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Homogeneity and flexural properties of SiC/SiC composites prepared by CVI method

Hiroshi Araki [a,*], Tetsuji Noda [a], Wen Yang [b], Akira Kohyama [b]

[a] *National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[b] *Institute of Advanced Energy, Kyoto University, CREST, Gokasho, Uji, Kyoto 611-0011, Japan*

Abstract

Several SiC/SiC composites reinforced with either Nicalon-CG or Hi-Nicalon fibers were fabricated by chemical vapor infiltration (CVI) process. Two kinds of reactant gases, methyltrichlorosilane (MTS) and ethyltrichlorosilane (ETS), were used as the source gases for SiC matrix. The space homogeneities of the composites were investigated with statistic density measurements and microstructure examinations. The flexural properties were studied using three-point bending tests. About 35 bending tests were conducted for each composite and the effects of the space homogeneity were studied using the Weibull distribution analysis. High-density composite with the highest individual bending specimen density of 2.85 Mg/m^3 was obtained. Hi-Nicalon/SiC composite prepared with MTS showed a Weibull modulus of 7.43 with average fracture strength of 665 MPa. Similar situation was observed for the Hi-Nicalon/SiC composite prepared with ETS. The Nicalon-CG/SiC composite showed lower fracture strengths with much lower Weibull modulus of 2.08.

1. Introduction

Chemical vapor infiltration (CVI) has advantages in high purity, minimizing damage to fibers and making near-net shape products of composites and is therefore widely used for producing SiC/SiC composites [1,2]. Fabrication of high-density SiC/SiC composites with homogeneous matrix densification, which is very important for the evaluation of the performance of the materials, is one of the primary goals for current CVI process. Recent progress in researches on the CVI process with small size samples of disk shape with 40 mm∅ made it possible to produce dense and homogeneous SiC/SiC composites with much improved strength and toughness [3]. However, when the composite size is scaled up, the process conditions for the small sized one are not necessarily applied and it becomes difficult to get uniform matrix densification with high density.

* Corresponding author. Tel.: +81-298 59 2848; fax: +81-298 59 2801.
E-mail address: araki.hiroshi@nims.go.jp (H. Araki).

In the present paper, several SiC/SiC composites reinforced with either Nicalon-CG or Hi-Nicalon fibers were fabricated by the CVI process. The space homogeneities of the composites were investigated with statistic density measurements and microstructure examinations. The flexural properties were studied using three-point bending tests and the effects of the space homogeneity were studied using the Weibull distribution analysis.

2. Experimental

2D plain-woven Nicalon-CG and Hi-Nicalon SiC fiber cloths laminated with 7–14 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%. The general dimensions of the preforms were 120 mm∅ × 2–4 mm. The preforms were densified with SiC matrix using the thermal decompositions of methyltrichlorosilane (MTS) or ethyltrichlorosilane (ETS) having a purity higher than 99 vol.%. MTS/ETS were carried by hydrogen with a reduced pressure of 14.4 kPa in the CVI reactor. The CVI

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temperature was 1273 and 1323 K for ETS and MTS respectively, with the process time of 60–80 h.

Bending test specimens were cut parallel to one of the fiber bundle directions of the fabric cloth from the composites after the CVI process. Both surfaces of the specimens were polished to remove the surface chemical vapor deposition-SiC layer that was formed at the end of the CVI. The resulting specimen size were 25 mm in length, 4.0 mm in width and ~2.0 mm in thickness. The density of each specimen was measured from its weight and volume. About 35 bending tests (with a span of 16 mm) were conducted for each composite at room temperature with the load in the vertical direction to the laminates. The cross-head speed was adjusted to 0.0083 mm/s. The microstructure and fracture surfaces were examined with scanning electron microscope (SEM).

