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# Process, microstructure and flexural properties of reaction sintered Tyranno SA/SiC composites

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**Abstract**

The preparation routes of fiber preform for the fabrication of RS-SiC/SiC composites have been investigated, based on the mechanical property–microstructure correlations. Tyranno SA SiC fiber reinforced SiC composites have been fabricated by a reaction sintering process, which is associated with the consecutive slurry infiltration process of low pressure slurry impregnation with various filler particles and with the magnitudes of the cold pressures. The characterization of RS-Tyranno SA/SiC composites was evaluated by means of SEM, EDS and three point bending test. The consecutive slurry infiltration process of low impregnation pressure and cold pressure for the preparation of fiber preform provided the required density for RS-Tyranno SA/SiC composites (>2.9 mg/m$^3$), even if there was a large amount of Si rich SiC phases in the matrix of the intra-fiber bundle. The flexural properties of RS-Tyranno SA/SiC composites depended on the magnitudes of cold pressure used for the preparation of the fiber preform.


## 1. Introduction

SiC fiber reinforced SiC matrix composites (SiC/SiC) have been extensively studied as structural material for a new approach in fusion energy systems such as first wall or divertor coolant channels and advanced gas turbine engines [1–3]. For fusion applications of SiC/SiC composites, a high density, an appropriate thermal conductivity and a low induced radioactivity must be still secured through the process optimization. SiC/SiC composites have been fabricated by various manufacturing techniques including chemical vapor infiltration (CVI), polymer impregnation and pyrolysis (PIP), hot pressing (HP) and reaction sintering (RS) [4–14]. The RS process can be considered as a promising technique because it offers a high density, a high-purity SiC matrix and a good thermal conductivity. The characterization of RS-SiC/SiC composites is closely related with the preparation methods of the fiber preform. Several studies showed that RS-SiC/SiC composites, in which the fiber preform was prepared by the high slurry impregnation pressure, possessed a thermal conductivity higher than 50 W/m K and a density higher than 2.8 mg/m$^3$ [15,16]. The previous study also showed that the consecutive slurry infiltration process of low pressure impregnation and constant cold pressure was effective to make a sound fiber preform for high dense RS-SiC/SiC composites [17]. However, the magnitudes of cold pressure used for the consecutive slurry infiltration process will affect the property of RS-SiC/SiC composites significantly. The properties of fiber preform for the RS process will also depend on the size of the SiC particles and the composition ratio of SiC/C matrix slurry, since the high-purity SiC matrix is obtained from the

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homogeneous blending of starting SiC and C particles. Therefore, it is important to guarantee the required preparation condition of fiber preform for RS-SiC/SiC composites.

The purpose of the present study is to investigate the effect of the preparation route of the fiber preform associated with the magnitude of the cold pressure and the size of the SiC particle on the microstructure and the flexural properties of RS-Tyranno SA/SiC composites. The fracture mechanism of composites was also examined.

## 2. Experimental

### 2.1. Composite fabrication

The reinforcing material was a plain-woven Tyranno SA fiber without a fiber surface coating layer (Ube Co., Ltd.). The matrix slurry was a mixture of SiC particles, C particles and water with some dispersant. The composition of SiC and C particles in the matrix slurry was 10:5 weight ratio. The preparation parameters of the fiber preform were varied by the size of raw SiC particles and the magnitude of cold pressures. Three kinds of SiC particles, with an average size of 0.03, 0.3 and 1.0 μm were used. The average size of the C particles was 85 nm. The magnitudes of cold pressures were 3.5, 7.0 and 10.5 MPa, respectively. The fiber preform was prepared by compacting with different cold pressures, after injecting the matrix slurry into a fiber structure under a constant impregnation pressure of 0.9 MPa. RS-Tyranno SA/SiC composites were fabricated by infiltrating molten Si into the fiber preform under a vacuum atmosphere. The reaction sintering temperature and the holding time of all composites were 1450 °C and 2 h. The volume fraction of Tyranno SA fiber was about 10% in this composite system.

### 2.2. Characterization evaluation

The microstructure analysis of RS-Tyranno SA/SiC composites was carried out using scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS). Especially, the chemical composition of the SiC phases created by the reaction of molten Si and C particles was identified to examine the homogeneity of the matrix region. The composite density was also determined by the Archimedes method. In order to investigate flexural properties of RS-SiC/SiC composites, three point bending tests were performed at room temperature. Five pieces of samples were used in this test. The dimension of a test sample was $(2(T) \times 4(W) \times 25(L)$ $mm^3$. The span length and the crosshead speed were 18 mm and 0.5 mm/min, respectively.

