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High-performance SiC/SiC composites by improved PIP processing with new precursor polymers

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Abstract

As they are potential candidates for fusion reactor structural materials, R&D are being conducted on SiC-based composite materials (CREST-ACE program). To improve the efficiency of the polymer impregnation and pyrolysis (PIP) process for SiC/SiC composite fabrication, a new precursor polymer, poly-vinylsilane (PVS) with SiC filler addition, was adopted as a matrix precursor and process optimization was performed. Consequently, high-density SiC/SiC composite with high mechanical properties was efficiently fabricated. Importantly, near-stoichiometric SiC matrix was developed by blending of poly-carbosilane (PCS) and poly-methylsilane (PMS). Remarkable improvements in tensile properties and fatigue characteristics (at 1573 K) were attained when inorganic powder fillers, BMAS or $ZrSiO_4$, were added to the polymer mixture as the matrix precursor. These results are encouraging to make economically and environmentally attractive fusion reactors utilizing SiC/SiC composites as major structural materials.

1. Introduction

It is essential to achieve a balance among our increasing need for energy at a reasonable price and our commitment to a safer environment, and to reduce dependence on potentially unreliable energy suppliers [1,2]. It is also important to have more flexibility and efficiency in the way energy is transformed and used. As a key technology to establish high-efficiency and environmentally conscious (low impact on the environment) energy conversion systems, multi-functional (structural) materials R&D is emphasized in the CREST-ACE program. The acronym CREST-ACE stands for CREST-Advanced Material Systems for Conversion of Energy. This program focuses on R&D of high performance materials and materials systems for severe environments. The final goal is to produce model components for high-efficiency and environmentally conscious systems of energy conversion [3,4].

As important energy options for the future, nuclear fission energy and nuclear fusion energy cannot be ignored. In these materials systems, nuclear reactions, and transformations by the high-energy beams and particles such as neutrons and γ-rays have strong impacts on the environment through the production of radioactive elements and emissions of electromagnetic waves. Therefore, low-activation materials R&D has been a major effort in fusion and fission energy research [5–7].

2. SiC/SiC composite materials R&D for fusion

There is a strong demand to make high-performance ceramic matrix composites (CMC) for advanced energy systems such as nuclear fusion reactors and advanced gas turbine engines. SiC/SiC composites are considered to be potential candidates for them because of their advantages: (1) high specific strength, (2) high

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temperature strength, (3) fracture toughness compared with monolithic ceramics, (4) insulating property (prevent energy loss by conduction), (5) controllability to improve conductivity, (6) low induced radioactivity under nuclear environments, etc. These characteristics are beneficial to achieve high plant efficiency in nuclear fusion systems with higher reliability on safety, which makes fusion an attractive energy option for the future.

R&D of SiC/SiC under the CREST-ACE program can be divided into three tasks: (1) process development of material production into composite material, (2) evaluation and prediction of materials performance and (3) design and fabrication of multi-functional components for energy conversion systems. The first task consists of three sub-tasks, namely, (1) improvement and innovation of SiC fibers, (2) process development of composite material production including matrix materials R&D, (3) design and control of interfacial microstructure to optimize material performance. Fig. 1 provides a brief outline of the tasks. The second task concerns (1) mechanical properties, (2) thermal and electrical properties, (3) establishment of evaluation test methodology for SiC/SiC composite materials and fibers. In this task, studies on irradiation effects and on severe environmental effects are emphasized. As the third task, elements of energy conversion components for fusion reactors and high-temperature gas reactors will be designed and fabricated as the goal of this program, which should verify the specifications of the elements. Low-activation characteristics are the most important technological challenges and selection of low-activation elements and elimination of harmful elements (to produce high purity SiC or SiC(X), where X is element(s) to improve thermal and electrical properties) are extensively carried out.

