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Fabrication and flexural properties of Tyranno-SA/SiC composites with carbon interlayer by CVI

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Abstract

Strength reliability and thermal stability of SiC/SiC composites are important as structural candidates for nuclear fusion reactor. Several CVI-Tyranno-SA (plain-woven)/SiC composites were fabricated and the flexural strength and the effects of the high temperature heat treatment in vacuum were investigated. The flexural strength and statistical properties of the as-fabricated composites showed a dependence on composite density. The highest average strength, 640 ± 69 MPa, with the highest Weibull modulus, $m = 12.2$, was obtained by the composite with the highest density among the several composites. No significant change of the strength of the composite was noticed against heat treatment at temperature up to 1973 K in vacuum of $\sim 3 \times 10^{-4}$ Pa for 1 h, beyond which the strength decreased with the increasing of the heat treatment temperature.

1. Introduction

It has been well recognized that SiC/SiC composite is one of the major candidates for nuclear fusion power reactors because of its advantages such as radiation resistance, excellent high temperature fracture, creep, corrosion, and thermal shock resistance, etc. [1–3]. SiC/SiC composites also possess safety advantages arising from their low induced radioactivity and after-heat. The successful development of advanced SiC fibers such as Tyranno-SA fiber made the SiC/SiC composites even more attractive [4]. SiC/SiC composites usually exhibit relatively large scatter in strength because of the statistical distributions of the flaws and pores in the materials. Therefore, the fabrication of dense SiC/SiC composites with homogeneous matrix densification and the evaluation of the strength reliability are necessary and important.

Thermal stability of SiC/SiC composites is also an important issue to be concerned since the materials are to be operated at high temperature in fusion and many other applications for high thermal cycle efficiency. The thermal stability of Tyranno-SA fiber is markedly improved over the old-generation Nicalon fibers. Therefore, improved thermal stability of the SiC/SiC composites reinforced with Tyranno-SA fibers rather than the Nicalon fibers is expected.

In the present work, several Tyranno-SA fibers-reinforced SiC/SiC composites were fabricated by the chemical vapour infiltration (CVI) process. Flexural properties were investigated with the main numerical interests in the statistical properties of the strength. Heat treatment at elevated temperatures in vacuum was also performed to study the effects of the heat treatment on the strength.

2. Experimental

2.1. Composite fabrication

2D plain-woven Tyranno-SA fiber cloths laminated with 18 sheets were used as the composite preforms. The preforms were compressed with a set of graphite fixtures to keep a fiber volume fraction of ~30%, resulting in a dimension of the preforms 120 mm in diameter and

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~3 mm in thickness. The preforms were densified with SiC-matrix using the thermal decompositions of methyletrichlorosilane (MTS). MTS was carried by hydrogen with volume ratio about 0.5 and a total hydrogen flow rate 2.01 min^{-1}. The CVI densification processes were carried out at 1323 K for about 80 h for each composite at reduced pressure of 14.4 kPa in the CVI reactor. Prior to the CVI matrix densification, the preforms were precoated with pyrolytic carbon (PyC) as fiber-matrix interlayer from methane (CH_4) using the CVI process, to modify the interfacial shear/sliding strength.

Totally four composites were fabricated, as shown in Table 1. No PyC interlayer was deposited on the fibers in composite SA-0, while 20, 60 and 120 nm PyC layer were deposited in composite SA-20, SA-60 and SA-120, respectively.

2.2. Heat treatment and mechanical tests

Twenty to thirty five bars with a surface area of 25 mm × 4.0 mm were cut parallel to one of the fiber bundle directions of the fabric clothes from composite SA-0, SA-60 and SA-120, respectively, to investigate the ultimate flexural strength statistical properties. Both surfaces of the specimens (bars) were carefully ground to remove the surface chemical vapour deposition (CVD)-SiC layer that was formed at the end of the CVI, and to guarantee a same surface condition of the specimens for the following bending test. The resulting specimen size was 25 mm in length, 4.0 mm in width and 2.0 mm in thickness. The density of each bar was measured from its mass and volume before bending test. Heat treatments in vacuum of $\sim 3 \times 10^{-4}$ Pa for 1 h at temperature range from 1273 to 2273 K were carried out for composite SA-20 (4 bars for each temperature).

