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Reaction-bonded silicon carbide tube fabricated by continuous sintering of double-walled preform

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Abstract

A reaction-bonded silicon carbide radiant tube has been successfully fabricated by the continuous sintering of a double-walled preform which was composed of inner Si/C and outer SiC/C layers. Sequential centrifugal casting was employed to develop double-walled preform and process shrinkages were minimized by adjusting the particle packing characteristics with multimodal particle size distribution. Debinding behavior was optimized in a two-step process consisting of the capillary migration/surface evaporation of the thermoplastic resin and subsequent thermal pyrolysis of the thermosetting resin. Reactive infiltration of liquid silicon was carried out in vacuum, during which liquid agglomeration of the liquid silicon by surface tension was prevented by in-situ formed porous silicon carbide network structure. Uniform and rapid infiltration was achieved with double-walled preform method due to reduced infiltration distance and increased area of infiltration front.

Keywords: RBSC; Particle size distribution; Debinding; Infiltration; Continuous sintering

1. Introduction

Due to their excellent properties at elevated temperature, silicon carbide ceramics have been widely used for high temperature applications [1,2]. Among various silicon carbide ceramics, reaction-bonded silicon carbide (RBSC) ceramics have considerable advantages from economical viewpoint since the costs of production and raw materials are relatively low compared to other ceramic materials [2–4]. Above all, the RBSC ceramics have an extraordinary advantage over common ceramic fabrication techniques in that they can be readily fabricated into the near-net-dimension components by infiltrating reactive liquid into porous solid performs.

On the other hand, reaction-formed silicon carbide (RFSC) ceramics have been extensively studied to further improve mechanical properties at ambient and elevated temperatures. These were produced by reactive infiltration of silicon melt into carbonaceous porous preforms [3–6]. Despite the vastly improved properties of RFSC ceramics, an extreme care should be taken to overcome considerable dimensional change during the resin curing and debinding processes in order to fabricate a large component [6,7]. Dimensional changes associated with the curing process could result in various macro-defects such as distortion and cracking.

In the present study, efforts were made to reduce dimensional change throughout curing and debinding processes by adding a substantial amount of SiC powders to form network structure in the resin mixture. At the same time, the complexity of silicon melt delivery through the fine capillaries of the pyrolyzed body was considerably simplified by employing a double-walled tube preform.

2. Experimental procedures

Starting powders used in this study were three grades of α-SiC powders with mean particle sizes in the range 5–150 μm (GC #100, #400, #2500, Showa Denko, Japan)

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and two grades of silicon powder with mean particle sizes of 70 and 2000 μm. Polymeric component used in this study as binder as well as an additional carbon source were furfuryl alcohol resin (KF-975, Kolon Chemical, Korea). In addition, ethylene glycol was used as a fugitive phase for the purpose of forming an interconnected pore structure before thermal pyrolysis. Xylene sulfonic acid (KH-10 Kolon Chemical) and Triton X-100 (Union Carbide, USA) were used as a catalyst and a liquid dispersant, respectively.

Powder composition used for forming the outer SiC/C layer was 50, 25 and 25 wt.% of SiC powders with mean particle sizes of 150, 35 and 5 μm, respectively. The binder resin mixture was composed of a 1:1 mixture of furfuryl alcohol and furfuryl alcohol resin as thermoset components and ethylene glycol as a fugitive thermoplastic component. The weight fractions of the thermoset and thermoplastic resins were 54.5 and 45.5%, respectively. Final mixture of high solid loading, e.g. 62.5 vol.%, was employed to prevent particle segregation during consolidation. Blending of SiC powders and resin was carried out for 3 h using a high-speed mixer in a stainless steel container cooled to below 4 °C to avoid premature polymerization of the resin mixture. The viscosity of the mixture was measured using a rotation viscometer at shear rate up to 1000 s^{-1}. Degassing in vacuum was followed.

The same procedures as described for the outer layer formation were applied to prepare the silicon/resin mixture for the inner layer of the double-walled preform. The mixing ratio of 70 and 2000 μm silicon powders was 80:20 by weight. The silicon powder with a mean particle size of 70 μm was added to enhance the flow characteristics of the mixture. The solid loading of the silicon/resin mixture was 57.5 vol.% and the same resin mixture was used as for the SiC/resin mixture of the outer layer.

A two-step centrifugal casting, outer silicon carbide/resin layer formation followed by inner silicon/resin layer, was performed at 250–400 RPM for 1 h at room temperature in a steel mold with 20 cm inner diameter and 100 cm length. Then, the casting mold was heated to 55–60 °C and maintained for 1 h to partially cure the resin mixture. After the partial curing was completed, further heat treatment up to 70 °C was performed over 12 h to complete the curing in a drying chamber.

