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High temperature characterization of reaction sintered SiC based materials

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Abstract

Monolithic SiC and SiC_f/SiC composite materials have been fabricated by a reaction sintering process. The mechanical properties of RS-SiC_f/SiC composites reinforced with Hi-Nicalon SiC fiber have been investigated at elevated temperatures, in conjunction with a detailed analysis of their microstructures. The effect of heat treatment on the microstructure and strength of RS-SiC material was also examined. The characterization of RS-SiC based materials was evaluated by means of SEM, EDS and three point bend test. The RS-SiC material showed an average density of 3.0 Mg/cm^3 and an average strength of about 550 MPa. However, the strength of RS-SiC material decreased with increasing heat treatment times. The RS-SiC_f/SiC composite also experienced a reduction of room temperature strength at a test temperature of 1300 °C, owing to the creation of internal defects such as matrix oxidation, interfacial debonding and fiber degradation.

1. Introduction

SiC fiber reinforced SiC matrix composites (SiC_f/SiC) have been studied for a new approach in the fusion power plant systems such as first wall or divertor coolant channel, because of its excellent high temperature property, remarkable dimensional stability and low induced radioactivity [1–3]. For fusion applications of SiC_f/SiC composites, both a high-purity SiC phase and a high-density SiC matrix with improved thermal conductivity and irradiation property must be still developed through the optimization of manufacturing process. With the rapid development of high crystalline SiC fibers, SiC_f/SiC composites have been fabricated by various methods [4–8]. The reaction sintering (RS) process is recognized as an attractive technique because it offers high density, good thermal conductivity and low cost production [6,9]. In general, RS-SiC based materials have inhomogeneous microstructures, since the molten silicon remained as fine residual silicon, filling the pores or voids formed in the porous preform. The major research interests for RS-SiC based materials are focused on the suppression of residual silicon content and the preparation route of various fabric preforms prior to the infiltration of molten silicon. The residual silicon content in the RS-SiC material can be decreased by the reduction of starting SiC particle sizes and the proportion of SiC and C particles in the preparation of C/SiC complex slurries [10,11]. Previous studies also showed that the slurry infiltration process by a combination of gas pressure impregnation and cold pressing was effective in making a sound fiber perform for high-density RS-SiC_f/SiC composites [12,13]. However, in order to promote the applications of RS-SiC based materials, the mechanical property–microstructure correlation must be

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investigated at the elevated temperatures. It is also important to examine the high temperature behavior of residual silicon phase.

The purpose of the present study is to investigate the effect of test temperatures on the mechanical properties of RS-SiC$_f$/SiC composites, in conjunction with the analysis of their microstructures. The characterization of RS-SiC materials changed by the heat treatment was also examined.

2. Experimental procedures

2.1. Fabrication of RS-SiC based materials

A porous compact preform for RS-SiC$_f$/SiC composites was prepared by injecting C/SiC complex slurry into fabric structures mounted in a rectangular shaped mold under a gas pressure of 6.0 MPa. The C/SiC complex slurry, which was a mixture of SiC powder, carbon powder and water, was prepared by ball milling. The average sizes of commercial SiC and carbon particles were 4.0 μm and 85 nm, respectively. The blending ratio of C and SiC particles in the complex slurry was maintained at 0.4 wt%. A braiding fabric of Hi-Nicalon SiC fiber was used for the fabrication of RS-SiC$_f$/SiC composites. A double coating of BN and SiC layers was deposited on the surface of SiC fiber using a chemical vapor deposition process. The volume fraction of SiC fiber in the composite was fixed at about 30 vol.%. RS-SiC and RS-SiC$_f$/SiC composite materials were fabricated by infiltrating molten silicon into each porous preform. The fabricating temperature and holding time were 1450 °C and 2 h in vacuum atmosphere, respectively. The dimensions of RS-SiC and RS-SiC$_f$/SiC composite materials were $3(t) \times 4 \times 40$ mm^3 and $1(t) \times 10 \times 40$ mm^3, respectively.