## 3. Results and discussion

### 3.1. Density and microstructure of RS-Tyranno SA/SiC composites

Fig. 1 shows the effects of the magnitudes of cold pressure and the sizes of raw SiC particle on the density of RS-Tyranno SA/SiC composites. The application of cold pressure for the preparation of fiber preform was obviously effective to increase the density of the composites. The composite density had a similar level with the increase of cold pressure, even if it was affected by the size and the porosity distribution in the fiber preform before the infiltration of molten Si. However, the composite density had a slight variation with the size of the SiC filler particles. The RS-Tyranno SA/SiC composite exhibited a density higher than about 2.9 $mg/m^3$, when the fiber preform containing SiC particles of 0.3 μm was prepared by the consecutive slurry infiltration process of an impregnation pressure of 0.9 MPa and a cold pressure of 3.5 MPa.

Fig. 2 shows cross-sections of RS-Tyranno SA/SiC composites depending on different preparation routes of the fiber preform associated with an impregnation pressure of 0.9 MPa and various cold pressures. The size of raw SiC particles for the matrix slurry was 0.3 μm. The preparation route of the fiber preform by an impregnation pressure of 0.9 MPa obviously created large amounts of matrix crack and debondings. On the other hand, when the fiber preform was prepared by the consecutive slurry infiltration process, the composites exhibited a good morphology without matrix cracks or debondings. However, the application of excess cold pressures higher than 3.5 MPa produced some large pores at the intersections of woven fibers.

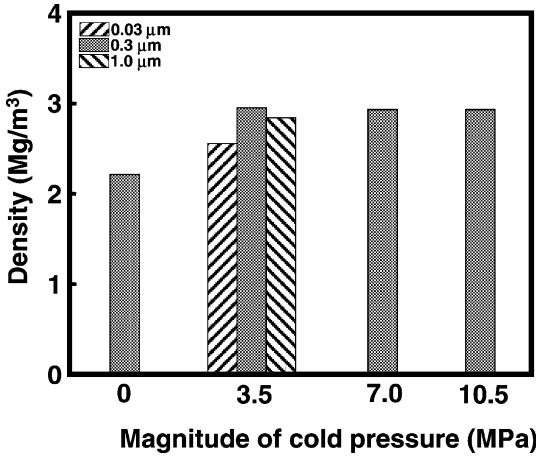


Fig. 1. Effects of the cold pressure and the sizes of raw SiC particles used for the preparation of fiber perform on the density of RS-Tyranno SA/SiC composites.

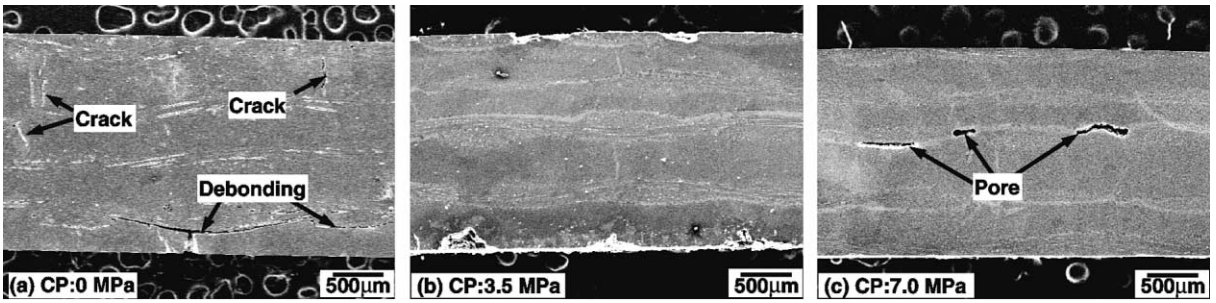


Fig. 2. Cross sections of RS-Tyranno SA/SiC composites depending on different preparation routes of the fiber preform associated with an impregnation pressure of 0.9 MPa and various cold pressures.

