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Densification of SiC_f/SiC composites by electrophoretic infiltration combined with ultrasonication

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An electrophoretic deposition (EPD) technique was used to infiltrate a SiC-based matrix phase into the fine voids of a Tyranno^{TM}-SA SiC preform with/without the application of ultrasound. The zeta potential and viscosity of the suspension were controlled to achieve a uniform and simultaneous deposition of all constituents. EPD was performed under a 10 V DC electric field for 30 minutes after adjusting the suspension pH to 3, in which the zeta potentials for all constituents were ≥ + 40 mV. The composites fabricated by EPD combined with ultrasonication showed a much higher degree of infiltration due to the minimized surface sealing effect than those by EPD only. After hot pressing at 1750 °C for 2 hours, the density of the composites by the combined process was 99.5%, which is the highest SiC_f/SiC density ever reported.

Key words: SiC_f/SiC composites, Electrophoretic deposition, Zeta potential, Slurry infiltration

Introduction

Continuous SiC fiber-reinforced SiC composites (SiC_f/SiC) can be used under extreme conditions, such as for aerospace and gas turbines, owing to their excellent thermal and mechanical properties [1, 2]. They have also been proposed as structural materials for the first wall of a fusion reactor, which is exposed to a high temperature plasma, because of their low levels of damage and activation under neutron irradiation [3, 4]. The aim of fiber reinforcement of these composites is to enhance the damage tolerance from catastrophic fracture, compared to monoliths or particulate composites, by deflecting the crack propagation path at the interface between the matrix and fibers. The prerequisites for achieving a damage-tolerant composite are a dense microstructure and the presence of a weak interface, which is generally acquired by depositing a pyrolytic carbon (PyC) or boron nitride layer on a SiC fiber [5].

Currently, the main limitation for producing a dense SiC_f/SiC composite is the lack of a suitable manufacturing technique. A range of techniques have been used to infiltrate the matrix phase into the voids of a fiber-preform, such as chemical vapor infiltration (CVI), polymer impregnation and pyrolysis (PIP), reaction sintering (RS), nano-infiltrated transient eutectoid (NITE), and combinations of these processes [6-9]. Although CVI can minimize the level of fiber damage on account of its low processing temperature of approximately 1000 °C, it is slow, expensive and difficult to infiltrate thick preforms due to preferential deposition at the surface, which is known as the 'surface sealing effect' [10, 11]. Moreover, composites fabricated by CVI usually contain 10-20% pores. While PIP is more economical than CVI due to the utilization of a pre-ceramic polymer precursor, this method leads to a porous microstructure, a lower purity SiC matrix and the presence of a glass phase that deteriorates the mechanical properties of the composites [7]. The NITE process, which employs SiC slurry infiltration into the voids between the fibers, appears to be most suitable technique for fabricating dense SiC_f/SiC [9, 12, 13]. However, the existence of a glass phase originating from approximately 10 wt.% Al_2O_3-Y_2O_3 sintering aids and the difficulty of infiltration into the fine voids between the fibers is still a challenge.

Another suitable method for slurry infiltration into a tightly woven structure is electrophoretic deposition (EPD), which has been demonstrated to be a good thick-film formation technique in the fields of electronic devices [14]. This technique can be used as a fast, simple and efficient infiltration method regardless of the shape of the preform, in which charged colloidal particles dispersed in a liquid medium migrate and deposit onto a conducting preform of an opposite charge under a DC electric field. In spite of these advantages, there are only a few reports on EPD application for SiC_f/SiC composite fabrication so far, showing a poor density of 85-90% and a flexural strength of 80-120 MPa [15-17]. However, it is believed that high density composites could be acquired by minimizing the surface sealing effect and optimizing many parameters related to the suspension and process [14]. The parameters related to the suspension include the particle size and zeta potential of the powder, the dielectric constant of the liquid, the conductivity and viscosity of suspension, and its long-term dispersion stability. On the other hand, the parameters related to the process include the deposition time, applied

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voltage, solid loading in suspension, and conductivity of the preform.

