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The effects of SiC whiskers and an SiC film coating deposited by chemical vapor infiltration (CVI) on a porous cordierite substrate

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Abstract This study was performed with the goal of reducing environmental pollution caused by nano-particle materials. SiC whiskers were grown on a porous cordierite substrate to enhance its filtering efficiency, performance, and durability by controlling pore morphology. We investigated two different methods: SiC whisker growth (A) and SiC film coating after the SiC whisker growth (B). These experiments were performed using the chemical vapor infiltration (CVI) process to grow the whiskers in the inner pore without closing it. After a 1 h deposition at 1200 °C, the compressive strength of the whiskered porous cordierite body increased from 24 MPa to 60 MPa (250%) in experiment (A) and to 82 MPa (342%) in experiment (B). The mean pore size was reduced after whisker growth (A) as well as after additional film coating (B). The adhesion strength between the whiskers and the cordierite substrate increased with the additional film coating (B). Consequently, the separation of whiskers from the substrate was minimized. N_2 gas was injected and a permeability change was observed which explains the separation of the whiskers from the substrate. This method makes the filtration of nano-sized particles feasible.

Introduction

The reduction of pollutant emissions such as particulates and nitrogen oxides from diesel automobiles has become a critical issue in recent years, so the legal regulations regarding diesel automobiles are being strengthened [1, 2]. Hence, diesel particulate filters (DPF) made of ceramic materials have been developed to eliminate these particulates. Commercially available diesel particulate filters (DPF) are produced today from cordierite and silicon carbide. Cordierite DPFs are used because cordierite has a low thermal expansion and excellent thermal shock resistivity [3, 4]. However, the cordierite DPFs with a 5 μm mean pore size which are currently on the market do not efficiently capture nano-particulates of less than 50 nm in size [5]. This makes them insufficient for capturing nano-sized particulates to achieve the goal of atmospheric environmental protection. The purpose of our method is to filter off the nano-particulates to compensate for the filter's inefficiency. We tried to form a smaller pore size on the cordierite body by growing SiC whiskers inside the pore through a vapor–solid reaction using the CVI process [6, 7]. Then, we analyzed the micro structure, the mechanical strength, the pore size distribution, the gas permeability, and the change in permeability after N_2 gas injection.

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Experiments

The whiskers were grown by the chemical vapor infiltration (CVI) process using low pressure chemical vapor deposition (LPCVD) in a horizontal hot-wall furnace [8, 9]. A cordierite honeycomb (VHoneycomb, Ceracomb, Korea) with a porosity of 35%, and a mean pore size of 5 μm was used as a substrate. The substrate dimension was 4 (W) × 4 (L) × 8 mm^3 (H). The substrate was cleaned using ultra sonic waves in methyl alcohol and DI water for 1 min each, and then dried at 100 °C. Methyltrichlorosilane (CH_3SiCl_3, MTS, Acros Organics Co., U.S.A) was used as a source, and high-purity hydrogen (H_2) gas was used as the dilute- and carrier-gas. The MTS source was bubbled at a temperature of 0 °C [10]. In our experiment, the applied input gas ratio, α, is defined as the ratio of the total hydrogen gas flow to the MTS source flow. The SiC whiskers were deposited at an input gas ratio of 100, and a total pressure of 5 torr. The deposition temperature was 1200 °C, and the deposition times were 10, 30, and 60 min. The additional SiC film coating was performed at an input gas ratio of 4, and a total pressure of 5 torr. The deposition temperature was 1200 °C, and the deposition time was 10 min. After the deposition process, scanning electron microscopy (SEM) (FESEM, Hitachi S-4200) and a universal testing machine (H10 K-C, Hounsfield Test Equipment Ltd., U.K.) were used to measure the microstructure and compressive strength. The sizes of the pores were analyzed using a mercury porosimeter (AutoporeIII v3.02, Micromeritics Co., U.S.A), and the gas permeability was measured with an injection of N_2 gas at a pressure of 1 atm 28 °C. Line density was measured to define growth density of whiskers in specific area. To measure the line density, SEM image was enlarged on A4 paper (256 × 192 mm^2) as Fig. 1 shows, and five lines (L_1–L_5) were drawn on the image with same space (10 μm) then summed up the area of whiskers occupying the line (L_1–L_5). To reduce error,

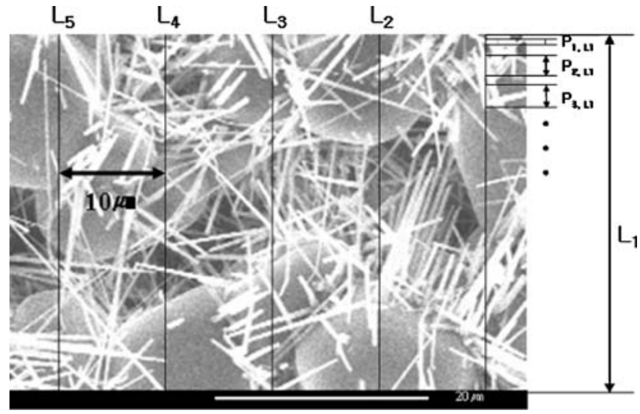

Fig. 1 SEM image for determination of line density of whiskers, line density (‰) = (Σ PLi/Σ Li) × 1000