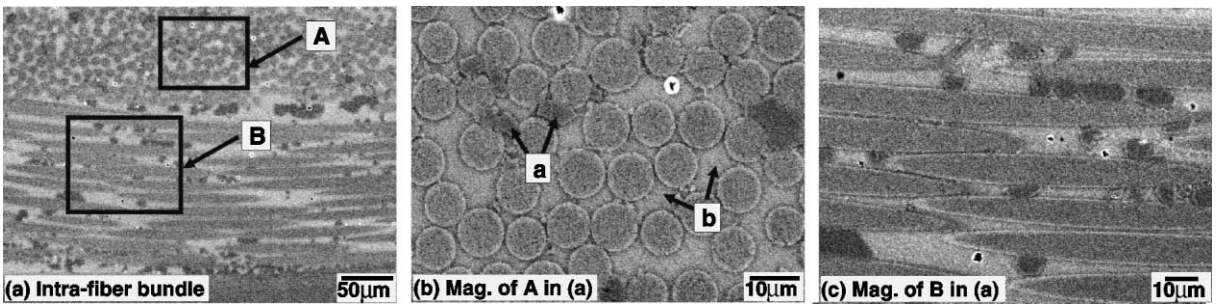


Fig. 3. Intra-fiber bundle microstructure of RS-Tyranno SA/SiC composites in which the fiber preform was prepared by the consecutive slurry infiltration process at an impregnation pressure of 0.9 MPa and a cold pressure of 3.5 MPa.

Fig. 3 shows the intra-fiber bundle microstructure of RS-Tyranno SA/SiC composites. In this case, the fiber preform was prepared by the consecutive slurry infiltration process of an impregnation pressure of 0.9 MPa and a cold pressure of 3.5 MPa. The size of the raw SiC particles for matrix slurry was 0.3 μm. The composition of each portion in this figure is shown in Table 1. The consecutive slurry infiltration process obviously provided a dense SiC matrix with some pores in the composite. The cold pressure of 3.5 MPa also has no effect on the damage of Tyranno SA fibers (Fig. 3(c)). However, as shown in Fig. 3(b), Si rich phases with a Si/C ratio of about 1.7, were greatly created in intra-fiber bundles of composites, even if there were near-stoichiometric SiC phases. This is maybe because the molten Si flows easily between Tyranno SA fibers during the RS process, and then fills large matrix pores and openings, accompanying the creation of crystallized SiC phases.

Table 1
Composition of each portion displayed in Fig. 3 and Fig. 4, as identified by EDS quantitative analysis (detector counts)

| Element | Concentration (at.%) | | | | |
|---|---|---|---|---|---|
| | a | b | c | d | e |
| Si | 47 | 63 | 46 | 48 | 67 |
| C | 53 | 37 | 54 | 52 | 33 |

Fig. 4 shows the inter-fiber bundle microstructure of RS-Tyranno SA/SiC composites fabricated by the matrix slurry containing raw SiC particles of 0.3 and 0.03 μm. The fiber preform was prepared by the consecutive infiltration process of an impregnation pressure of 0.9 MPa and a cold pressure of 3.5 MPa. The chemical composition at the positions c, d and e determined by EDS analysis is shown in Table 1. The composite mainly showed near-stoichiometric SiC phases in the matrix region of the inter-fiber bundles, when raw SiC particles of 0.3 μm were used for the preparation of the matrix slurry. However, the composite containing SiC particles of 0.03 μm exhibited the coexistence of near-stoichiometric SiC phases and Si rich SiC phases in the inter-fiber bundle matrix. Such a chemical inhomogeneity seems to be related with the non-uniformity of matrix slurry by the decrease of the SiC particle size, since the size was very small, which favored the formation of agglomerates.

### *3.2. Flexural properties of RS-Tyranno SA/SiC composites*

Fig. 5 shows the effect of the magnitudes of cold pressure on the flexural properties of RS-Tyranno SA/

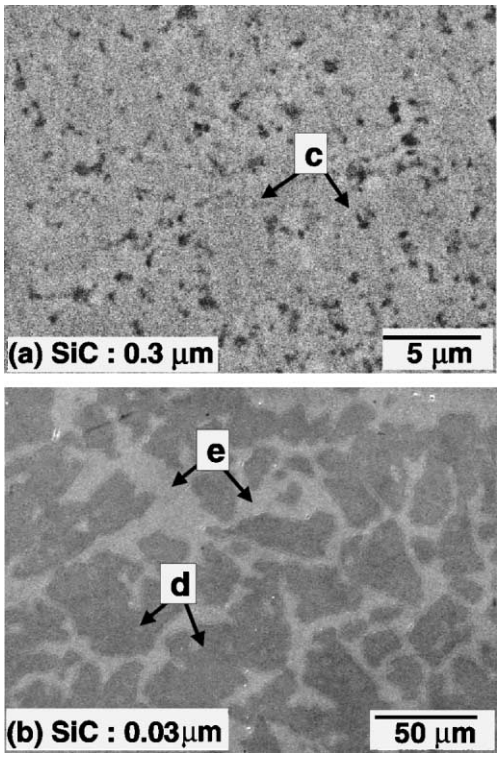


Fig. 4. Inter-fiber bundle microstructure of RS-Tyranno SA/SiC composites fabricated by the matrix slurry containing different sizes of raw SiC particles.