3. Results and discussion

3.1. Composites prepared with MTS

Two composites, Nicalon-CG/SiC and Hi-Nicalon/SiC, were fabricated with MTS at 1323 K and 14.4 kPa. The densification time was 80 and 60 h for the Nicalon/CG/SiC and Hi-Nicalon/SiC, respectively. Fig. 1 shows the SEM images of the appearances and microstructures of the surface and cross-section of the Nicalon-CG/SiC composite. The intrafiber bundle was quite well densified while relatively large interfiber bundle pores were occasionally found on the cross-section image. The densities and space distributions of the composite are shown in Fig. 2. Very high densities, 2.65–2.85 Mg/m^3, corresponding to a porosity of 12–5%, were achieved by this composite although no clear space dependence of the densities is shown in the figure. The density and space distributions of the Hi-Nicalon/SiC composite were also studied in a similar manner. The Hi-Nicalon/SiC composite yielded a slightly lower density of 2.38–2.72 Mg/m^3. The lower density was considered to be due mainly to the shorter CVI time, as mentioned before.

Fig. 3 shows typical stress–displacement curves of the bending tests for the two composites. The specimen from Hi-Nicalon/SiC composite yielded an ultimate strength as large as 815 MPa and showed a gradual decrease in stress after reaching the maximum. The stress did not become zero after the large deformation since the specimens were not torn off owing to the tolerance of fibers. On the other hand, apparent plasticity was not observed for the specimen from the Nicalon-CG/SiC composite and the ultimate strength was 493 MPa, in spite of its high density as shown in the figure. The SEM images of the fracture surfaces and fiber pullouts of the two specimens were shown in Fig. 4. Interfacial debonding and fiber pullouts are clearly evident on the fracture surface of the specimen from the Hi-Nicalon/SiC composite (Fig. 4(a) and (b)) while the fracture surface of the specimen from the Nicalon-CG/SiC composite was

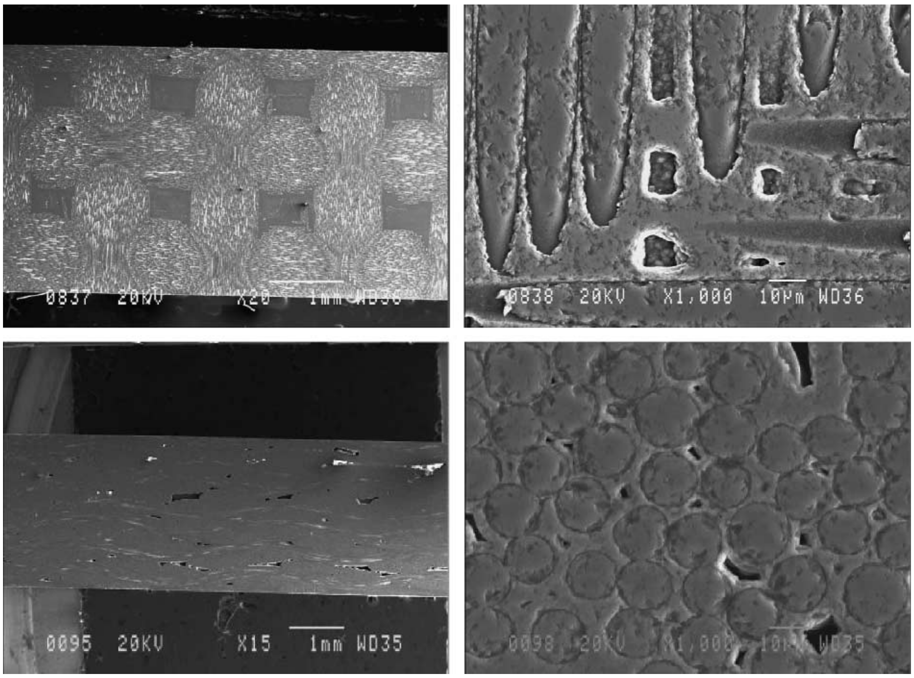

Fig. 1. Appearance of surface and cross-section of Nicalon-CG/SiC composite prepared with MTS.