3. New PIP processes for high-performance SiC/SiC production

3.1. Utilization of PVS and PCS with SiC filler as matrix precursor

The polymer impregnation and pyrolysis (PIP) method has advantages in the viewpoint of large-scale components fabrication with complicated shapes, microstructural control, and low fabrication cost for SiC/SiC composite. However, it is difficult to obtain a composite with high density and fine and uniform fiber distribution due to volume shrinkage and gas evolution of the polymer precursor during the ceramization process. In addition, the composite microstructure fabricated by the PIP process is strongly influenced by the precursors used and process conditions [8–11]. Therefore, it is essential to produce appropriate polymers with small volumetric shrinkage and to optimize process parameters utilizing filler materials [12–15]. In this report, a systematic process optimization utilizing poly-vinylsilane (PVS) is described. The characteristics of PVS, i.e., low-viscosity liquid form at ambient temperature and its thermosetting property, are advantages for reducing pores by pressurization during pyrolysis. Mass reduction and morphological change occurred from 380 to 800 K, especially from 600 to 700 K. It was found that the transformation to a SiC structure starts around 700 K. Solidification followed by an increase in viscosity occurs simultaneously. Based on these characteristics, PIP process design and optimization was performed.

The first optimization step of processing conditions was conducted by varying process conditions, such as curing temperature (K), heating rate (K/h), and pressure for consolidation (MPa). In the optimized conditions,

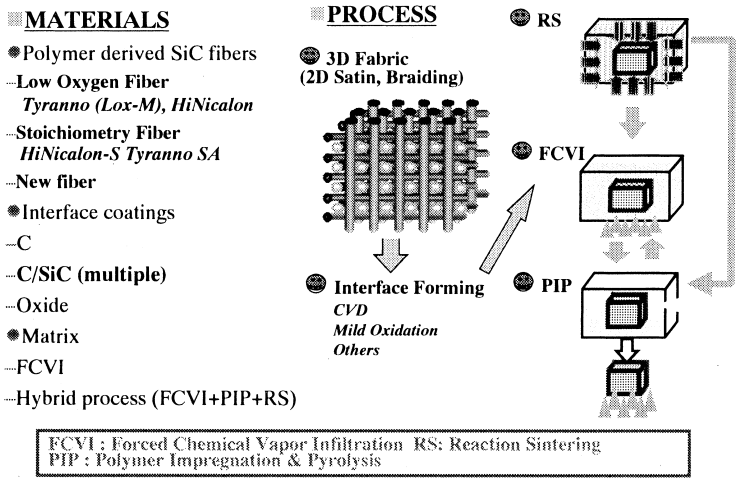

Fig. 1. R&D of SiC/SiC under CREST-ACE program.