Based on previous research on the optimization of the suspension dispersion and process parameters [18, 19], the present paper describes an efficient method for fabricating a dense SiC_f/SiC composite using EPD by increasing the degree of infiltration into the fine voids between the fibers. In particular, EPD combined with ultrasonication was used to enhance the degree of matrix phase infiltration while minimizing the surface sealing effect, and the density, microstructure and mechanical properties of the composites fabricated by the combined process were compared with those by EPD only.

Experimental

A nano-sized β-SiC (D_m = 52 nm, 97.5% pure, 4620 KE, NanoAmor Inc., USA) and 12 wt.% Al_2O_3 (D_m = 150 nm, 99.9% pure, Baikowski, Japan) : Y_2O_3 (D_m = 220 nm, 99.99% pure, Acros Organics, USA) : MgO (D_m = 160 nm, 99.9% pure, Sigma-Aldrich, USA) mixture at a 6.4 : 2.6 : 1.0 weight ratio were used as the matrix phase and sintering aids, respectively. High energy milling (MiniCer, Netzch, Germany) was performed for the sintering aids using 0.8 mm ZrO_2 beads at 3,000 rpm for 3 hours to reduce the particle size to that of SiC (≈ 100 nm). Two-dimensionally woven Tyranno^{TM}-SA grade-3 fabrics (Ube Industries LTD., Japan) were used as reinforcements after coating with a 400 nm-thick PyC layer through the decomposition of CH_4 at 1,100 °C. The fabrics with a 0/90° plain woven structure containing 1,600 filaments per yarn were punched into 5 cm diameter discs.

Polyvinyl butyral (PVB) resin with a mean molecular weight of 55,000 g/mole (Butvar B-98, Solutia, USA) was used as a binder phase. After dissolving 6 g of PVB resin in 300 g ethanol, 60 g of SiC powder containing 12 wt.% of the sintering aids and 3 wt.% of a polyester/polyamine co-polymeric dispersant (Hypermer KD1, ICI, UK) with respect to the weight of SiC were added to the binder solution to form a suspension. The suspension was further ball-milled for 36 hours using 6 mm SiC balls to ensure particle dispersion. Suspensions containing SiC, Al_2O_3, Y_2O_3, and MgO were prepared at the same time to check the zeta potential of each particle. The zeta potential was measured using an electroacoustic-type zeta potential analyzer (Zeta Probe, Colloidal Dynamics, USA) after adjusting the pH of the suspension using NH_4OH and HCl.

EPD was performed using a dual electrode system for a disc-shaped SiC preform under an applied voltage of 10 V for 30 minutes with/without the application of ultrasound for the suspension, as shown in Fig. 1. The distance between the SiC fabric and the stainless steel electrode was 20 mm. The 10 W ultrasonic pulses with a 1 second cycle were applied only for the first 20 minutes to enhance the infiltration using a probe-type ultrasonicator (HD 2070, Bandelin, Germany). The degree of infiltration for the green sample was evaluated after cryo-fracturing of infiltrated fabric using

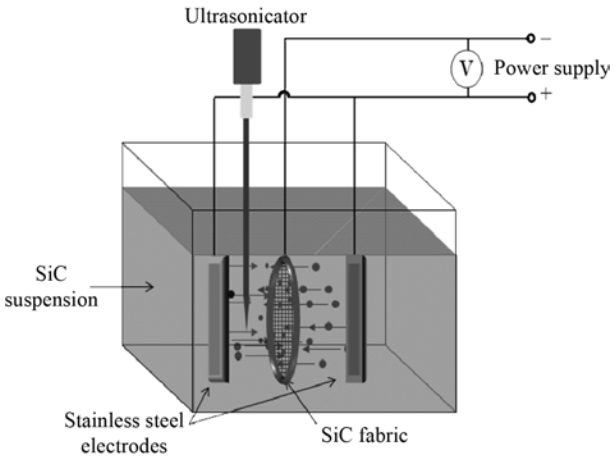

Fig. 1. Schematic diagram of the experimental apparatus for infiltration using EPD combined with ultrasonication.

liquid N_2. After drying the infiltrated fabrics at 70 °C for three hours, 15 layers of fabrics were stacked and laminated uni-axially under a pressure of 10 MPa at 80 °C. All samples underwent a binder burn-out process at 400 °C for two hours in air. Hot pressing was then carried out at 1,750 °C for 2 hours in an Ar atmosphere at a pressure of 20 MPa.