2.2. Evaluation of RS-SiC based materials

The microstructural analysis for RS-SiC and RS-SiC$_f$/SiC composite materials was carried out using SEM with EDS. The mechanical properties of all materials were evaluated by three point bend tests. In order to examine the high temperature stability of RS-SiC material, its strength after the heat treatment was measured at room temperature. The heat treatment test was performed at a temperature of 1400 °C. The holding times for the heat treatment were 1.0, 3.0 and 5.0 h under a vacuum atmosphere (2×10^{-3} Pa), respectively. The flexural strength of RS-SiC$_f$/SiC composites was examined at room and elevated temperatures (25, 1000, 1100 and 1300 °C). The thermal exposure time heated up to each temperature before three point bend tests was constant as about 4 h. In order to obtain a uniform test atmosphere, the test sample was also maintained at each test temperature for 1 h. The dimensions of test samples for RS-SiC and RS-SiC$_f$/SiC composite materials were $3(t) \times 4 \times 25$ mm^3 and $1(t) \times 4 \times 25$ mm^3, respectively. The span length and the crosshead speed for the three point bend tests of all materials were 18 mm and 0.5 mm/min, respectively. Four pieces of test samples were also used for the strength evaluation of RS-SiC based materials.

3. Results and discussion

3.1. Characterization of RS-SiC material

Fig. 1 shows the microstructure of RS-SiC materials following the heat treatment test. The temperature and its holding time for the heat treatment test were 1400 °C and 5 h, respectively. RS-SiC materials without the heat treatment exhibited a dense morphology with some amount of void or porosity, even if they were mainly composed of SiC phase and residual silicon. The density

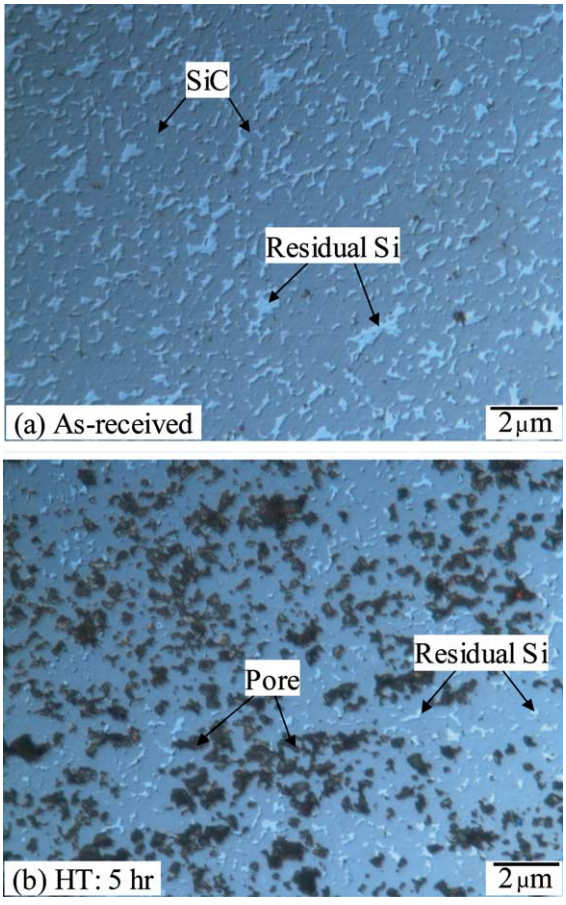

Fig. 1. Microstructures of RS-SiC materials as a function of heat treatment time at 1400 °C.

and the residual silicon content of the as-received RS-SiC material were about 3.0 Mg/m^3 and about 20%, respectively. It was found that the RS process could provide a good density for monolithic SiC materials. The morphology of RS-SiC material was greatly affected by the heat treatment. In other words, an increase in porosity was observed in RS-SiC material after the heat treatment (black area in Fig. 1(b)). This is likely caused by the evaporation of residual silicon phases during the high temperature exposure.

Fig. 2 shows the effect of the heat treatment time on the density and the porosity volume fraction of RS-SiC materials. The heat treatment temperature was 1400 °C. It was found that the heat treatment time had a significant effect on the density and the porosity amount of RS-SiC materials. The density of RS-SiC materials greatly decreased with increasing the heat treatment time. This is because large amount of residual silicon phases were transformed into the porosity during the high temperature exposure, as shown in Fig. 1. Such an volume fraction of porosity in the microstructure increased with increasing the heat treatment time. The volume fraction of porosity after the heat treatment time of 5 h had about 42%, which corresponded to about seven times of the as-received RS-SiC material. The average size of porosity in the microstructure also grew from about 0.02 μm to about 0.05 μm after the heat treatment time of 5 h.

