Mechanical Properties and Microstructure of 3D 6-Directional Braided $\text{SiO}_{2\text{f}}/\text{SiO}_2$ Composites by Silicasol-Infiltration-Sintering Method

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Three dimensional (3D) 6-directional braided $\text{SiO}_{2\text{f}}/\text{SiO}_2$ were prepared by silicasol-infiltration-sintering method. The process parameters were optimized and the optimal parameters were as follows: the silicasol of 35 wt % of SiO_2 as slurry and sintering at 450 °C. The tensile and bending strength of the composite materials were investigated. The density and the flexural strength of the $\text{SiO}_{2\text{f}}/\text{SiO}_2$ composites were 1.72 g cm⁻³ and 94.8 MPa, respectively. The good strength was attributed to high strength structural of the 3D 6-directional braided perform which was higher than conventional 2D and 3D perform. The microstructures have been studied by SEM which revealed that the fracture mechanism of the composite was a mixture of ductile and brittle modes.

Key Words: 3D 6-Directional $\text{SiO}_{2\text{f}}/\text{SiO}_2$ composites, Silicasol-infiltration-sintering, Mechanical properties, Microstructure.

INTRODUCTION

Continuous fiber reinforced ceramic matrix composites (CFCCs), such as C/SiC, C/Si-C-N and SiC/SiC systems, have received considerable attention because of their higher performance at elevated temperature and higher fracture toughness compared with monolithic ceramics¹⁻³. For this reason, CFCCs are considered as the most potential to be used in advanced aero-engines, space and fusion power reactors.

Among various reinforcing fibers, silica fiber, which has properties of high melting point combined with high thermal shock resistance and excellent ablation resistance as well as low thermal conductivity, is promising and has been received considerable attraction, especially in the field of radom material^{4,5}. However, the mechanical properties of silica material in the monolithic form have restrained its further applications. Recently, attention has been focused on silica fiber-reinforced silica composites ($\text{SiO}_{2\text{f}}/\text{SiO}_2$). For the purpose of improving the mechanical properties, numerous studies have been conducted to reinforce silica matrix composites by adding silica shorter fiber, unidirectional silica fiber and conventional 3D braided structure. Xu *et al.*⁶ has studied the influences of the sintering temperature, atmosphere and pre-treatment on the properties of unidirectional silica fiber reinforced silica composite with pressureless sintering and hot pressing method. Chen *et al.*⁷ has manufactured Nextel 480 fiber preform reinforced SiO_2 matrix composites by APCVI. Chen *et al.*⁸

has investigated fused silica matrix composites reinforced with 3D braid *via* liquid phase infiltration deposition. It can be seen that the mechanical properties of silica matrix composites are closely related to the braided structure of reinforcement and the preparation method. Comparatively less reports in literature on the study of 3D 6-directional braided $\text{SiO}_{2\text{f}}/\text{SiO}_2$ composites, which have a new high-performance over the conventional 3D composites, including better out-of-plane stiffness, strength and high damage tolerance^{9,10}. It is necessary to conduct study on their microstructure and mechanical performances before they can be certified for use, especially in the fields of astronauts and aeronautics¹¹.

In this paper, 3D 6-directional braided $\text{SiO}_{2\text{f}}/\text{SiO}_2$ composites have been prepared *via* silicasol-infiltration-sintering method, which combined with infiltration, drying and sintering. Sol-gel infiltration processing is an easy and flexible process to achieve uniform distribution of materials, which can be applied to perform of complex and different shapes. The mechanical properties including tensile properties and flexural properties have been investigated and the microstructures of the composites were investigated by scanning electron microscopy (SEM).

EXPERIMENTAL

Processing of the samples: The 3D 6-directional braided silica reinforcements were provided by Sinoma Science & Technology Co. Ltd. The yarns specification is B type silica

fiber (190Tex) and the fiber volume fraction is *ca.* 47 %. A single unit of 3D 6-directional braided structure is illustrated in Fig. 1. 3D 6-Directional braided composites have been developed by adding the biaxial reinforced yarns along and cross braiding direction based on the 3D 4-directional braiding process.