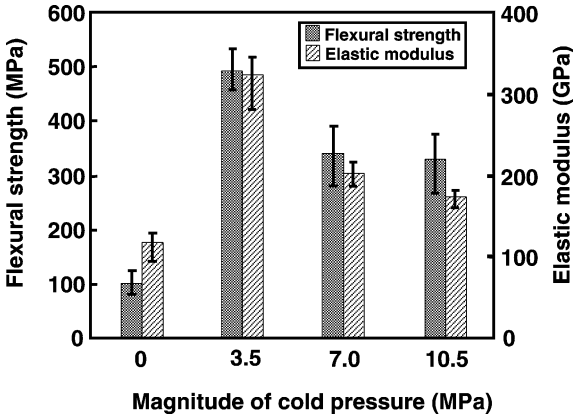


Fig. 5. Effects of the cold pressure used for the preparation of fiber preform on the flexural properties of RS-Tyranno SA/SiC composites.

SiC composites. The size of the raw SiC particles for the matrix slurry was 0.3 μm. All composites exhibited a catastrophic fracture behavior due to the absence of a fiber surface coating layer. The induction of cold press to the preparation of the fiber preform represented a significant increase in the flexural properties of composites. Especially, the average flexural strength and the average elastic modulus of composites showed about 500 MPa and about 320 GPa, respectively, when the fiber preform was prepared by the consecutive slurry infiltration process at an impregnation pressure of 0.9 MPa and a cold pressure of 3.5 MPa. However, the increase of cold pressure had a tendency to decrease flexural properties of the composites. This is may be because the increase of cold pressure resulted in large scale matrix pores at the intersection of woven fibers as shown in Fig. 2.

Fig. 6 shows the effect of the size of the SiC particles used for the preparation of matrix slurry on the flexural properties of RS-Tyranno SA/SiC composites. The impregnation pressure and the cold pressure for the preparation of the fiber preform were 0.9 and 3.5 MPa, respectively. The average flexural strength and the average elastic modulus of composites showed the maximum value at the addition of the SiC particles of 0.3 μm. In this limited study, the decrease of the SiC particle size for the preparation of matrix slurry seemed to improve the flexural properties of composites. The drastic property degradation of composites by the addition of SiC particles of 0.03 μm is caused by the formation of numerous matrix cracks or debondings and an inhomogeneous matrix, which is associated with the blending technique of the SiC/C matrix slurry.

Fig. 7 shows the representative fracture surface of RS-Tyranno SA/SiC composites in which the fiber preform was prepared by the consecutive infiltration process at an impregnation pressure of 0.9 MPa and a cold pressure of 3.5 MPa. The size of the raw SiC particles for the matrix slurry was 0.3 μm. The composite showed a brittle fracture surface without interfacial debonding

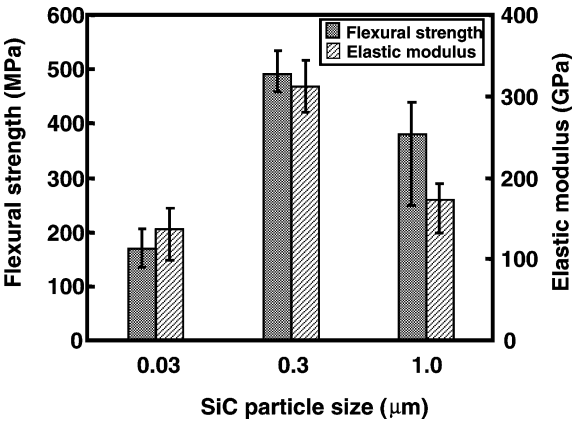


Fig. 6. Effect of the sizes of raw SiC particle used for the preparation of matrix slurry on the flexural properties of RS-Tyranno SA/SiC composites.

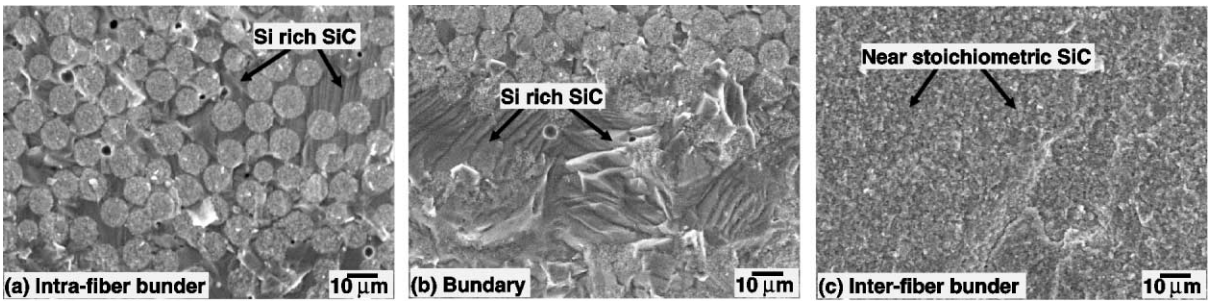


Fig. 7. Fracture surface of RS-Tyranno SA/SiC composites without fiber surface coating layer.