Fig. 3 shows the flexural strength of RS-SiC materials as a function of the heat treatment time at 1400 °C. RS-SiC materials showed a typical brittle fracture behavior. The strength of RS-SiC materials dramatically decreased with increasing the heat treatment time. The RS-SiC materials retained an average strength of about 320 MPa after a heat treatment of 5 h. Such a strength level was corresponded to about 60% of the as-received RS-SiC material. It is found from these results of Figs. 1 and 2

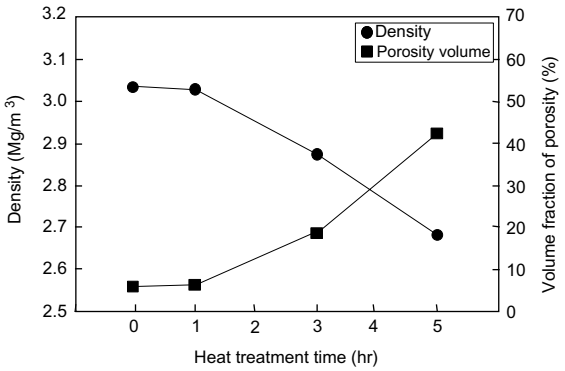

Fig. 2. Effect of heat treatment time on the density and the porosity volume fraction of RS-SiC materials (heat treatment temperature: 1400 °C).

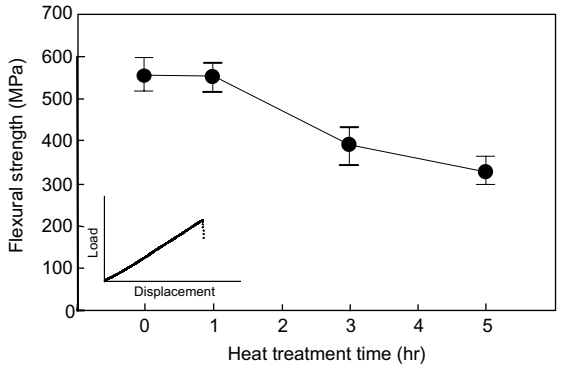

Fig. 3. Flexural strength of RS-SiC materials as a function of heat treatment time at 1400 °C.

that the strength of RS-SiC material depends on the variation of its density and microstructure from the heat treatment. In other words, the strength reduction of RS-SiC material by the increase of heat treatment time was due to the decrease of density, since the residual silicon phases in the microstructure evaporated to form increasing amount of porosity. Therefore, in order to extend the high temperature applications of RS-SiC materials, the residual silicon phase in the microstructure must be suppressed through the optimization of fabricating process.

3.2. Characterization of RS-SiC$_f$/SiC composites

Fig. 4 shows the representative microstructure of RS-SiC$_f$/SiC composites with a density of about 2.8 Mg/m^3. The microstructure of RS-SiC$_f$/SiC composites by the thermal exposure, corresponding to the duration of the three point bend test at 1300 °C, is also shown in this figure. The composition of each phase depicted in the figure was identified by EDS analysis. The matrix of RS-SiC$_f$/SiC composites before the thermal exposure consisted mainly of two types of SiC phases with different ratios of Si and C, even if it had a good morphology without matrix cracks or debondings. A large amount of Si rich SiC with a Si/C ratio of about 1.7 were created in the matrix of the RS-SiC$_f$/SiC composite, compared to that of near stoichiometric SiC with a Si/C ratio of about 0.9. Such a chemical fluctuation in the SiC matrix is due to the presence of fine unreacted carbon and residual silicon phases [12]. Moreover, as shown in Fig. 4(b), the RS-SiC$_f$/SiC composite exhibited a microstructural instability after the thermal exposure corresponding to the duration of the three point bend test (1300 °C). In other words, the extensive interfacial debonding between SiC fiber and interfacial coating layer as well as the damage of SiC matrix were observed. The SiC matrix also showed a Si/C ratio of about 0.7 due to the thermal exposure. This seems to be due to the