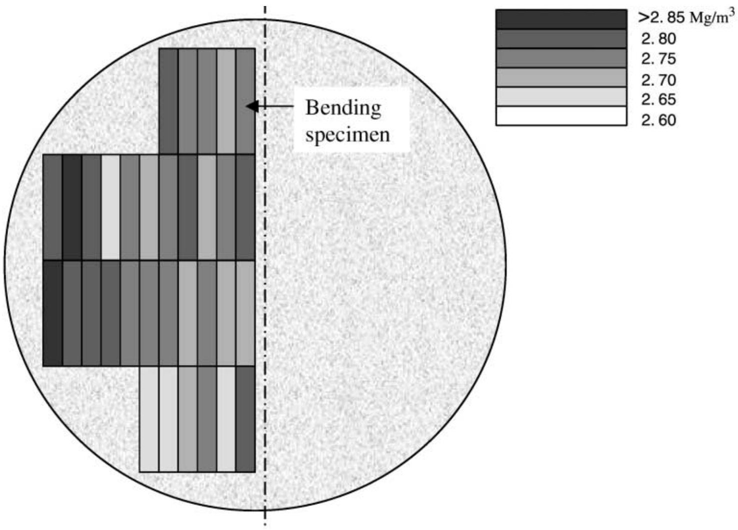

Fig. 2. Density map for the Nicalon-CG/SiC composite.

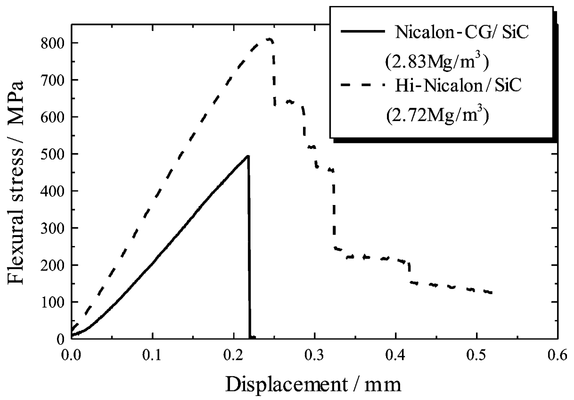

Fig. 3. Stress–displacement curves of the Nicalon-CG/SiC and Hi-Nicalon/SiC composites prepared with MTS.

relatively flat and pullout of fibers was hardly found (Fig. 4(c) and (d)). The Nicalon-CG fiber contains oxygen of 11.5 mass% with an amorphous structure, while the Hi-Nicalon fiber contains a much lower oxygen content of 0.5%, with a microcrystalline structure of around 5 nm of the grain size. Therefore, it is believed that some degradations of the Nicalon-CG fiber was occurred during the CVI densification process which continued for 80 h at 1323 K, owing to the deoxidation of the fiber [4] and crystal growth, etc. This is likely to be the main reason causing the almost brittle fracture behaviors of the Nialon-CG/SiC composite with low fracture strength.

Fig. 5 shows the relationship between fracture strength and density of the composites. The average strength of the Hi-Nicalon/SiC composite was $\sim$665 MPa, which is about two times higher than that of the Nicalon-CG/SiC composite. Fig. 5 shows that with increasing the density, the fracture strength increased with reduced scattering. The highest strength of the Hi-Nicalon/SiC composite (prepared with MTS) was obtained by the specimen with the highest density of 2.72 Mg/m^3.

The Weibull plots of fracture strengths of the two composites are shown in Fig. 6. The Weibull modulus was 7.43 for the Hi-Nicalon/SiC composite, versus a much smaller one of 2.08 for the Nicalon-CG/SiC composite. The main reason of the smaller Weibull modulus is due to the brittle fracture mode of the Nicalon-CG/SiC composite due to the degradation of the Nicalon-CG fiber. The degradation of the fiber will cause increased statistical strength distributions of the fiber itself and result in large scattering of the composite strengths. Furthermore, although the composite was highly densified with the matrix, there are still some inter/intrafiber bundle pores (Fig. 1, SEM images of cross-section and microstructure). Brittle fracture behavior results in increased sensitivity to the pores or possibly pre-existed matrix cracks or defects in the composite upon external loading. This might also be a reason for the small strength Weibull modulus of the composite.

