A COST-EFFECTIVE FABRICATION METHOD FOR CONTINUOUS FIBER CMCS WITH EXCELLENT FRACTURE TOUGHNESS

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Abstract
Si-Zr-C-O long fiber /Al₂O₃ laminated composites have been successfully developed using pre-impregnated (prepreg) sheets. The monolayer prepreg sheets were prepared via infiltration of alumina/glass aqueous slurry into aligned long fibers, then laminated and finally pressureless-sintered in the furnace (in air).

The key of this process is to add the SiO₂-B₂O₃-based glass powder into alumina slurry in order to avoid the degradation of fibers during sintering of the fiber contained green body.

The purpose of this work is to investigate the influence of alumina/glass weight ratio, sintering temperature and sintered density affecting the mechanical properties such as bending strength and fracture toughness. The Si-Zr-C-O long fiber /Al₂O₃ composite sintered at 900 ºC in alumina/glass weight ratio 6/4 showed the maximum bending strength of 405 MPa and fracture toughness of 20 MPa·m¹/², which suggests prospective applications to various structures (aerospace, automotive and others) under high temperature environment.

1 Introduction
Ceramic matrix composites (CMCs) have been developed to overcome the inherent low fracture toughness of ceramic materials. It is well-known that long fiber reinforced ceramics is most effective method to fulfill high toughness of ceramics. Much of the past effort has been concentrated on understanding toughening, the role of interfacial adhesion, and the development of novel fabrication techniques [2]. However, the techniques developed so far often produce matrix poor regions, or possess a problem in fiber/matrix interfacial characteristics due to degradation of fibers during processing and thus these materials do not meet the needs of demanding applications in terms of the material uniformity, reproducibility, superiority to monolithic ceramics and cost effectiveness.

The author developed a low-cost production route to CMC [3]. The fabrication process does not require any expensive fabrication facilities and is concluded to be cost-effective and have a good potential for significantly increasing mechanical properties such as static strength, fracture toughness, and fatigue resistance. The key of this process is to add the SiO₂-B₂O₃-based glass powder into alumina slurry in order to avoid the degradation of fibers during sintering of the fiber contained green body.

2 Fabrication Method and Experimental Procedures
The fabrication process is shown in Fig.1. The aqueous homogeneous slurry was prepared by ball milling the mixture of Al₂O₃ powder (α-alumina AL45-1, Showa Denko Co. Ltd, Japan) and SiO₂-B₂O₃ based glass powder (SNK-01, Senyo Glass Co. Ltd, Japan) and additives (binder, plasticizer, dispersant, ethanol, distilled water, etc) in a polyethylene jar using yttria stabilized zirconia milling media. The average particle size of Al₂O₃ was 1.1μm and SiO₂-B₂O₃-based glass was 4.0μm. The copolymer of acrylic acid and acrylic acid ester (AQ-2559, Lion Corporation, Japan) was used as binder and dispersant agent. The reinforcing material chosen for this study was Si-Zr-C-O fibers (ZMI-S1E08PX, Ube Industries Ltd, Japan). In this work, the simplified casting method based on a tape casting technique was utilized to prepare pre-impregnated (prepreg) sheets. The aqueous slurry was vacuum defoamed then cast uniformly on uniaxial aligned fibers setting on a coater. Then the cast fibers were vacuum-assisted to infiltrate the
slurry into the multifilament Si-Zr-C-O fibers. The thickness of prepreg sheet was determined by adjusting the clearance between coater and roller. The prepregs were then cut into specimen geometry, and laminated together to prepare the unidirectional multilayer-preforms.

The multilayer-preforms of fiber-containing prepreg sheet were pressureless-sintered at each temperature for 1h in the furnace (in air). For the purpose of lowering sintering temperature to avoid the degradation of fibers contained green body during sintering, the SiO2-B2O3-based glass powder was added to alumina powder. The weight ratio of added glass powder to alumina powder which is called alumina/glass weight ratio was varied for the optimum sintering temperature. Three-point bending test on the smooth flat specimen and single edge cracked fracture toughness test were performed at constant cross-head speed of 0.5mm/min, in order to evaluate the strength properties and fracture toughness of Si-Zr-C-O/Al2O3 composites. The sintered density of the Si-Zr-C-O/Al2O3 composites was measured by the Archimedes method. The cross-section of Si-Zr-C-O/Al2O3 composites was observed by Digital Microscope (Keyence VHX, Japan) and SEM (Quanta200, FEI, USA) before and after bending test.

### 3 Experimental Results and Discussion

#### 3.1 Sintered Density

Table 1 shows the sintered density of Si-Zr-C-O/Al2O3 composites which were sintered at different temperature in each alumina/glass weight ratio. Significant density reductions were observed in the specimens sintered at 830, 850 °C in 5/5 and 920 °C in 6/4. The density reduction of 5/5 occurred at lower temperature than 6/4. The 7/3 formed dense matrices and then density reduction was not confirmed up to 1000 °C. Fig.2 shows the sectional micrograph of Si-Zr-C-O/Al2O3 specimen sintered at 920 °C in 6/4. The specimen included a large number of spherical pores in the matrix. This is due to the fact that bloating, characterized by spherical pores in micrograph, takes place at the specimens [4]. The specimens in which bloating occurred swelled significantly in the laminated direction. In contrast, the Si-Zr-C-O/Al2O3 specimen sintered at 900 °C in 7/3 achieved dense matrix as shown in Fig.3.