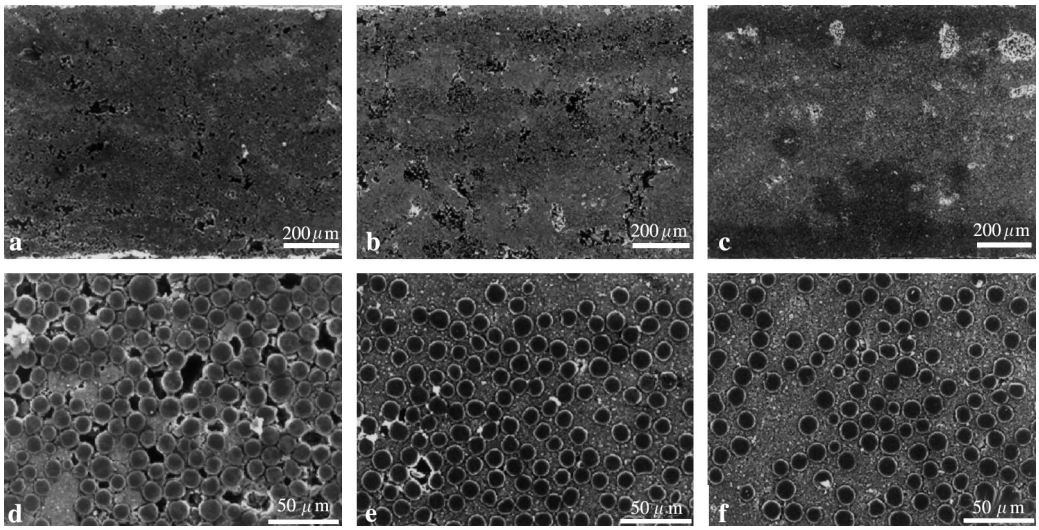

Fig. 2. SEM micrographs of unidirectional composites fabricated utilizing a slurry of each mass fraction of SiC powder as matrix precursor: (a) 25%; (b) 57%; (c) 67%.

where the polymer in curing sheets and the pressure were well balanced, a composite with high density was obtained. As the next step in optimization, the mass fraction of SiC powder added to PVS was optimized. Although the effective volume yield increases with higher mass fraction, the relative density could not be improved and had a peak near 60%. Also, the fiber volume fraction decreased as the mass fraction of SiC powder increased. Fig. 2 shows low magnification SEM micrographs of the composites fabricated with slurry containing various SiC powder mass fractions. Large pores are observed in (a) and (b) but not in (c). Many micropores between fibers can be seen in the higher magnification views (d), a few in (c) and almost none in (f). Fig. 3 is a typical load–displacement curve of the composite of 57% after six cycles PIP densification, showing the three-point bending property. The composite has average three-point bend strength of more than 600 MPa and displays semi-stable fracture behavior that is not found in conventional ceramics. Remarkable improvement in bend strength and toughness obtained using no interfacial fiber coating was applied in this composite.

Further optimization of the process conditions, including curing temperature, the pressure for consolidation and the mass fraction of filler material, and selection of fillers could improve the performances of SiC/SiC composites. Initial results encourage further work on the PIP process development for making high-performance SiC/SiC composites.

3.2. Utilization of PMS and PCS as matrix

Poly-methylsilane (PMS) with high molecular weight was synthesized by conventional reflux method, rather than by sonochemical synthesis [16,17]. The structural formula and synthesis flow of PMS is compared to the usual PCS synthesis method in Fig. 4. The structural formula of PMS was estimated to be $[(CH_3–SiH)_{0.5}–(CH_3–Si)_{0.5}]_n$ by calculation from the ^{1}H-NMR spectrum. PMS and PCS mixtures in various ratios were pyrolyzed at 1273 K in nitrogen to control the C/Si atomic ratio. Figs. 5(a) and (b) show the yield and the C/Si atomic ratio after pyrolysis as functions of PMS/(PMS + PCS) weight ratio, respectively. The yield was proportional to the calculated value based on the yields of PMS and PCS corresponding to 53.5% and

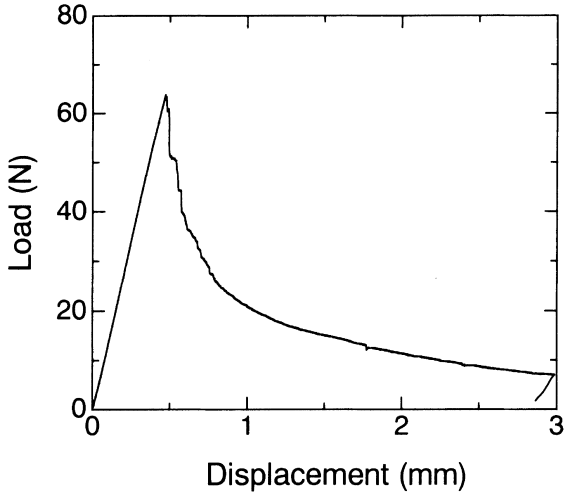

Fig. 3. Representing load–displacement curve of the composite after six times PIP densification.