The density of the composites was measured for 5 samples using the Archimedes method. The hot-pressed samples were cut into 4 × 2 × 40 mm^3 pieces and polished for a 3-point bending test (UTM AG-50E, Shimadzu, Japan), which was performed at a crosshead speed of 0.1 mm/minute and a span of 30 mm. The sample morphology was examined by scanning electron microscopy (SEM; Hitachi S-4100). Ten minutes of plasma etching was carried out to observe the grains by SEM.

Results and Discussion

Fig. 2(a) and (b) show SEM images of nm-sized SiC particles and a 2-dimesionally woven SiC fabric, respectively. The Tyranno^{TM}-SA fiber consisted mainly of β-SiC crystals

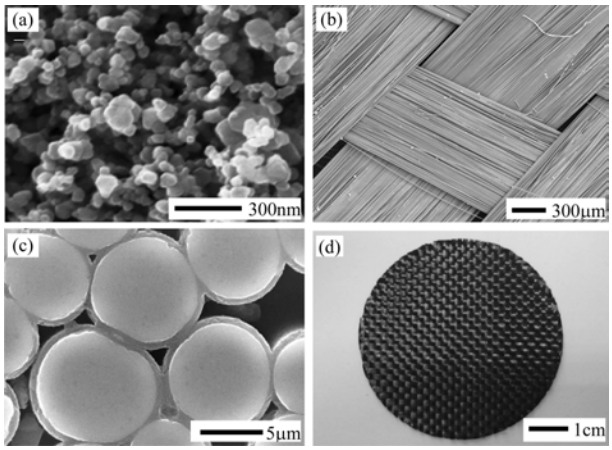

Fig. 2. Images of (a) SiC particles, (b) 0/90° woven Tyranno ^{TM}-SA fabric, (c) 400 nm PyC-coated fibers and (d) a fabric disc used for EPD.

with a C/Si atomic ratio of 1.08. Hence, good irradiation resistance is expected due to the highly crystalline structure and near stoichiometric composition. The SiC_f/SiC composites containing Tyranno^{TM}-SA fibers could be hot-pressed at 1750 °C because this fiber does not show any strength degradation or compositional changes up to 2,200 °C in an inert atmosphere [20]. The woven fabrics contain large inter-bundle voids and small intra-bundle ones between each fiber, as shown in Fig. 2(b). The efficient infiltration of the matrix phase composed of SiC powder and sintering aids into these voids is essential for fabricating dense SiC_f/SiC composites. The dual electrode system used in this study was expected to enhance the infiltration more than the widely used single electrode system due to deposition from both sides. On the other hand, the dispersion of nano-sized matrix particles is also an important factor for efficient infiltration because they have a strong tendency to agglomerate. A systematic approach for the dispersion of this system in terms of an electrostatic and steric mechanism can be found in a previous report [18]. Fig. 2(c) shows the uniform 400 nm-thick PyC coating layer on a SiC fiber, which was formed to increase the damage tolerance of composites by deflecting the crack propagation through the relatively weak matrix-fiber interface. However, the infiltration into the preform shown in Fig. 2(d) would be more difficult by decreasing the size of the gaps as a result of the formation of a PyC interphase.