3.2. Composite prepared with ETS

The relationship between fracture strength and density of the composite prepared with ETS is also plotted in Fig. 5. The composite was reinforced with 2D plain-woven Hi-Nicalon fiber, too. The CVI temperature, pressure, and time were 1273 K, 14.4 kPa, and 80 h. The density was in the range of 2.25–2.38 Mg/m^3. The ulti-

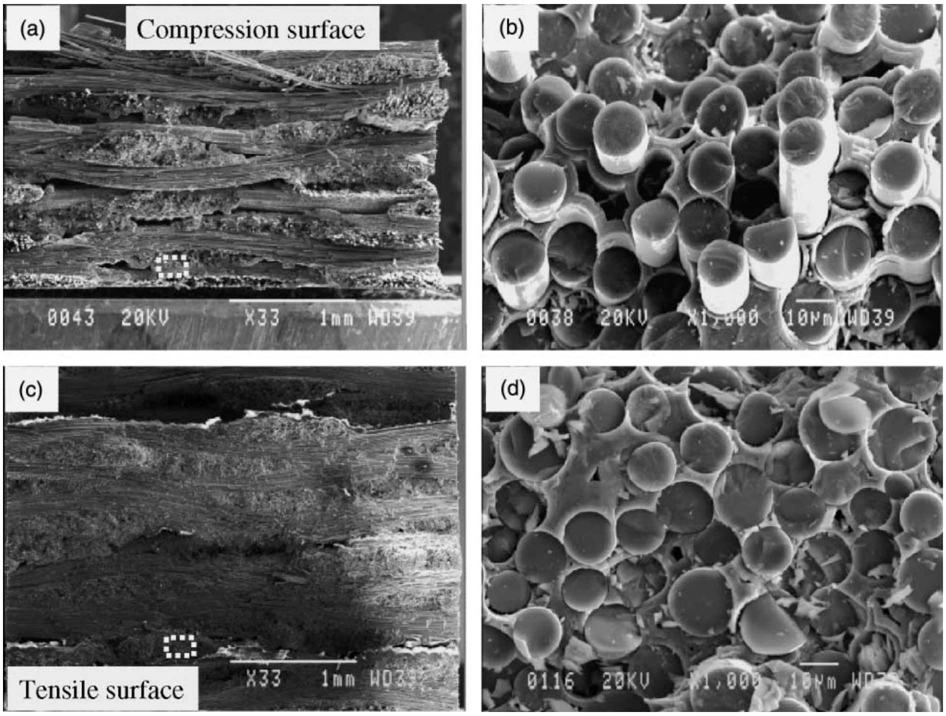

Fig. 4. SEM images of fracture surfaces and fiber pullouts of Hi-Nicalon/SiC (a,b) and Nicalon-CG/SiC (c,d) composites prepared with MTS.

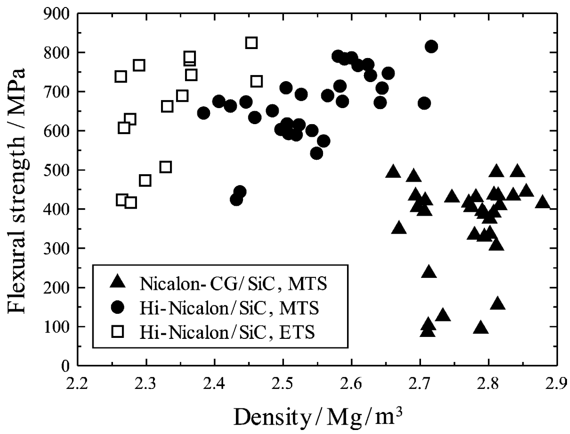

Fig. 5. Relation between fracture strengths and densities of the composites.

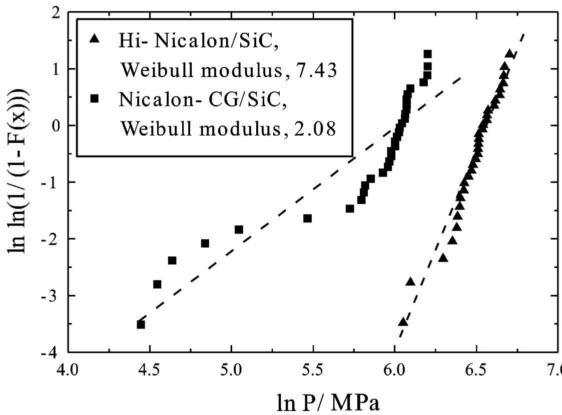

Fig. 6. Weibull plots of fracture strengths of the Nicalon-CG/SiC and Hi-Nicalon/SiC composites prepared with MTS.

mate flexural strength ranges from 400 to 850 MPa with a Weibull modulus of 7.24, which is almost same as that of the Hi-Nicalon/SiC composite prepared with MTS.