The flexural strength and fracture behaviours were investigated by three-point bending tests with support span 16 mm and cross-head speed 0.0083 mm/s. The micro-structures, PyC interlayers, and the fracture surfaces of all the composites were examined by means of scanning electron microscopy (SEM, JEOL JSM-6700F).

3. Results and discussion

3.1. Composites and flexural strengths

The average density and average ultimate flexural strength of the composites are given in Table 1. The ultimate flexural strengths were derived from the load–displacement curve of each specimen according to ASTM C 1341-97 [5]. Composite SA-0, SA-60 and SA-120 were used to investigate the statistical strength while composite SA-20 was used to study the effects of high temperature heat treatment on the flexural strength. Table 1 shows that among the composites for statistical properties, SA-0 has the lowest average density, 2.55 Mg/m^3, with the largest coefficient of variation (CV) of density, 0.020. The best CVI matrix densification was achieved with SA-60, which showed the highest average density, 2.98 Mg/m^3, and the smallest CV of density, 0.010. Composite SA-0 showed an average strength of 345 ± 70 MPa, which is much lower than that of composite SA-60 (640 ± 69 MPa) and SA-120 (590 ± 78 MPa). This is because of the lowest density and strong interfacial bonding (no PyC interlayer was deposited in the composite) in the composite. The composite exhibited brittle fracture behaviours with rather flat fracture surface, as shown typically in Fig. 1(a). Interfacial debonding and sound fiber pullouts occurred in the specimens from SA-60 and SA-120 (Fig. 1(b) and (c)).

3.2. Weibull statistic distribution of the strength

The ultimate flexural strengths are assumed to follow the flexible two-parameter Weibull distribution [6]. The Weibull plots of the flexural strengths of composite SA-0, SA-60 and SA-120 are shown in Fig. 2. The Weibull modulus are 6.4, 12.2 and 10.5, respectively. The low density and large CV of the density are likely to be the main reasons causing the smallest Weibull modulus of SA-0 among the three composites. In addition, the flat fracture surface (Fig. 1(a)) indicates strong interfacial bonding in this composite. Interfacial debonding/bridg-

Table 1
Density and flexural strength of the composites

Composite ID	Tested specimen	Density (Mg/m^3)	CV[a]	Flexural strength (MPa)	CV[a]	m[b]
SA-0	20	2.55 ± 0.05	0.020	345 ± 70	0.202	6.4
SA-60	33	2.98 ± 0.03	0.010	640 ± 69	0.108	12.2
SA-120	35	2.74 ± 0.04	0.015	590 ± 78	0.132	10.5
SA-20[c]	8[d]	2.70 ± 0.14	–	380 ± 113	–	–

[a] Coefficient of variation.
[b] Weibull modulus.
[c] For heat treatment test.
[d] As-received.

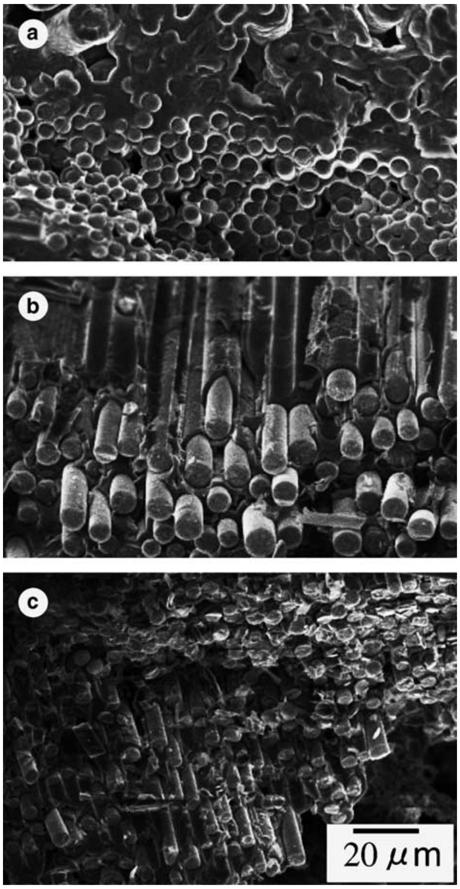

Fig. 1. Typical fracture surfaces of composite SA-0 (a), SA-60 (b), and SA-120 (c).