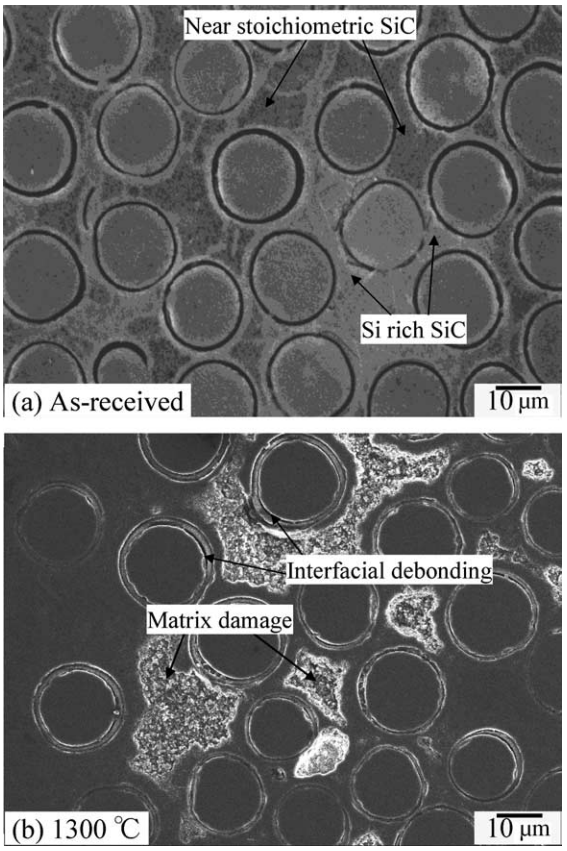

Fig. 4. Microstructures of RS-SiC_f/SiC composites by the thermal exposure at the test temperature.

oxidation of Si rich SiC phases and residual silicon phases formed in the SiC matrix.

Fig. 5 shows the effect of test temperature on the flexural strength of RS-SiC_f/SiC composites reinforced with SiC/BN double-coated Hi-Nicalon SiC fiber. RS-SiC_f/SiC composites showed a pseudo-ductile failure behavior with stable crack propagation beyond the maximum load, regardless of the test temperatures. This is because the crack propagation path depends on the correlation among interfacial delamination, fiber fracture and fiber pull-out after the crack is arrested at the interface. RS-SiC_f/SiC composites had a room temperature strength of about 330 MPa. The strength of RS-SiC_f/SiC composites decreased at test temperatures higher than 1100 °C, even though it slightly increases from room temperature to 1000 °C. RS-SiC_f/SiC composites had the strength of about 260 MPa at 1300 °C, which corresponded to about 80% of the room temperature strength. This is related to the variation of microstructure by the high temperature exposure, as shown in Fig. 4(b). That is to say, since the strength of Hi-Nicalon SiC fiber decreased at the temperature higher than 1000 °C, the high temperature strength reduction of RS-SiC_f/SiC composites was caused by the degradation of Hi-Nicalon SiC fiber as well as the microstructural instabilities such as matrix damage and interfacial debonding [3]. Therefore, the creation of crystallized SiC in the matrix region is basically required for the development of high performance RS-SiC_f/SiC composites, since the variation of microstructure during long-term thermal history will impose a severe limitation on the high temperature applications.

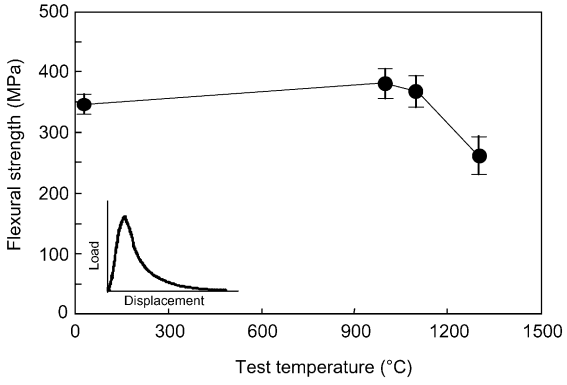

Fig. 5. Effect of test temperatures on the flexural strength of RS-SiC_f/SiC composites.

4. Conclusions

1. RS-SiC materials exhibited a good morphology with the density of about 3.0 Mg/m^3, even if there were large amount of residual silicon phases (about 20%). The density of RS-SiC material greatly decreased with increasing the heat treatment time due to the formation of pores by the evaporation of residual silicon.
2. RS-SiC materials showed a good flexural strength of about 550 MPa at room temperature. However, the strength of RS-SiC materials dramatically decreased with the increase of thermal exposure times, due to the drastic decrease of sintered density.
3. Large amount of Si rich SiC phases (Si/C ratio: about 1.7) were created in the matrix region of RS-SiC_f/SiC composites, in addition to the formation of crystallized SiC and residual silicon. RS-SiC_f/SiC composites also showed microstructural defects such as interfacial debonding and matrix oxidation, after the thermal exposure corresponding to the duration of three point bend tests at high temperatures.
4. RS-SiC_f/SiC composites had a flexural strength of about 330 MPa at room temperature. The strength of RS-SiC_f/SiC composites greatly decreased at test temperatures higher than 1100 °C due to

microstructural instabilities from the long-term thermal exposure.

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