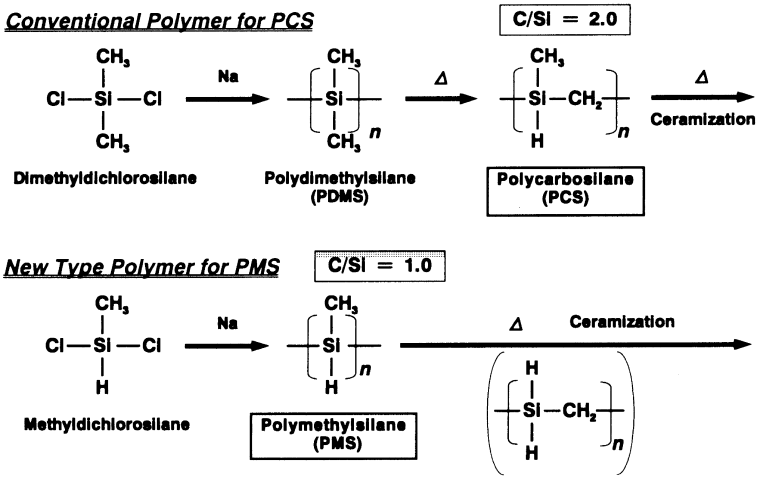

Fig. 4. Synthesis process of new-type polymer for PMS with a comparison with conventional polymer for PCS.

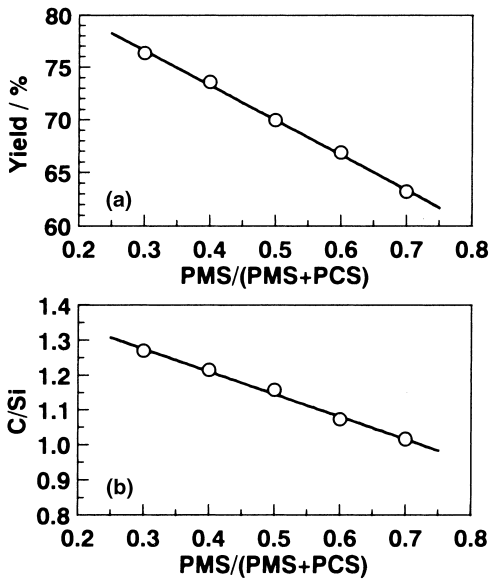

Fig. 5. Dependence on PMS/(PMS + PCS) of: (a) yield; (b) C/Si atomic ratio.

86.5%, respectively. The C/Si atomic ratio was proportional to the calculated value based on the C/Si atomic ratio of PMS and PCS corresponding to 0.79 and 1.45, respectively, and its ratio increased with a rise in the weight ratio of PCS. The C/Si atomic ratio showed a near-stoichiometric composition when the PMS/(PMS + PCS) weight ratio was 0.7. To make near-stoichiometric SiC by blending the two polymers is the point of this process R&D because stoichiometric SiC has excellent durability against liquid metals such as Li and Na [18] and radiation damage [19].

3.3. High-temperature strength improvement by BMAS or $ZiSiO_4$ addition to the matrix

Tensile strength and cyclic fatigue performance of conventional SiC/SiC composite are generally insufficient because of microcracks that developed at pores when loaded under high stress in the matrix of CMC. To improve the performance of CMC, the composites were fabricated with Tyranno-Lox M fiber with carbon interphase. The matrix was derived from the pyrolysis of poly-metaro-carbosilane including BMAS (BaO_2–MgO–Al_2O_3–SiO_2) or $ZrSiO_4$ particles. Remarkably improved tensile strength was obtained at both room and high temperatures, as shown in Fig. 6. The tensile