The debinding was carried out in a two-step process by heating up the cast tube to 400 °C in flowing argon. The first stage of the debinding was intended to remove ethylene glycol through capillary migration and surface evaporation and to provide continuous pore channels for the gaseous species generated in the second stage. Eventually, this process yielded the glassy carbon in both layers of the preform. The glassy carbon yield was about 25 wt.% after 36 h at 400 °C.

The debinded double-walled perform was sintered by pushing it through the hot zone with a speed of 5–10 mm/min under vacuum. The microstructure was investigated by observing polished and fractured surfaces of green, pyrolyzed and sintered preforms. The pore size distribution was measured by mercury porosimeter.

3. Results and discussion

Fig. 1 shows schematic illustrations of a double-walled preform structure and continuous sintering process. The double-walled preform consists of two layers: the outer layer of SiC/C composite and the inner of Si/C composite. Once the temperature exceeds the melting point of silicon, the silicon melt formed in the inner layer instantly reacts with carbon in the Si/C layer to form silicon carbide. This silicon carbide cage structure in the inner layer is responsible for preventing the silicon melt from agglomerating due to surface tension. Otherwise, the agglomerates of silicon melt can be readily separated from the outer SiC/C layer due to the gravity effect prior to complete infiltration. The silicon melt, transferred to the outer SiC/C layer through the in-situ silicon carbide cage structure, reacts with carbon to form newly generated silicon carbide which bonds together those original silicon carbide particles.

Fig. 2 shows plots of the suspension viscosity versus shear rate for the mixtures containing different powder compositions. Due to the sensor geometry of viscometer, viscosity measurements were carried out without the coarsest powders of 150 μm. The labels in Fig. 2 indicate the mixing ratios of

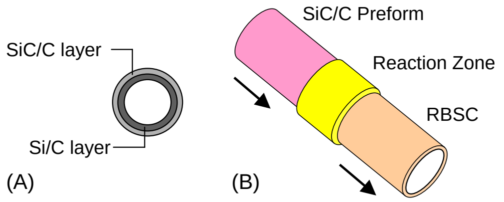

Fig. 1. Schematics of (A) double-walled tubular preform composed of Si/C inner layer and SiC/C outer layer and (B) continuous sintering process.

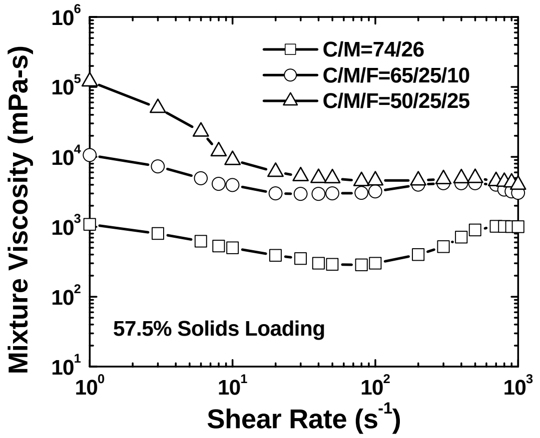

Fig. 2. Mixture viscosity of SiC/resin mixtures vs. shear rate for three powder/resin mixtures prepared with different powder mixing ratios. C/M/F represents the weight ratio of coarse, intermediate, and fine SiC powders.

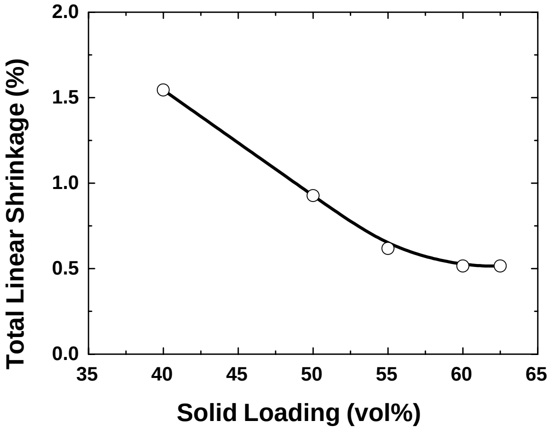

Fig. 3. Total linear shrinkage vs. solids loading of powder/resin mixture measured after resin curing and debinding.