Fig. 3 shows the zeta potentials of the SiC, Al_2O_3, Y_2O_3, and MgO particles in an ethanol suspension as a function of the pH. MgO showed a positive zeta potential over the measured pH range without an isoelectric point (IEP), while the others showed a decrease in zeta potential with increasing pH due to the effect of OH^- ions. The IEPs for SiC, Al_2O_3 and Y_2O_3 were pH = 6.3, 10.0 and 8.3, respectively. MgO tends to migrate to the cathode at pH > 10 due to its positive zeta potential, while the opposite is true for the other particles with a negative surface charge. Moreover, Al_2O_3 would have a very low driving force for migration under an electric field owing to its low zeta potential in the high pH region. On the other hand, all types of particles in the suspension would move to the cathode at pH < 6 due to their positive zeta potentials, even though there might be some difference in mobility. The principal driving force for EPD is the electrophoretic mobility of the particles, which is proportional to the surface charge, under an applied DC electric field. The suspension pH was set to 3 in order to maximize the surface charge, whereby the zeta potentials for all constituents were ≥+40 mV. In addition, the difference in mobility originating from the different zeta potentials of the constituents was minimized by increasing the viscosity of the suspension through the addition of 10 wt.% PVB. Since the difference in mobility in multi-component systems can induce a non-uniform distribution of each constituent due to the different deposition rates, it can be minimized by controlling the solid content, dispersion and viscosity of the suspension [14]. The addition of a PVB binder can enhance the adhesion of the matrix phase to the fabric and at the same time prevent cracks in the deposits. In addition, the binder can provide steric stabilization of the suspension due to the adsorbed polymeric layer.

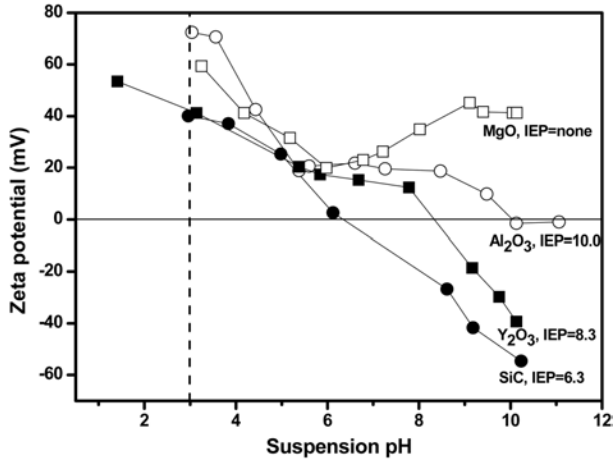

Fig. 3. Behavior of zeta potentials for SiC, Al_2O_3, Y_2O_3 and MgO particles in ethanol as a function of the suspension pH.

Fig. 4(a) and (b) compares the green composite microstructure fabricated by EPD only and EPD combined with ultrasonication after cryo-fracturing using liquid N_2. The matrix phase had infiltrated effectively into the fine voids of the composite fabricated using the combined process, showing the existence of a deposit surrounding the fiber and dense fragments. On the other hand, the composite fabricated by EPD only showed little matrix phase infiltration into the voids. The matrix phase deposits preferentially at the surface without penetrating into the deep voids inside during EPD, which is known as the surface sealing effect [10, 11]. As a result, there are many unfilled voids, resulting in a low green composite density. However, the application of ultrasound can minimize this surface sealing effect by releasing the surface adsorbed matrix phase during the EPD process. After 20 minutes of periodic ultrasound application for efficient infiltration, EPD without ultrasonication

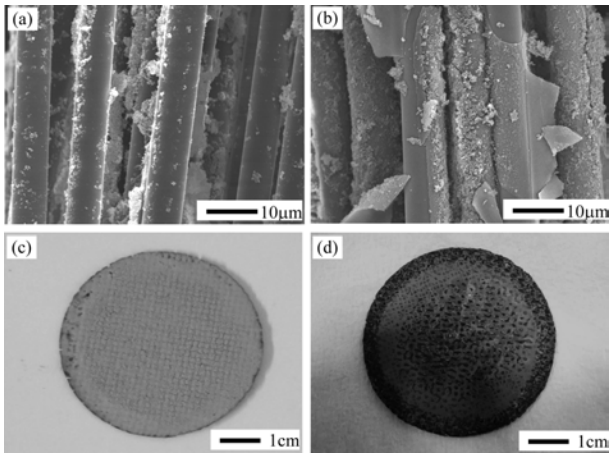

Fig. 4. Cryo-fractured images for the green composites fabricated by (a) EPD only and (b) EPD combined with ultrasonication. Images for (c) the green fabric after infiltration and (d) hot-pressed composite are also shown.

was performed for an additional 10 minutes for surface filling. Fig. 4(d) shows the SiC_f/SiC composites hot-pressed at 1750 °C, 20 MPa for 2 hours after stacking 15 infiltrated preforms shown in Fig. 4(c).