Table 1. Sintered density of Si-Zr-C-O/Al2O3 composites sintered at different temperature in each alumina/glass weight ratio.

<table>
<thead>
<tr>
<th>Alumina/glass weight ratio</th>
<th>Sintering temperature (°C)</th>
<th>Sintered density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/5</td>
<td>800 830 850</td>
<td>2.50 1.59 159</td>
</tr>
<tr>
<td>6/4</td>
<td>850 880 900 920</td>
<td>2.23 2.16 2.02 1.64</td>
</tr>
<tr>
<td>7/3</td>
<td>900 920 950 1000</td>
<td>2.63 2.63 2.71 2.62</td>
</tr>
</tbody>
</table>

Fig.1 Fabrication process of Si-Zr-C-O/Al2O3 composite.

Fig.2 Sectional micrograph of Si-Zr-C-O/Al2O3 specimens sintered at 920 °C in 6/4.
It has been reported that a balance in competitive kinetic process between the viscous flow and dissolution of alumina into glass is required to achieve a high densification in the alumina/glass system. It should be pointed out based upon the present investigation that glass softening point, glass composition, glass ratio and particle size play an important role to achieve densification of Si-Zr-C-O/Al$_2$O$_3$ composites.

### 3.2 Mechanical Properties

Fig. 4 shows the influence of sintering temperature and alumina/glass weight ratio on the bending strength. The highest bending strength was obtained in the specimen sintered at 900 °C in 6/4. It should be noted that the bending strength of 6/4 remarkably increased between 850 °C and 900 °C though the sintered density decreased. In addition, the bending strength of 7/3 drastically reduced from 920 °C to 950 °C despite of similar sintered densities. The above results indicate that the bending strength of Si-Zr-C-O/Al$_2$O$_3$ composites does not necessarily correspond to the sintered density and thus other parameters dominate the bending strength. 

Fig. 5 shows the influence of sintering temperature and alumina/glass weight ratio on the fracture toughness $K_{IC}$. The highest fracture toughness was obtained in the specimen sintered at 900 °C in 6/4. The specimens sintered between 880 °C and 920 °C in 6/4 only display the high fracture toughness above 10 MPa·m$^{1/2}$, while the specimens in 5/5 and 7/3 were low fracture toughness in comparison to 6/4. It is concluded that the high bending strength and fracture toughness of Si-Zr-C-O/Al$_2$O$_3$ composite has been brought about by an adequate fiber/matrix interface characteristic.

![Fig. 3 Sectional micrograph of Si-Zr-C-O/Al$_2$O$_3$ specimens sintered at 900 °C in 7/3.](image)

![Fig. 4 Comparison of the bending strength for Si-Zr-C-O/Al$_2$O$_3$ specimens sintered at different temperature in each alumina/glass weight ratio.](image)

![Fig. 5 Comparison of the fracture toughness for Si-Zr-C-O/Al$_2$O$_3$ specimens sintered at different temperature in each alumina/glass weight ratio.](image)

![Fig. 6 shows bending stress-deflection curves for the specimens sintered at 900 °C in 6/4 and 7/3. The 6/4 deflected twice as much as the 7/3 and showed higher ultimate stress than the 7/3. Furthermore nonlinear fracture behavior was obviously observed in 6/4.](image)
Fig. 6 Bending stress-deflection curves for Si-Zr-C-O/Al₂O₃ specimens sintered at 900 ºC in 6/4 and 7/3.

Fig. 7 and Fig. 8 indicates SEM micrographs of the bending fracture surface of Si-Zr-C-O/Al₂O₃ specimen sintered at 900 ºC in 6/4 and 7/3. The 6/4 exhibited extensive fiber pull-out during failure, which was approximately 0.5-1.0 mm. On the other hand, the pull-out length of 7/3 was short and the fibers were decoupled. It is considered that the addition of glass powder into Al₂O₃ matrix plays an extremely important role to create adequate fiber/matrix interfaces and thus Si-Zr-C-O/Al₂O₃ composite achieves the high strength and toughness.

**4 Conclusion**

The influence of alumina/glass weight ratio, sintering temperature and sintered density affecting bending strength and fracture toughness has been investigated in the present work. The Si-Zr-C-O long fiber /Al₂O₃ composite sintered at 900 ºC in alumina/glass weight ratio 6/4 showed maximum bending strength of 405 MPa and fracture toughness of 20 MPa·m¹/². It should be emphasized in conclusion that adding the glass powder to the alumina matrix play an important role not only to lower the sintering temperature, but also to provide an adequate fiber/matrix interfacial characteristic.

**REFERENCES**