SiC powders used in SiC/resin mixtures. C, M and F represent the SiC powders with mean particle sizes of 35, 5, 1 μm, respectively. The first two mixtures, e.g. C/M = 74/26 and C/M/F = 65/25/10, represent the compositions to provide the maximum packing density calculated by packing model of multi-modal powders using experimentally determined packing density of individual powder [8]. On the other hand, the other mixture of C/M/F = 50/25/25 contains additional fine powders. As usually observed with suspensions of high solids loading, all three mixtures of 57.5 vol.% solids showed shear thinning behavior at relatively low shear rate, e.g. up to ~100 s^{-1}. With increasing shear rate, there occurs a significant dilatant flow for the mixtures of maximum packing conditions. In contrast, the mixtures with additional fines did not show any indication of dilatant flow, which has been widely applied in castable refractories [9,10]. Therefore, the mixture used in this study was the composition of C/M/F = 50/25/25 using 150, 35 and 5 μm SiC powders.

Fig. 3 shows a plot of process shrinkage associated with curing and debinding as a function of SiC powder addition. It is clear that the process shrinkage could be considerably reduced in the presence of rigid SiC network structures. In particular, the shrinkage was almost negligible when the amount of SiC addition exceeded 60 vol.%. Since the reported shrinkage in RFSC ceramics are close to 30%, it is very important to reduce process shrinkage to a negligible level using SiC particle network in order to minimize the shrinkage-related defects [11,12].

Fig. 4 shows a SEM micrograph of double-walled preform after curing, where the inner layer is composed of Si/resin composite and the outer layer is composed of SiC/resin composite. Since the cured resin matrix is continuous, it is difficult to distinguish the inner layer from the outer layer based on the particle size of the component powders. Instead, there exists a resin-rich layer between two component layers, which is believed to form by capillary migration of resin phase during consolidation of the outer layer.

Fig. 5 shows a polished section of the double-walled preform after thermal pyrolysis. It is more evident that there exists a large difference in size between the component particles used in both layers. Additionally, there was observed a carbon-rich interface between the component layers with approximately 300–400 μm thickness. Except the component segregation present in the preform, there were no major defects, such as cracks and/or delamination, observed in the pyrolyzed perform tubes.

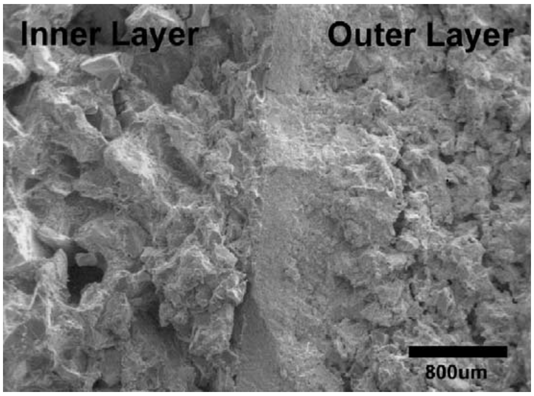

Fig. 4. SEM micrograph showing the interface region of double-walled preform after resin curing.

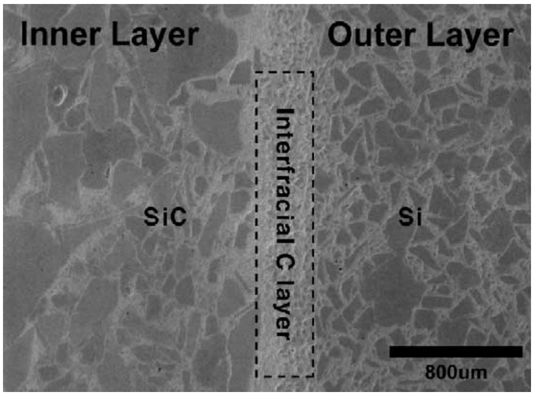

Fig. 5. SEM micrograph showing the interface region of double-walled preform after thermal pyrolysis.

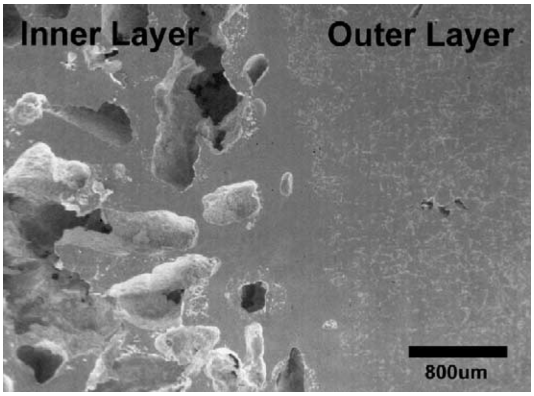

Fig. 6. SEM micrograph showing the interface region of double-walled preform after reaction infiltration.