The hot-pressed composite had an alternating layered structure of fiber- and matrix-rich layers, as shown in Fig. 5, due to the surface-adsorbed matrix phase. The fiber content of this composite was approximately 45 vol.%. Fig. 6 shows the flexural strength-displacement behavior of the composites fabricated by EPD only and EPD combined with ultrasonication. The composite fabricated by the combined process and EPD only showed a flexural strength of 491 and 247 MPa, respectively. These values are a significant improvement over those obtained for fully densified SiC monolith in a previous report (198 MPa) [21]. Since the displacement of the composite by the combined process was much larger than that by EPD only, the damage tolerance was also much larger. However, both composites showed an abrupt decrease in load after fracturing, which indicates the brittle nature of these composites. The brittle nature of the composite is due to the relatively strong matrix-PyC-fiber interface because a weak interface between the matrix and fiber is essential for a damage-tolerant ceramic composite if a high density is preserved [5]. When the interface is too strong, a crack passes the interface as in a monolithic ceramic without deflecting crack propagation. On the other hand, a weak interface increases the toughness by crack deflection, showing a significant amount of fiber pull-out from the fractured surface [5]. However, the composite fabricated in this study showed little fiber pull-out, as shown in Fig. 5, indicating the need for interface phase optimization.

Fig. 7 shows SEM images of the composites fabricated by the two different methods. The composite fabricated by EPD only showed incomplete infiltration of the matrix phase into the fine voids. The voids at the border between the fiber bundles and matrix were filled to some degree, while many of the voids inside were not filled due to a surface sealing effect [10, 11]. This composite showed 92% of the theoretical density, which was calculated by considering the density of SiC powder = 3.22 g/cm^3, Tyranno^{TM}-SA fiber = 3.10 g/cm^3, and a 45 vol.% fiber content. On the other hand, the composite fabricated by the combined process showed no unfilled voids, as shown in Fig. 7(c) and (d). A dot line is drawn at the boundary in Fig. 7(c) to clarify the boundary between the matrix and fiber. PyC, fiber and matrix phase filled the fine voids in Fig. 7(d), indicating the effectiveness of EPD combined with ultrasonication for matrix phase infiltration into the fine voids. Moreover, the fibers maintained their original round shape after hot pressing at 1750 °C. The density of the composite fabricated by this combined process was 3.15 g/cm^3, i.e., 99.5% of the theoretical density, which the highest SiC_f/SiC density reported thus far.

Fig. 8 shows SEM images of the fiber and matrix phase after plasma etching. The grains of the matrix phase in Fig. 8(a) showed a broad size distribution and extra-large grains more than a few micrometers in size. On the other

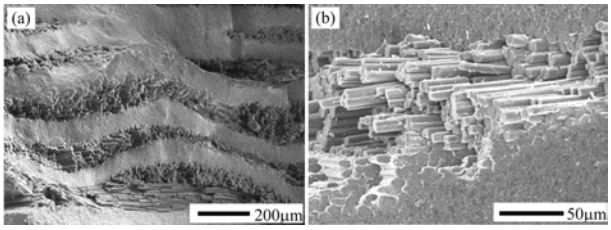

Fig. 5. SEM images of the fractured composite surface after the 3-point bending test, showing the alternating matrix- and fiber-rich layers with little fiber pull-out.

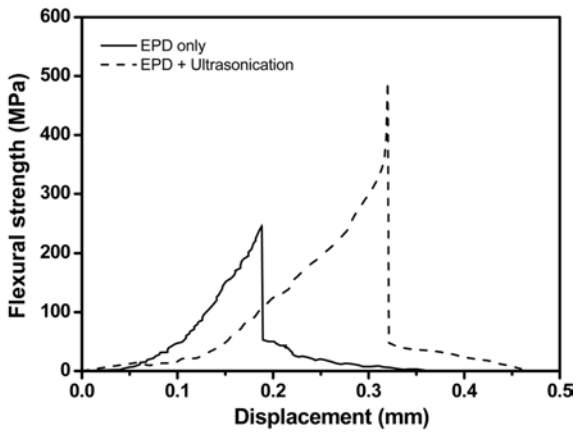

Fig. 6. Flexural strength -displacement behavior of the composites fabricated by EPD combined with/without ultrasonication.

