THE ROLE OF A POLYMER-DERIVED MATRIX ON THE TENSILE PERFORMANCE OF SIC/SIC COMPOSITE

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ABSTRACT

In order to get an important basis for the process design of the polymer impregnation and pyrolysis method to manufacture SiC/SiC composite, the role of a matrix made by polymer pyrolysis on the tensile strength of a composite was investigated. As basic process factors for polymer-derived matrix production, the number of matrix densification processing, filler addition rate, and preceramic polymer used were focused on. Evaluations were carried out by using unidirectional mini-composites through tensile test, push-out test, and the statistical evaluation for fracture mirror. As the results, it was found that filler distribution, polymer-derived microstructure and matrix density influenced in-situ fiber strength, effective fiber ratio and both of them respectively. The increase of the in-situ fiber strength was mainly attributed to the density and uniformity of matrix, and the effective fiber ratio could be improved by decreasing interfacial shear strength. By controlling them appropriately, a composite of high tensile strength could be obtained.

1. INTRODUCTION

Continuous SiC fiber reinforced SiC matrix (SiC/SiC) composite is one of a representative CMC and has been a promissing candidate for heat-resistant structural material for use in future transportation system and advanced energy system [1].

Similarly to FRP, many mechanical characteristics of CMC are governed by the performance of reinforcing fiber [2]. There would be two main factors of fiber performance which directly determine composite strength; i.e. the stress at which a fiber broke in fracture process ‘in-situ strength’ and the ratio of mechanically contributory fiber ‘effective fiber ratio’ [3]. The properties of fiber in composite are based on that of original fiber and are known to decline due to heat and handling in manufacture [4]. These factors should be significantly dependent on the fracture process of composite which is comprised of the debonding and sliding at fiber/matrix interface and consequential crack deflection and bridging [5]. These fracture mechanisms are determined by the conditions of interface and matrix.

Polymer impregnation and pyrolysis (PIP) method is very useful technique in making a CMC component of various sizes and shapes at relatively low cost. There have been many R & D on the air frame and engine components by using PIP [6,7]. Polymer-derived matrix by PIP can potentially be controlled by changing the raw materials and the process conditions at wide range.

The objective of this work is to get a useful guideline for designing PIP process by clarifying the role of a polymer-derived matrix on the tensile strength of a composite. The unidirectional mini-composite samples for which the number of matrix densification processing, filler addition rate, and preceramic polymer used were systematically changed were prepared and evaluated by tensile test, push-out test, and the statistical evaluation for fracture mirror. By correlating the matrix features with in-situ fiber strength, effective fiber ratio and interfacial shear strength, preferable process conditions to increase composite’s strength were examined.

2. EXPERIMENTS

As the samples, unidirectional mini-composites which were composed of a fiber bundle with interface layer and matrix were prepared in various conditions of the number of the matrix densification processing, filler addition rate and preceramic polymer. As the raw materials, Tyranno-ZMI® SiC fiber bundle (11 μm, 800 fil./yarn, Ube Industries LTD., Japan) for the reinforcement, allylhydridepolycarbosilane (AHPCS, Starfire Systems Inc., USA) and polycarbosilane (PCS, Nippon Carbon Co., Ltd., Japan) for the precursor polymer, and ultra-fine grade of β-random™ SiC particle of 270 nm diameter (Ibiden Co., Ltd., Japan) for the filler were used. The interface layers of inner 1000 nm thickness carbon and outer 100 nm thickness SiC were formed by CVI technique for all preforms. In the PIP process, the filler particle was added to the polymers only at the first processing. The samples for the number of matrix densification processing and preceramic polymer were prepared at the filler addition rate of 30 wt.%. PIP processing was carried out totally eight times to densify the matrices, because it was confirmed that the density of a composite was almost saturated after 8 times of PIP processing in the previous work [8]. Consequently, stick composite samples of more than 150 mm length with a diameter of around 1mm were obtained.

For the samples, tensile test, push-out test and fracture mirror measurement were performed. The tensile test was conducted for more than 5 specimens for each fabrication condition in 90 mm of gage length at 0.5 mm/min of displacement rate. The push-out test was conducted using a Berkovich-shape indenter with flat bottom at the loading rate of 20 mN/s. The disc specimens of around 200 μm thickness with both sides polished were prepared for the test. At least 20 effective data points were obtained for each condition. The interfacial shear strength, τ, was calculated from a load at which a flat area appeared in a load-displacement curve being divided by the debonding-related interface area. It corresponds to the fiber/matrix interface debonding strength.