The SEM microstructure examination revealed carbon layer formations around the fibers in the composite with ETS, as evidenced in Fig. 7. Such carbon layers are considered to be formed from the excess carbon content in the ETS via the chemical reaction as

$$C_2H_5SiCl_3 = SiC + C + 3HCl + H_2 \quad (1)$$

A thin carbon interfacial layer was found to be able to yield the SiC/SiC composite with improved strength [3]. This might be the main reason for the Hi-Nicalon/SiC composite prepared with ETS to achieve a comparable strength to that of the one prepared with MTS, in spite of its lower density. However, as seen in Fig. 5, the scattering of the data is narrowed with increasing the

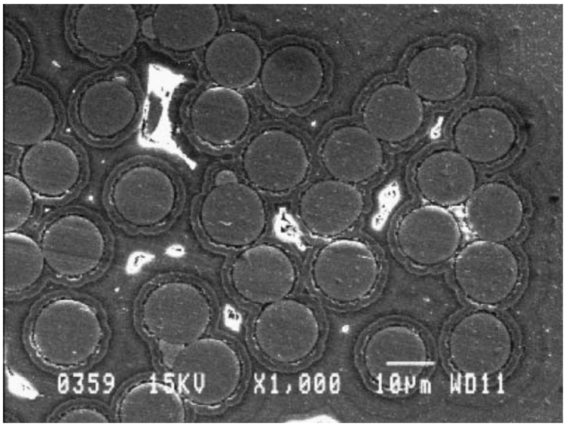

Fig. 7. SEM image of the microstructure of Hi-Nicalon/SiC composite prepared with ETS, showing the carbon layers around the fibers.

density. Therefore, even larger Weibull modulus is then expected if the composite with a higher density than 2.5 Mg/m^3 are constantly fabricated.

4. Summary

Several SiC/SiC composites reinforced with either 2D plain-woven Nicalon-CG or Hi-Nicalon fibers were fabricated by the CVI process. The space homogeneities of the composites were investigated with statistical density measurements and microstructure examinations. The flexural properties were studied using three-point bending tests. The effects of the space homogeneity were studied using the Weibull distribution analysis. The followings are summarized.

1. Quite high-density composite with the highest individual bending specimen density of 2.85 Mg/m^3 was fabricated with the MTS as source gas under appropriate CVI conditions.
2. The Hi-Nicalon/SiC composite fabricated with MTS and ETS showed flexural strength Weibull modulus of 7.43 and 7.24 respectively, with average value of 665 and 610 MPa.
3. The Nicalon-CG/SiC composite yielded much lower average flexural strength of 360 MPa with smaller Weibull modulus. This is attributed mainly to the brittle fracture behavior related with the degradation of Nicalon-CG fibers during the CVI process.
4. It is expected that for the Hi-Nicalon fiber reinforced composites, the flexural strength could be further improved with even larger Weibull modulus when the composite is uniformly densified with a density higher than 2.5 Mg/m^3 and an appropriate fiber/matrix interlayer is deposited.

References

[1] T. Noda, H. Araki, F. Abe, M. Okada, J. Nucl. Mater. 191–194 (1992) 539.
[2] R.H. Jones, L.L. Snead, A. Kohyama, P. Finici, Fus. Eng. Des. 41 (1998) 41.
[3] W. Yang, Development of CVI Process and Property Evaluation of CVI-SiC/SiC Composites, Doctoral thesis, Institute of Advanced Energy, Kyoto University, 2002.
[4] H. Araki, H. Suzuki, W. Yang, S. Sato, T. Noda, J. Nucl. Mater. 258–263 (1998) 1540.