Fig. 6 shows a polished section of the radiant tube after silicon melt infiltration at 1500 °C in vacuum. It clearly shows that the silicon melt formed in the inner layer completely penetrated into the outer layer, leaving behind in-situ SiC cage structure with continuous pore channels. It is also apparent that the interface between the inner and the outer layers was preserved relatively well without major defects.

The in-situ SiC porous structure, in the inner layer of the double-walled preform, played a critical role as a silicon melt reservoir, preventing the silicon melt from agglomerating. In addition, the continuous in-situ SiC porous channels evidenced in Fig. 6 was believed not only to provide continuous flow channels for silicon melt flow from inner layer to the outer layer but also to trigger simultaneous infiltration of silicon melt throughout the contact area between the component layers. It should also be noted that the double-walled perform used in the present study has several advantages over the conventional RBSC fabrication process with an isolated melt reservoir. These advantages include the increased area of infiltration front, substantially reduced infiltration depth, simultaneous and homogeneous infiltration due to the intimate contact area formed between the component layers. For the RBSC components with considerable infiltration distance, it takes a quite a long time to infiltrate the components with silicon melt. At a given condition, the infiltration kinetics could be readily optimized only by controlling the pressure gradient generated by the particle size differences between the component layers without the adjustment of infiltration temperature or time.

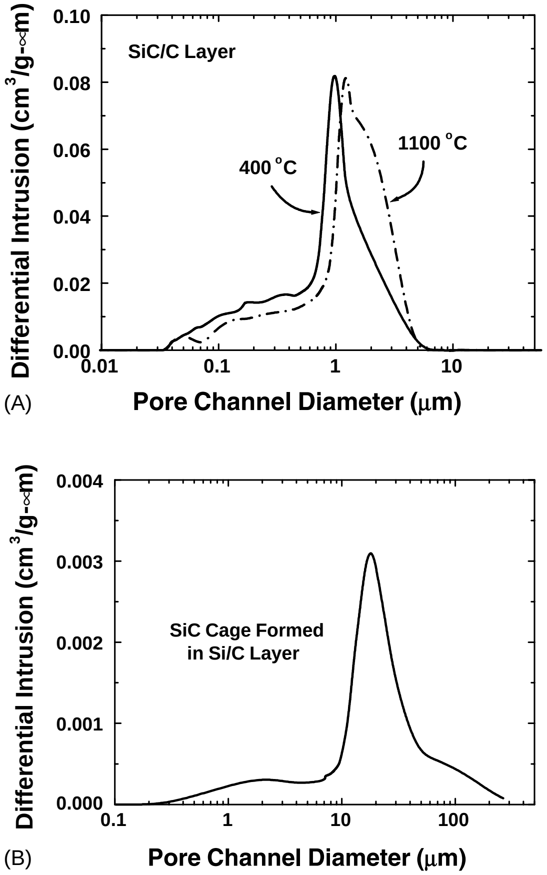

Fig. 7. Pore size distributions of (A) the SiC/C layer after thermal pyrolysis and (B) the SiC cage structure formed in Si/C layer after reactive infiltration.

In fact, it can be confirmed from the pore size distributions in Fig. 7 that both layers of the double-walled preform have a significant difference in capillary structure to provide sufficient pressure gradient for the simultaneous infiltration of silicon melt. That is, the mean pore size in the outer SiC/C layer was about 1–2 μm, while that of the in-situ formed SiC cage structure in the inner layer was close to 20 μm. This reflects that a significant difference in capillary size between both layers could be maintained throughout reaction infiltration process. In addition, it is noted that the contact angle between silicon melt and solid carbon is zero while that between silicon melt and silicon carbide is ∼30° [13]. The difference in contact angle might provide additional pressure gradient between the component layers, promoting infiltration of silicon melt from the inner layer to the outer layer. It should be recognized in Fig. 7A that further heat treatment after thermal pyrolysis up to 400 °C significantly changes pore size distribution with little or no linear shrinkage. This indicates that the densification of very reactive carbon is severely constrained and localized in the presence of rigid SiC network structure, assuring the dimensional stability of the preform tubes.

4. Summary

A reaction-bonded silicon carbide tubes with a large diameter have been fabricated by a continuous sintering using a double-walled preform. Centrifugal casting and curing of the preform was followed by two-stage debinding and continuous sintering. The two-stage debinding consists of capillary migration and surface evaporation of the thermoplastic resin and subsequent thermal pyrolysis of the thermoset resin. Reactive infiltration of the silicon melt was carried out in a vacuum or an inert atmosphere during which liquid agglomeration of the silicon melt by surface tension was prevented by in-situ formation of a silicon carbide cage structure.

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