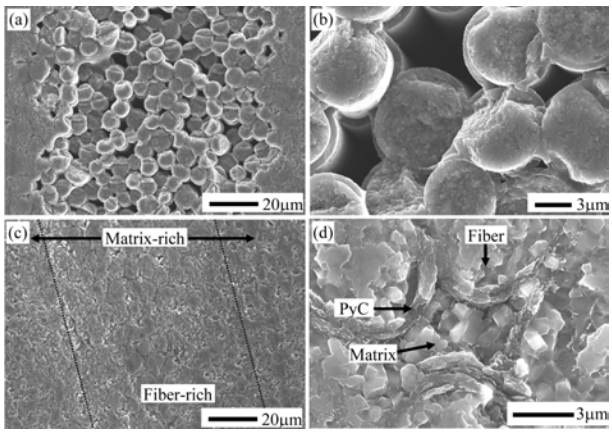

Fig. 7. SEM images of the SiC_f/SiC composites fabricated by (a), (b) EPD only and (c), (d) EPD combined with ultrasonication.

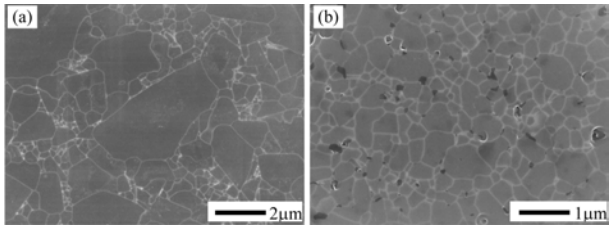

Fig. 8. Microstructures of (a) matrix and (b) fiber, showing a larger grain size with a broader size distribution with the matrix region compared to the fiber.

hand, the SiC grains in the fiber were fine and uniform; the largest grain did not exceed 1 μm. This larger grain size of the matrix phase was attributed to the 12 wt.% of Al_2O_3-Y_2O_3-MgO sintering aids with respect to the matrix SiC, which transformed to a liquid phase and enhanced grain growth during high temperature hot-pressing. Moreover, segregation of the liquid phase at the grain boundaries can deteriorate the high temperature properties of the composite by re-melting. Since the existence of a liquid phase and large grains hinders the mechanical properties, it is important to maintain the small grain size by reducing the sintering aids or controlling the sintering conditions. Further experiments to improve the mechanical properties of the hot-pressed SiC_f/SiC composites, including the optimization of an interface phase, sintering conditions and a search for effective sintering aids, are currently underway.

Conclusions

This study examined the effectiveness of EPD combined with ultrasonication for the infiltration of a nm-sized SiC-based matrix phase into the fine voids of a Tyranno^{TM}-SA SiC preform to fabricate dense SiC_f/SiC composites. The matrix suspension composed of SiC, Al_2O_3-Y_2O_3-MgO as a sintering aid, ethanol as a solvent, and PVB as a binder phase was infiltrated into the preform by EPD under a 10 V DC electric field with/without the application of ultrasound. The pH of the suspension was set to 3 to achieve positive zeta potentials +40 mV for all constituents in the multi-component system and ensure that all particles migrated to the cathodic SiC fabrics. Moreover, the difference in mobility induced from the different zeta potential values was minimized by increasing the suspension viscosity through the addition of a PVB binder. EPD combined with ultrasonication enhanced the degree of infiltration significantly compared to the conventional EPD process. The densities of the composites fabricated by the combined process and EPD only were 99.5 and 92%, respectively, indicating the effectiveness of the combined process. On the other hand, the composites showed brittle properties with little fiber pull-out during fracture, which was attributed to the relatively strong matrix-PyC-fiber interface and broad grain size distribution with extra-large grains in the matrix. Overall, the combined process resulted in the highest SiC_f/SiC density ever reported. However, the damage tolerance of the composites requires improvement.

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