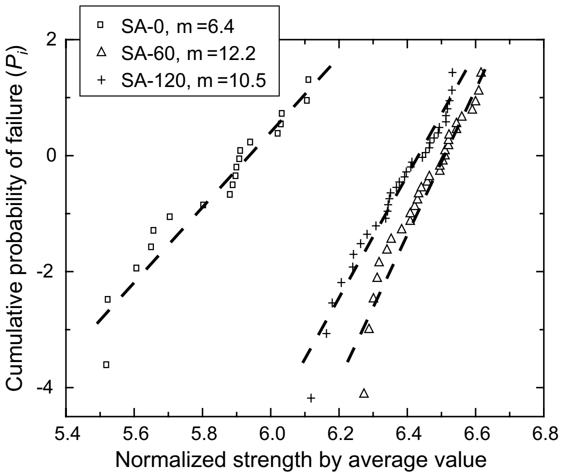

Fig. 2. Weibull plots for the flexural strength of the Tyranno-SA/SiC composites.

ing of matrix cracks at interfaces in this composite are unlikely to occur upon external bending loading, and hence, likely resulting in increased sensitivity of failure of the composite to the matrix cracks and pores in the material. The two PyC-interlayered composites showed much increased statistical reliability of the flexural strength. The highest Weibull modulus, 12.2, was achieved by SA-60, which corresponds with the highest density and lowest CV (Table 1). This value is much higher than that of plain-woven Nicalon-CG (2.1) and Hi-Nicalon (7.4) fibers reinforced SiC/SiC composites that were fabricated with the similar CVI process as the current ones [7].

3.3. Effects of heat treatment

As shown in Table 1, although the average density of composite SA-20 is 2.70 ± 0.14, near to that of composite SA-120, the average as-fabricated strength is 382 ± 113 MPa, much less than that of SA-120. Less PyC interlayer and poor matrix space homogeneity (the standard deviation of the density is 0.14 Mg/m^3, much higher than the other composites) are main reasons for its low average strength. The effect of the heat treatment temperature on the strength is graphically illustrated in Fig. 3. Although the error bars are relatively large, Fig. 3 shows a clear trend of the strength against heat treatment temperature. The strength remains stable up to 1973 K, beyond which a decrease occurred with increasing heat treatment temperature. Over 50% of the strength was lost after the specimen was heat-treated at 2273 K in vacuum of $\sim 3 \times 10^{-4}$ Pa for 1 h.

Fig. 4(a) and (b) shows the SEM images of the fracture surfaces of a specimen after heat treatment at 2273 K. Some changes of morphologies at the fracture surface at the area near to the surface of the specimen are evident, indicating that some damages have occurred in the specimen before the bending test. This damage is believed to result from the heat treatment at 2273 K.

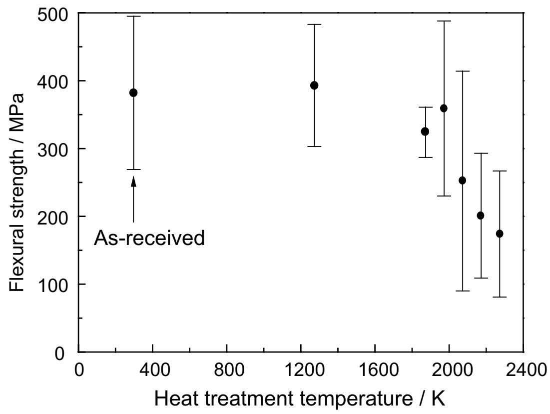

Fig. 3. Effects of heat treatment temperature on the flexural strength.

