized through fabricating monoliths. Then, SiC/SiC composites were fabricated using optimized inter-bundle matrix slurries in each process for the first inspection of process requirements.

1. Introduction

Continuous SiC fiber reinforced SiC composite (SiC/SiC composite) has been developed as a promising candidate for use in advanced energy systems such as fusion power reactor and gas turbine engine recently [1–3]. Silicon carbide engineering ceramics have been conventionally prepared by reaction sintering, hot pressing or hot isostatic pressing utilizing ceramic powder [4]. In the fabrication of ceramic matrix composites (CMC), an impregnation technique to fill intra- and inter-bundle area with matrix without any fiber damage is necessary. Among the fabrication processes of CMC, the polymer impregnation and pyrolysis (PIP) method offers such advantages as high impregnation efficiency, microstructural control, low cost, and the technical applicability of FRP production to make a large-scale component with complicated shape [5–11]. Although the potential application of polymer-derived composite had been limited for use without irradiation so far because of insufficient crystallization of polymer-derived matrix, recent improvement of processing temperature owing to the development of high-thermal resistant SiC fiber such as Tyranno-SA™ made PIP process a promising technique to fabricate SiC/SiC composite for fusion. However, the pyrolyzed product of organometallic polymer includes a lot of pores formed due to the shrinkage and gas evolution of polymer during decomposition, which often degrade the performance of a composite. Reaction sintering (RS) is an advantageous technique to obtain high-crystallized dense SiC without hot pressing [12–14]. Therefore, the hybridization of PIP and RS is attractive approach to obtain a high-strength and homogeneous matrix. Also the process development with pressureless consolidation is much more useful for near-net-shape fabrication.

The purpose of this work is mechanical improvement of SiC/SiC composite by process improvement of PIP in combination of RS. Fibrous prepregs were prepared by polymeric intra-bundle densification technique similar as that previously reported [15]. For intra-bundle matrix, four kinds of process options were studied. Those are as follows: (i) pyrolysis of SiC precursor, (ii) pyrolysis of C precursor and subsequent reaction sintering between polymer-derived C and Si particles, (iii) reaction sintering between Si and C particles, (iv) reaction sintering between C particles and liquid Si impregnated. The process optimizations such as mixing ratio and forming condition were systematically conducted to reduce porosity and strengthen final products in each option

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without fiber. Then, trial fabrications of two-dimensional SiC woven laminate composites were carried out to obtain process requirements of composite fabrication with optimized matrices.

2. Experimental

2.1. Materials and fabrication procedure

Polycarbosilane (PCS) and MSP-1™ were used as polymeric precursors for SiC and C, respectively. As reinforcement, the plain-woven fabric of Tyranno-SA™ developed by Ube Industries was employed because of its excellent thermal stability owing to a high-crystallized microstructure and near stoichiometric composition. For inter-bundle densification, polyvinylsilane (PVS)-based slurry was used.

For the preparation of monoliths, materials were mixed in acetone for more than 2 h using a magnetic stirrer. The mixtures of 3–4 g were packed to prepare green compacts and compressed under appropriate conditions for each process. The compacts were consolidated up to 1773 K without pressurization in Ar. Then, the consolidated bodies expect those prepared by liquid Si impregnation process were subjected to PIP process cycles for densification.

For the fabrication of composites, the plain-woven sheets were cut to the size of 40×40 mm^2 to prepare fibrous preforms. The preforms were first impregnated with the polymeric slurry and then cured to prepare compound prepregs. To make green bodies, the mixtures for inter-bundle matrix were impregnated into the prepregs and then compressed. The green body was consolidated up to 1773 K in Ar and finally subjected to PIP process cycles similar to monolith. No pressure was applied during the consolidation processing.

2.2. Evaluations

The apparent density of monoliths was calculated using the weight and dimensions of the rectangular specimen measured by calipers. Archimedean method was utilized to measure the density of composites. Microstructural analysis was carried out using optical microscope (OM) and scanning electron microscope (SEM). Flexural strength (σ) and flexural elastic modulus (E) of monoliths and composites were measured by three-point bending test. Ultimate flexural strengths were determined from the peak load on the load-displacement curve. The cross-sectional area of specimens and the span were 4 mm width $\times$ 2 mm thickness and 18 mm, respectively. The crosshead speed of 0.5 mm/min was employed in this work.