Fig. 1. Single unit of 3D 6-directional braided structure

The composites were prepared by silicasol-infiltration-sintering, as shown in Fig. 2. Firstly, the braided silica reinforcement was put into a sealed container and the container was vacuumed to 0.1 Pa. Then, the pure silica sol (35 wt %, average particle size 10 nm, pH 9, Yuda Chemical Company, China) was sucked into the container meanwhile the pressure was maintained at 0.1 Pa. After 0.5 h, the pressure was increased to 10 atm and kept for 1 h. After that the composites were dried at 80 °C for 1 h and 110 °C for 1h, respectively. During this drying process, water content of the matrix gel solution is gradually descended. Then dried preforms were heated in an oven at 450 °C for 2 h as to remove the coupling agent and bound water. The process was repeated 10 cycles to enhance the properties of the 3D 6-directional SiO_{2f}/SiO₂ composites. Photographs of the 3D 6-directional braided preform before infiltration (a) and after sintering (b) are showed in Fig. 3.

Fig. 2. Schematic diagram of sol-gel method

(a)

(b)

Fig. 3. Photograph of the 3D 6-directional braided preform before infiltration (a) and after sintering (b)

Measurements: The as-processed samples were cut parallel to the direction of fiber and then ground into bars of 94 mm in length, 23 mm in width and 3.5 mm in thickness for tensile test. The samples used for bending test were rectangular bars of 5 mm width, 3.5 mm thickness and 40 mm length. The tensile test and bending tests were measured at SANS CMT5105 electronic universal testing machine with a constant loading rate of 0.3 mm/min. The specimens of tensile testing were reinforced by aluminum strengthening plates. There was a preload about 5N before the test. The load-displacement curve for the composites was recorded to fracture. Density and porosity measurements were performed based on the Archimedes principle. Microstructure and failure mechanism was examined by scanning electron microscopy (Jeol JSM-6360). The specimen was coated with thin gold to prevent charging effect.

RESULTS AND DISCUSSION

As shown in Fig. 4, after 10 cycles, the weight of the reinforcement increased from 190-415 g, but almost stopped increasing after 8 cycles. The reason is that, as cycle times increase, infiltration paths of the slurry has being jammed which will lead to the size of the silica sol particle gets too big to infiltrate into the composites fully, so the infiltration efficiency is debased. The porosity and density were 0.228 and 1.72 g cm^{-3} , respectively for the as-processed composites.

Fig. 4. Weight-cycle curves of 3D 6-directional $\text{SiO}_2/\text{SiO}_2$ composites

Fig. 5 shows a typical load-displacement curve for silica composites. The values for mean strength and Young's modulus were 33.7 MPa and 31.5 GPa, respectively. The curves could be generally divided into three regions: a very small initial linear region followed by a low gradient region and finally a steep stress drop region. It was observed that the specimen did not fall apart after the load was removed. It should be pointed out that the steep drop-step which also could be found in Fig. 6 means that there are some brittle failures in the specimen¹². As the 3D 6-directional braided composites which is similar to 3D 5-directional braided composites to a great extent can be considered as transversely isotropic materials in a macro-scale. The tensile failure behaviour of the composites, which haven't suggested the delamination of the composite, is a little different from conventional 2D reinforced composites¹¹.

Fig. 5. Tensile load-displacement curve of 3D 6-directional $\text{SiO}_2/\text{SiO}_2$ composite

Fig. 6. Flexural stress-deflection curve of 3D 6-directional $\text{SiO}_2/\text{SiO}_2$ composites

During the three-point bending test (Fig. 6), the composite initially showed an elastic response with deflection increasing linearly with increase in load, followed by an extended unelastic regime. A stress-drop point was observed which is responsible for stress unloading resulting from the matrix crack and interface debonding within the specimen. It can be seen that the failure was not catastrophic. The composites exhibit good strength and typical composites behaviour, *i.e.*, failed gradually with fiber pull-out. The flexural strength of the specimen was about 94.8 MPa, which is quite high, relative to this low sintering temperature. As known, the fused-silica fiber tends to get damaged after high temperature treatment. Jia *et al.*¹³ has founded that the silica fiber is impaired during the process by high temperature.