After the tensile test, fracture mirror evaluation for the fibers at the fracture surface was performed by using SEM. Here the mirror radii of more than fifty fibers were measured for each condition. Then Weibull moduli, m, and in-situ fiber strengths, σ_c, were calculated by following the procedure presented by W. A. Curtin [5,9]. Since it is difficult to define the cross section and accordingly fiber volume fraction of the mini-composites by an excess deposition of a polymer-pyrolyzed product, the strengths of the composites were compared in maximum load, ϕ_{theory}, which can be theoretically estimated by using m and σ_c with the following equation.

$$\phi_{theory} = \sigma_c \left(\frac{2}{m+2} \right)^{1/(m+1)} \frac{m+1}{m+2} \times A_{all,f} \qquad (1)$$

where $A_{all,f}$ means the cross section of all fibers embedded in the composites. ϕ_{theory} corresponds to maximum load of a composite in case that all fibers have the strength of σ_c effectively in the statistic distribution which can be representatively expressed by m. This can be compared with the maximum load obtained in the tensile test, $\phi_{experiment}$, as the following equation.

$$\rho = \frac{\phi_{experiment}}{\phi_{theory}} \times 100 \quad (\%) \qquad (2)$$

There could be observed many fibers that have smooth fracture surfaces, not showing a fracture mirror. It can be considered that those fibers were broken at very low stress level by something irregular incidence [3]. The in-situ fiber strength was estimated from only the fibers in which fracture mirror morphology was seen. Therefore ρ

corresponds to the ratio of fibers that really exhibit the in-situ strength in the '*m*' distribution and formed a stress-related fracture mirror. The ρ is expressed as 'effective fiber ratio' in this paper.

3. RSULTS AND DISCUSSIONS

As a big influence on the density of a composite, the effect of the number of matrix densification processing is described below.

For comparison of strength, the maximum tensile loads of the composites after respective time of densification processing are shown in Figure 1. The sample of n=0 was only a fiber bundle with CVI-coating layer. The maximum load could be largely improved after the first matrix forming processing. It also increased as the matrix was densified by subsequent processing up to 8 times. Being densified highly with the matrix, the fiber bundle could be improved almost twice. Relatively large scattering of the load shown for the composites of n=1 might be attributed to unreliable matrix formation in this stage of densification.

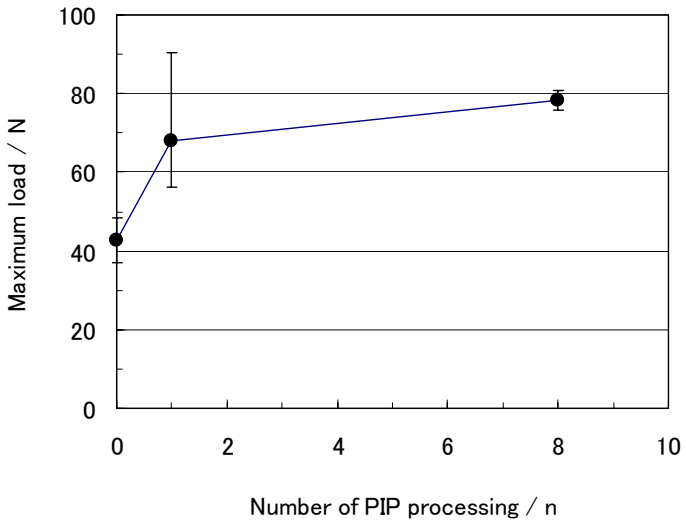

Figure 1: Maximum loads of the composites of various numbers of the densification processing.

Figure 2 exhibits the distribution of fiber breakage location in the gage area. In the samples of n=0, each fiber was mechanically highly independent, so that the fibers could be broken randomly at those weakest points of the entire gauge areas. On the other hand, fiber breakage was limited in some ten millimeters in the samples of n=1 and further within a millimeter for n=8 samples. This result preliminary suggests that as a matrix surrounding fibers be densified, the fibers became mechanically more fixed and accordingly the breaking at each weakest point was suppressed so that the fiber breakages were limited around the final crack area, resulting in the increase of the maximum load. An importance of matrix densification from the aspect of strength was confirmed.

The in-situ fiber strengths and effective fiber ratios of the composites are exhibited in Figure 3. Compared with those of the fibrous preforms at n=0, in-situ strengths of the samples which were put to the matrix forming processing once increased by 30 %. Noticeable improvement of the strength was not shown by densifying a matrix further. For both the samples at n=1 and n=8, similar in-situ strength of about 2 GPa was obtained. Thus in-situ fiber strength in a composite could be significantly increased by only the first rough matrix forming.