3. Results and discussion

3.1. Process optimization of inter-bundle matrix

Fig. 1 shows relative densities of as-consolidated bodies prepared from SiC precursor and SiC particle as a function of initial volume fraction of SiC precursor. It was gradually improved as the polymer content increased and reached 60% at the polymer content of 36%, and then declined a little. Fig. 2 shows the microstructure of as-pyrolyzed body at the polymer content of 74%, where the cracks were initiated due to the shrinkage and gas evolution of the polymer all around the body. Many cracks were induced during densification processing for the specimens with the polymer content less than 22%. It was found that initial polymer content of mixture should be optimized so as to avoid

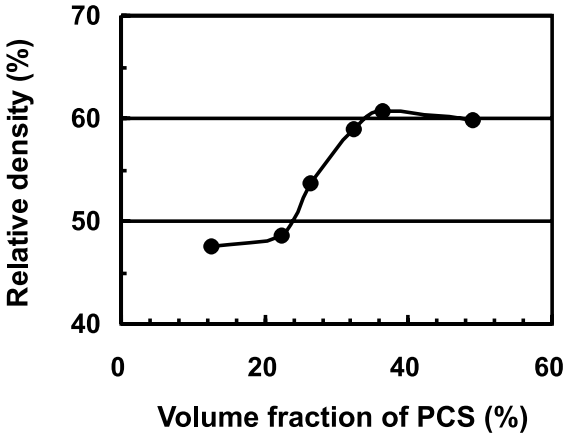

Fig. 1. Relative density of as-consolidated bodies with PCS and SiC particles.

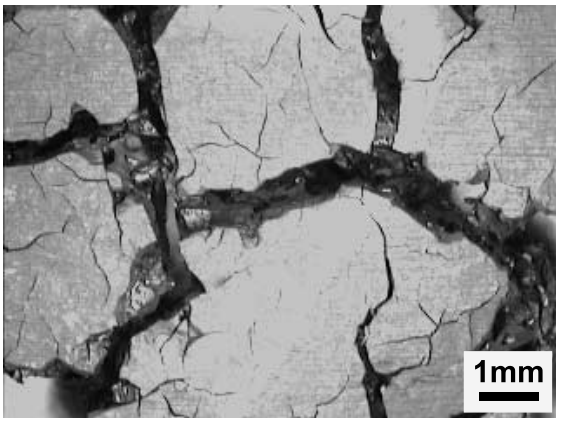

Fig. 2. Optical micrograph of as-pyrolyzed body from PCS and SiC particles at the polymer content of 74%.

crack generation during both consolidation and densification steps. Similar behaviors as relative density and the crack initiation were presented in flexural strength, as shown in Fig. 3. At the optimized polymer content (36%), a flexural strength of about 70 MPa could be obtained.

In the process optimization of C precursor, Si and SiC particle system, relative density increased with the increasing volume fraction of C precursor in raw material, as shown in Fig. 4(a). With more than 30% of C precursor, the relative density reached 55%. From this behavior, C precursor was found to act as an efficient densification aid. According to microstructural observation, no apparent cracks were detected in all specimens. Further optimization of composition and microstructural uniformity are necessary as an important aspect of the process establishment. Fig. 4(b) presents the relationship between density and flexural strength of this process. Increased density yielded increased flexural strength. As an important achievement for this process, the flexural strength about 130 MPa was obtained for the specimens with high relative density, which was almost two times as high as those produced with SiC precursor and SiC particle.

Fig. 5 shows the relative density of as-consolidated bodies prepared by reaction sintering among Si, C and SiC particles as a function of Si particle content in raw material. It increased with the increasing volume fraction of Si particle up to nearly 55%. However, increased density did not yield increased flexural strength and the flexural strength of all specimens remained below 50 MPa. Further process condition survey is necessary in this system.

With a little preliminary study of liquid Si impregnation-type RS, monolithic SiC with high density (2.9 Mg/m^3) and fair flexural strength (372 MPa)