and fiber pullout. The composite also exhibited different fracture profiles according to the chemical composition of the SiC matrix. The inter-fiber bundle with a near-stoichiometric SiC matrix represented the granular fracture profile. On the contrary, the intra-fiber bundle and the boundary between inter-fiber bundle and intra-fiber bundle, in which the Si rich SiC matrix is mainly created, showed a cleavage fracture profile. In order to improve the characterization of RS-Tyranno SA/SiC composites, it will be necessary to create stoichiometric SiC phases in the matrix region and to apply a weak interphase capable of promoting a favorable fracture behavior.

## 4. Conclusions

1. The consecutive slurry infiltration process combined by low impregnation pressure and a cold pressure can be selected as another preparation route of fiber preform for the fabrication of high performance RS-Tyranno SA/SiC composites.
2. RS-Tyranno SA/SiC composites showed a density higher than about 2.9 mg/m$^3$ and an average flexural strength of about 500 MPa, when the fiber preform containing the SiC particle of 0.3 μm was made by the consecutive slurry infiltration process at an impregnation pressure of 0.9 MPa and a cold pressure of 3.5 MPa.
3. RS-Tyranno SA/SiC composites exhibited near-stoichiometric SiC phases in the inter-fiber bundle matrix, with the exception of the addition of raw SiC particles of 0.03 μm for the preparation of the matrix slurry. On the contrary, the intra-fiber bundle matrix of composites still showed significant compositional fluctuations.
4. RS-Tyranno SA/SiC composites showed a brittle fracture surface without interfacial debonding and fiber pullout, accompanied by different fracture profiles according to the chemical composition of the SiC matrix. In this composite system, an appropriate interphase is necessary to enhance the fracture toughness.

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## References

[1] L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, J. Nucl. Mater. 233–237 (1996) 26.
[2] P. Fenici, A.J. Frias Rebelo, R.H. Jones, A. Kohyama, L.L. Snead, J. Nucl. Mater. 258–263 (1998) 215.
[3] D. Brewer, Mater. Sci. Eng. A 261 (1999) 284.
[4] T. Noda, H. Araki, H. Suzuki, J. Nucl. Mater. 212–215 (1994) 823.
[5] T.M. Bresmann, J.C. McLaughlin, H.T. Lin, J. Nucl. Mater. 219 (1995) 31.
[6] K. Yoshida, M. Imai, T. Yano, J. Ceram. Soc. Jpn. 108 (2000) 224.
[7] T. Tanaka, N. Tamari, I. Kondo, M. Iwasa, Ceram. Inter. 24 (1998) 365.
[8] M. Kotani, A. Kohyama, K. Okamura, T. Inoue, Ceram. Eng. Sci. Proc. 20 (4) (1999) 309.
[9] M. Takeda, Y. Kagawa, S. Mitsuno, Y. Imai, H. Ichikawa, J. Am. Ceram. Soc. 82 (1999) 1579.
[10] K. Park, T. Vasilos, J. Mater. Sci. 32 (1997) 295.
[11] T. Yano, Y. Yoshida, T. Seki, Fus. Eng. Des. 41 (1998) 157.
[12] L. Hozer, J.R. Lee, Y.M. Chiang, Mater. Sci. Eng. A 195 (1995) 131.
[13] A. Sayano, S. Suyama, Y. Itoh, S. Nakagawa, J. Nucl. Mater. 271&272 (1999) 467.
[14] T. Kameda, S. Suyama, Y. Itoh, N. Nishida, J. Ceram. Soc. Jpn. 107 (1999) 622.
[15] T. Kameda, S. Suyama, Y. Itoh, Y. Goto, J. Ceram. Soc. Jpn. 107 (1999) 327.
[16] S.P. Lee, Y. Katoh, A. Kohyama, Scripta Mater. 44 (2001) 153.
[17] S.P. Lee, Y. Katoh, J.S. Park, S.M. Dong, A. Kohyama, S. Suyama, H.K. Yoon, J. Nucl. Mater. 289 (2001) 30.