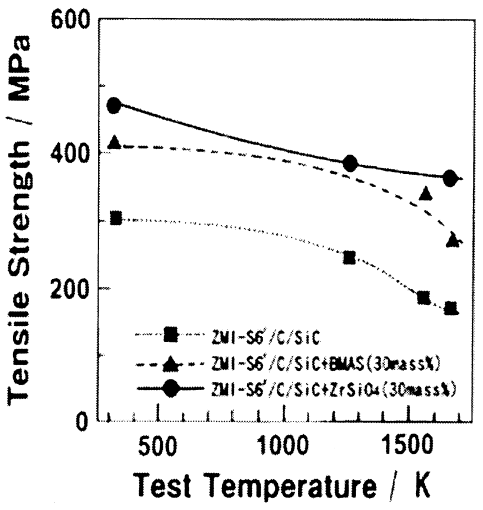

Fig. 6. Tensile strength of SiC_f/SiC composites with the matrices included oxide particles in air.

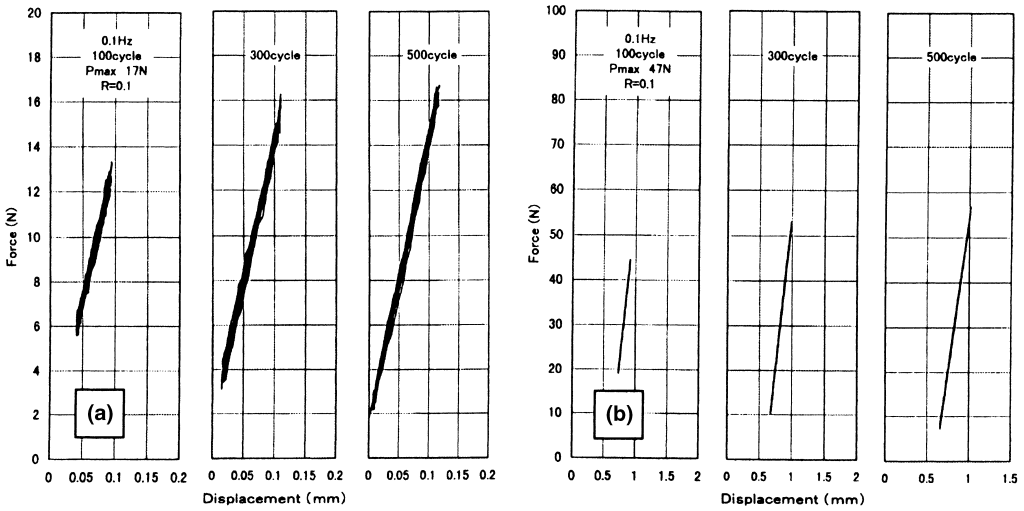

Fig. 7. Cyclic fatigue characteristic of: (a) usual CMC; (b) new CMC with matrix at 1573 K in Ar gas.

strength values of the specimen with 30% $ZrSiO_4$ was 470 MPa at room temperature and 380 MPa at 1673 K, more than two times stronger than without particles. Figs. 7(a) and (b) show the cyclic fatigue characteristics at high temperature. The cyclic stress–strain curves show the hysteresis loop in the conventional CMC. In contrast, hysteresis was not observed in the new type of CMC tested by the same manner.

4. Conclusions

For the application of SiC/SiC to fusion reactors, PIP process design and optimization was performed. The new SiC/SiC composites made by the new PIP processes showed excellent improvements in mechanical properties and attractive potential for large size component fabrication. The results can be summarized as follows.

In order to improve the efficiency of the PIP process, a new precursor polymer, poly-vinylsilane (PVS) with SiC filler, was adopted as a matrix precursor and process optimization was performed. Consequently, high-density SiC/SiC composite was efficiently produced, which exhibited excellent strength improvement.

Near-stoichiometric SiC was developed by blending PCS and PMS. The Tyranno-Lox M/SiC composites with near-stoichiometric matrix showed excellent improvement in tensile properties and fatigue characteristics at 1573 K, which was attributed to the use of PMS and PCS polymers with inorganic powder fillers, BMAS and $ZrSiO_4$, as the matrix precursor.

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