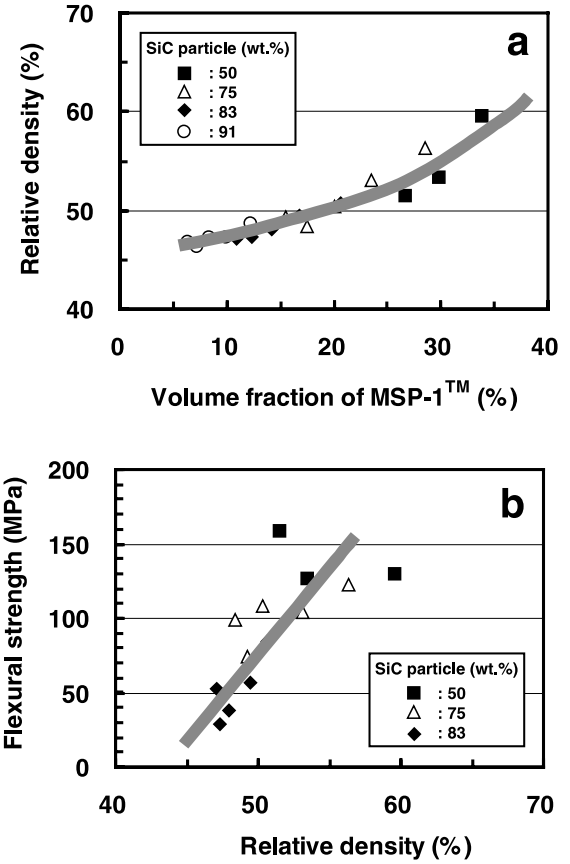

Fig. 4. Characteristics of specimens prepared using C precursor-based Si and SiC particle slurry: (a) volume fraction of MSP-1™ versus relative density of as-consolidated bodies; (b) relative density versus flexural strength of monoliths after densification processing.

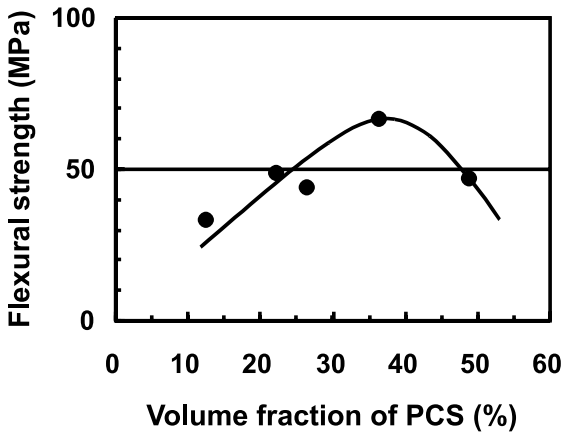

Fig. 3. Flexural strength of monoliths prepared with PCS and SiC particles.

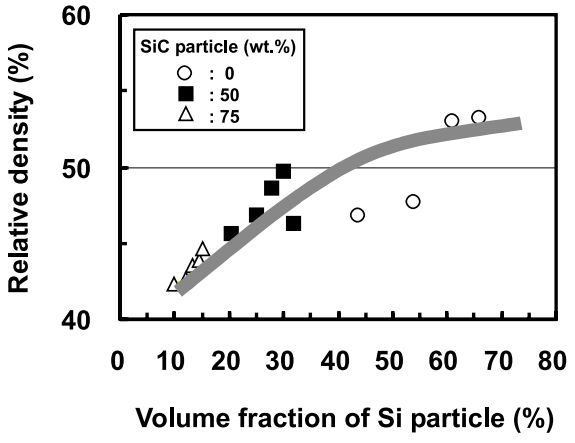

Fig. 5. Relative density of as-consolidated bodies prepared by reaction sintering among Si, C and SiC particles.

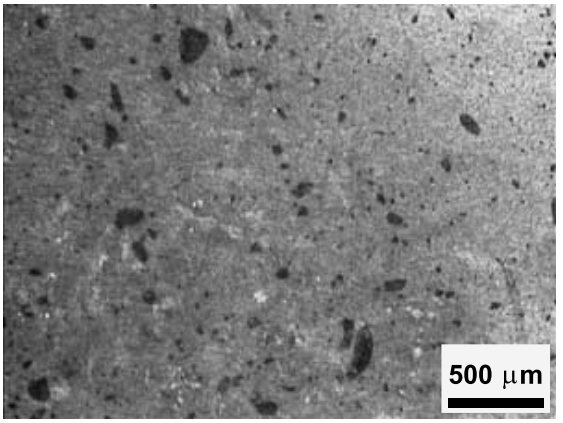

Fig. 6. Optical micrograph of the monolith prepared by liquid Si impregnation reaction sintering.

was successfully produced. Because the process optimization was not performed sufficiently so far, insufficiently homogeneous microstructure was obtained, as shown in Fig. 6. Further mechanical improvement would be achieved by the systematic optimization of process conditions. In mechanical property, liquid Si impregnation process was approved to be most advantageous.