As for the effective fiber ratio, it was found that around a half of the fibers acted as mechanically effective reinforcement. The ratio continuously increased by totally about 20 % due to the densification processing eight times. For this parameter, subsequent densification processing after the first matrix forming was useful for improving composite strength.
Overall, the in-situ fiber strength significantly increased at the first matrix forming processing, remaining constant in the subsequent processing stage, whereas the effective fiber ratio continuously increased in both the first processing and the subsequent processing. These two influences directly reflected to the composite strengthening by matrix densification, as shown in Figure 1.

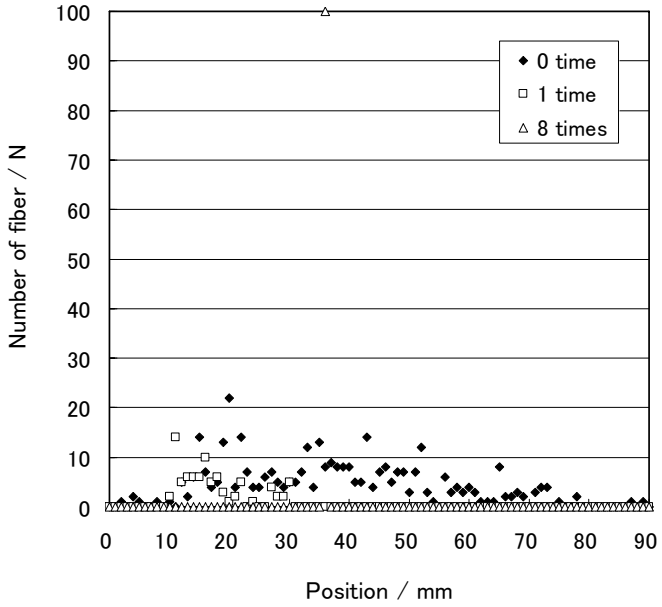

Figure 2: Distributions of fiber breakage location in the gauge area of the samples after various numbers of the densification processing.

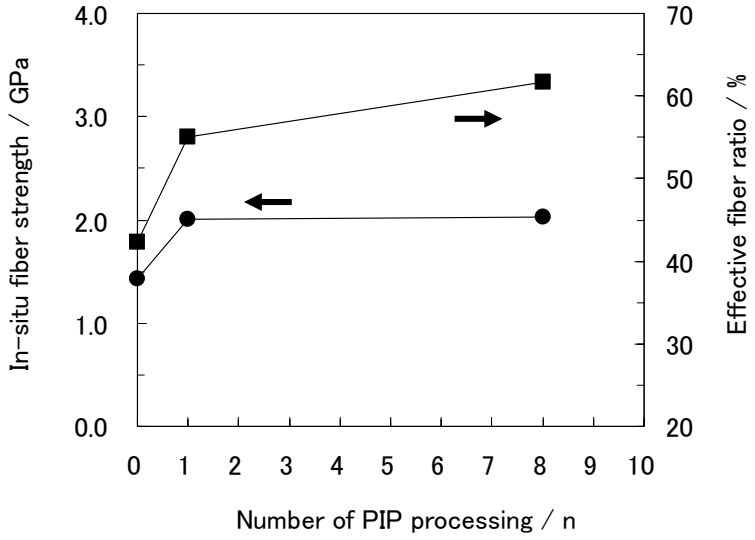

Figure 3: In-situ fiber strengths and effective fiber ratios of the samples after various numbers of the densification processing.

The evaluation of tensile strength in conjunction with fracture mirror measurement was carried out likewise for the effects of filler addition rate and preceramic polymer. These parameters change the filler distribution density together with matrix density and a polymer-pyrolyzed microstructure respectively. There, push-out test was also performed to evaluate the interfacial shear strength.
Through the systematic evaluation for these three process parameters, it was found that filler distribution, polymer-derived microstructure and matrix density influenced in-situ fiber strength, effective fiber ratio and both of them respectively. By correlating the parameters with matrix characteristics, it was revealed that in-situ fiber strength could be increased by improving the density and uniformity of matrix, and the effective fiber ratio could be improved by decreasing interfacial shear strength.

4. CONCLUSIONS

In order to get an important basis for designing PIP process, systematic investigation for the role of a polymer-derived matrix on the tensile strength of a composite was performed. The followings were clarified.

1. Tensile strength of a PIP-composite was determined by in-situ fiber strength and an effective fiber ratio.
2. In-situ fiber strength was dependent on the density and uniformity of matrix, whereas effective fiber strength was governed by interfacial shear strength.
3. By controlling them appropriately, high strength composite could be obtained.

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