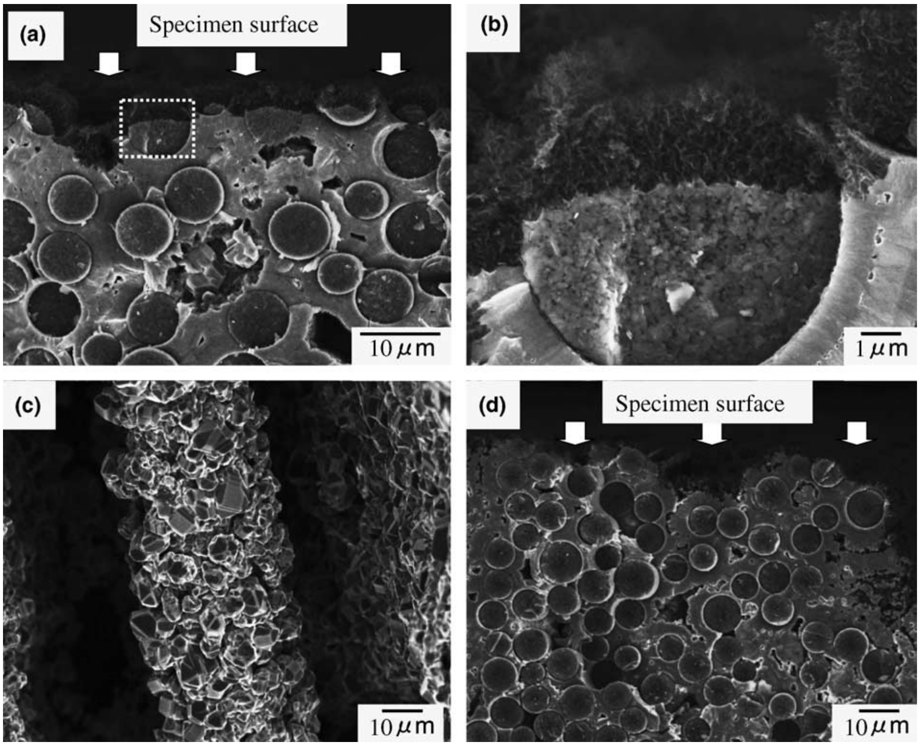

Fig. 4. Fracture surface of specimens after heat treatment at 2273 K ((a)–(c)) and 2173 K ((d)).

Interfacial debonding and short fiber pullouts at the fracture surface far from the surface of the specimen are similar as that of as-received specimens, indicating that damage to the specimen from the heat treatment was mainly at the regions near to the surface of the specimen, with a depth of about several micro-meters. Further examination revealed that significant recrystallization of the CVI-matrix in the specimen have occurred at the surface areas of the specimen as well as the outmost regions of some fiber bundles where relatively large interbundle pores (which are intrinsic with the CVI-SiC/SiC composite with plain-woven fabric as the reinforcement) exists, as shown in Fig. 4(c). Similar but much less damage was also observed in the specimens after heat treatment at 2073 and 2173 K (Fig. 4(d)) but not in those at temperatures lower than 2073 K. Obviously, the recrystallized SiC matrix is porous with very weak grain boundary, and therefore, possesses low fracture strength. This might be the main reason causing the decrease of the strength of the composite against heat treatment temperature when it was over 1973 K. The damage to the Tyranno-SA fibers near to the specimen surface is also a reason causing the decreased strength of the composite upon heat treatment. The detailed mechanism of the recrystallization behaviour of the CVI-SiC matrix upon high temperature heat treatment currently remains unclear. However, it is considered that such recrystallization behaviour is accompanied by sublimation of the matrix as [8]:

$$\mathrm{SiC} \rightarrow \mathrm{SiC}\ \text{(sublimation)}$$

The recrystallization of the matrix might also be affected by trace oxygen (from either the heat treatment chamber or the composite that was incorporated in pores in the composite during the CVI process) through [8]:

$$\mathrm{SiC}_{1+x} + \mathrm{O}_{\mathrm{trace}} \rightarrow \mathrm{SiC} + \mathrm{CO}$$

4. Conclusion

Several plain-woven CVI-Tyranno-SA/SiC composites with various PyC interlayers were fabricated. The flexural strength and the effects of the heat treatment were investigated. The conclusions are:

1. The flexural strength and statistic properties of the as-fabricated composites showed composite density dependence. Among the several composites, the highest average strength, 640 ± 69 MPa, with the highest Weibull modulus, $m = 12.2$, was obtained by the composite with the highest density, 2.98 ± 0.03 Mg/

m^3. This Weibull modulus is much larger than those of the Nicalon-CG/SiC and Hi-Nicalon/SiC composites.

2. The thickness of the PyC interlayer showed significant affects on the strength and fracture behaviour of the composites. The strength of the two composites with thicker PyC layer (60 and 120 nm, respectively) are much higher that of the composite with thinner (20 nm) PyC layer and that without a PyC layer.
3. No significant changes of the strength of the composite occurred via the heat treatment temperature up to 1973 K, beyond which the strength decreased with increasing the heat treatment temperature, which was attributed to a recrystallization-induced deteriorate of the CVI-matrix as well as the degradation of the Tyranno-SA fibers during the heat treatment.

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