3.2. Fabrication of composites

SiC/SiC composites were fabricated by impregnating inter-bundle matrix into the compound prepregs under same condition as monolith. Cross-sectional micrographs of the composites fabricated with SiC precursor and SiC particle are shown in Fig. 7. A well-densified intra-bundle matrix obtained by PIP was seen in micrograph (a). It was found that the intra-bundle densification technique that previously was optimized for unidirectional architecture was efficient even for wavy textile. Though the bulk density of 2.4 Mg/m^3 was obtained, a lot of large inter-bundle pores were observed due to insufficient impregnation of slurry as shown in (b). To achieve high mechanical properties, improved impregnation technique and efficient compressing conditions are necessary.

As the matrix derived from C precursor-based Si and SiC particle slurry was about 3.1 Mg/m^3, successful preparation of near-stoichiometric SiC with MSP-1™ and Si particles was confirmed. However, many inter-bundle cracks were seen to propagate and insufficient wettability of the C-precursor with fiber-prepreg were observed in Fig. 8. Further optimization of pressure to make a green body and the selection of solvent are necessary.

By the liquid Si impregnation process, densification of inter- and intra-bundle was highly achieved despite insufficient process optimization. Further process development was necessary to avoid residual Si formed in intra-bundle spaces.

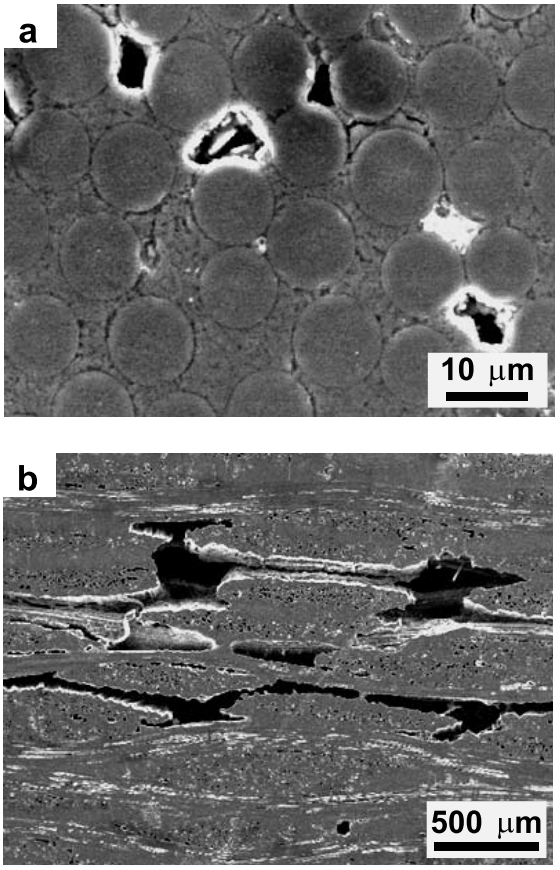

Fig. 7. SEM micrographs of the composite fabricated using PCS and SiC particle slurry for inter-bundle matrix.

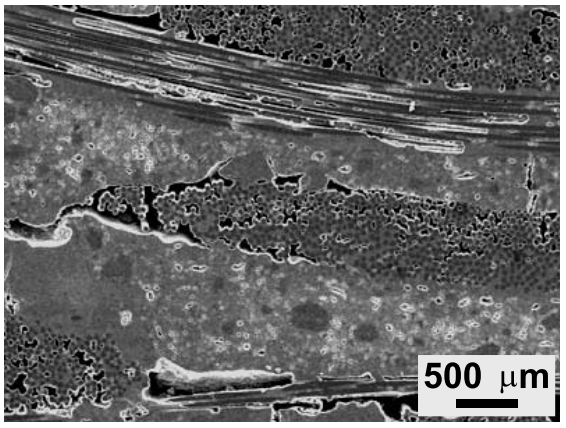

Fig. 8. Cross-sectional SEM micrograph of the composite fabricated using C precursor-based Si and SiC particle slurry for inter-bundle matrix.

4. Summary

The mechanical improvement of SiC/SiC composite was examined by developing improved inter-bundle matrix. Four kinds of process options were studied. The process optimizations involving mixture ratio and pressure to make a green body were systematically performed in each option. Then, two-dimensional SiC/SiC composites were fabricated with optimized inter-bundle matrices to inspect their validity as inter-bundle matrices. These preliminary studies clarified many useful process requirements for this process development and selection.

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