The nature of the fiber/matrix interface can be seen by examining the fracture surface of the composite specimens after the three point test. Fig. 7 shows the SEM micrographs of the composites. From Fig. 7(a) it is seen that there were some fiber bundles had been pulled out from the matrix. Also, in Fig. 7(b) extensive fiber pull-out was observed in the fracture surface. But there were also some flat fracture surfaces of the fiber bundles which mean that in some part fibers are bonded well to the matrix. Because of the fact that the porous matrix between the fibers disintegrated into smaller pieces during the fracture process, as shown in Fig. 7(c), there were a noticeable amount of matrix debris attached to the fibers. Also we can see that the length of pull-out fiber was more than $15 \mu\text{m}$. The micrograph also shows that not all fibers were bonded well to the matrix and therefore not all the fibers participated in strengthening the composite. The poor bonding is due to incomplete sintering. If the silica matrix was bound too tightly with the silica fiber system, that will cause fiber damage. Also, as the matrix disintegrates during fiber pull-out and the fiber pulls from the matrix will absorb energy of stress concentrations, thus increasing the fracture energy¹⁴. The SEM fractography in Fig. 7(d) shows that the matrix was separated layer by layer which illustrate that silica matrix was deposited for many cycles. Although the sintering temperature was 450°C , the silica matrix presented large particles and good crystallization. This mechanism will disintegrate additional stress because the matrix microcracks can be better off deflected.

Fig. 7. SEM micrographs of the fracture surfaces of the 3D 6-directional $\text{SiO}_2/\text{SiO}_2$ composites

Conclusion

3D 6-Directional braided $\text{SiO}_2/\text{SiO}_2$ were prepared via silicasol-infiltration-sintering method employing 3D 6-directional braided silica fiber fabrics as reinforcements and high pure silica sol as slurry. Mechanical properties of the composite materials were investigated under flexural and tensile loading. The density of the composites was 1.72 g cm^{-3} after the preform was infiltrated and sintered.

The composites exhibited excellent mechanical properties at room temperatures. The tensile strength was 33.7 MPa and the values of flexural strength were 94.8 MPa. This good strength was attributed to high strength structural of the 3D 6-directional braided perform and relatively low sintering temperature. SEM examinations revealed fracture process of the specimen encompasses both brittle and ductile ruptures. The toughening mechanisms of the composites were micro-debonding at the fiber/ matrix interface and fiber pulled out.

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REFERENCES

1. Y.D. Xu, L.F. Cheng, L.T. Zhang, H.F. Yin and X.W. Yin, *Mater. Sci. Eng. A*, **318**, 183 (2001).
2. S. Jacques, A. Guette, F. Langlais, R. Naslain and S. Goujard, *J. Eur. Ceramic Soc.*, **17**, 1083 (1997).
3. G.-J. Qi, C.-R. Zhang and H.-F. Hu, *Trans. Nonferrous Met. Soc. China*, **16**, 824 (2006).
4. N.E. Prasad, S. Kumari, S.V. Kamat, M. Vijayakumar and G. Malakondaiah, *Eng. Fracture Mechanics*, **71**, 2589 (2004).
5. T. Vasilos, T. Erurk and R. Ambatim, *Ceramic Eng. Sci. Proceed.*, **14**, 955 (1993).
6. C.-M. Xu, S.W. Wang, X.X. Huang and J.K. Guo, *Ceramics Int.*, **33**, 669 (2007).
7. Z. Chen, L. Zhang, L. Cheng, Y. Xu and R. Gao, Nextel 480/Silica Composites by Atmosphere Pressure Chemical Vapor Infiltration, Wiley-VCH Verlag GmbH & Co. KGaA (2006).
8. H. Chen, L.M. Zhang, G.Y. Jia, W.H. Luo and S. Yu, *Key Eng. Mater.*, **249**, 159 (2003).
9. K. Xu and X. Xu, *Mater. Sci. Eng. A*, **487**, 499 (2008).
10. F. Zhang, Z.G. Liu, Z. Wu and G.Q. Tao, *Chin. J. Aeronautics*, **23**, 61 (2010).
11. D.-S. Li, Z.-X. Lu, C. Li and J.-L. Li, *Int. J. Solids Struct.*, **46**, 3422 (2009).
12. Y.D. Xu, L.T. Zhang, L.F. Cheng and D.T. Yan, *Carbon*, **36**, 1051 (1998).
13. D.C. Jia, Y. Zhou and T.Q. Lei, *Aerospace Mater. Technol.*, **31**, 29 (2001).
14. H. Chen, L.M. Zhang, L.M. Hu, G.Y. Jia, W.H. Luo, S. Yu and Z.Q. Cheng, *Key Eng. Mater.*, **249**, 163 (2003).