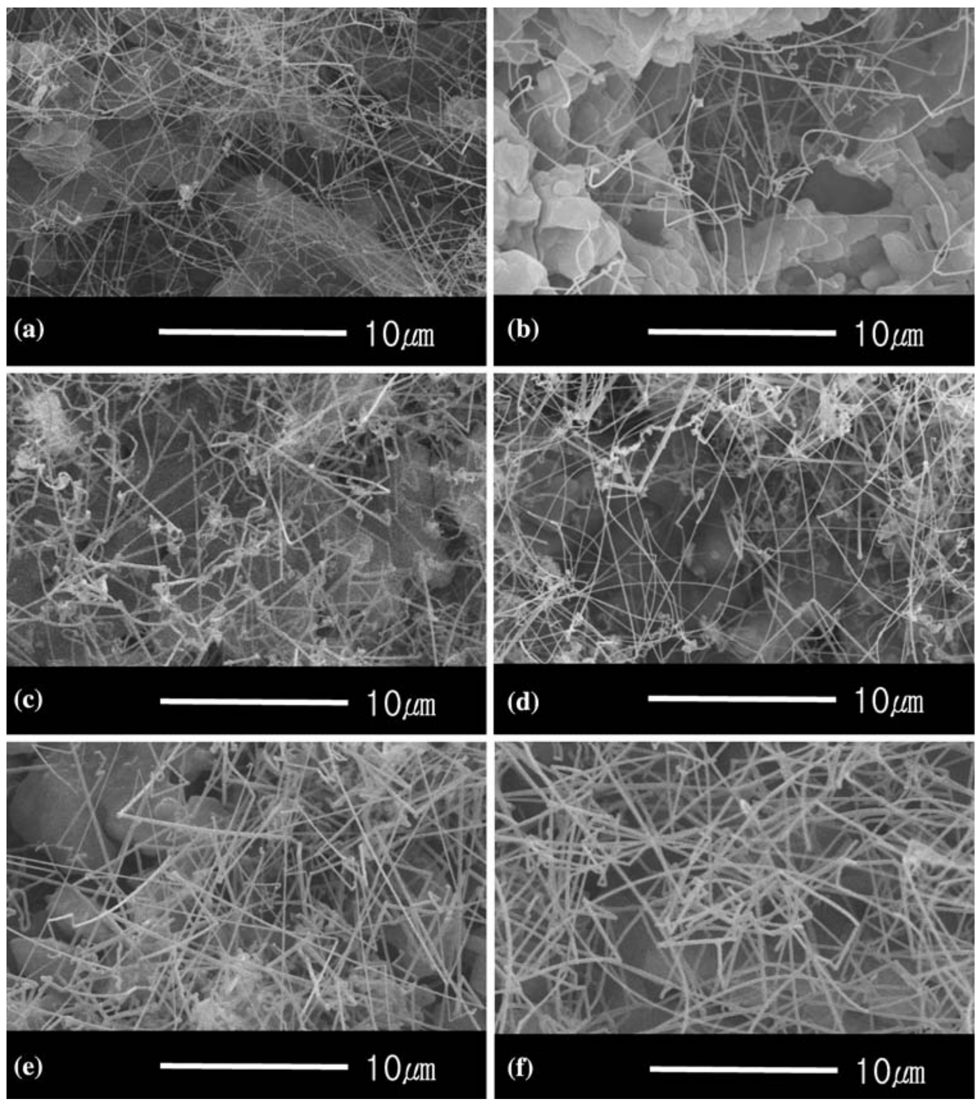

Fig. 2 SEM images of the SiC whiskers [A (**a**–**c**)] in the inner pores, and the additional SiC film coating [B (**d**–**f**)] after whisker deposition as a function of deposition time (**a**), (**d**) 10 min, (**b**), (**e**) 30 min, (**c**), (**f**) 60 min (T_{dep} = 1200 °C, for α = 100)

Table 1 The mean diameters and line densities of whiskers growth (A) and additional SiC film coating (B) (T_{dep} = 1200 °C, for α = 100)

	Deposition time (10 min)		Deposition time (30 min)		Deposition time (60 min)	
	(A)	(B)	(A)	(B)	(A)	(B)
Mean diameter (nm)	103	160	192	234	237	313
Line density (‰)	102	391	480	524	706	725

mean value of line density from four different SEM images was measured.

Results and discussions

Figure 2 shows the SEM images of the SiC whiskers a, b, c in the pores in experiment (A), and the additional SiC film coating d, e, f in experiment (B), at various deposition times. The mean diameters and line densities were measured and listed in Table 1. As the deposition time increased from 10 min to 60 min, the mean diameter of the whiskers in experiment (A) increased from 103 nm to 237 nm (230%), and the mean diameter of the whiskers in experiment (B) increased by about 58 nm with the additional SiC film coating. Figure 3 shows the variation in the compressive strength of the cordierite body after growing whiskers (A) and after additional film coating (B). As the deposition time increased, the compressive strength of whiskered cordierite body (A) increased. It seems that the networking of whiskers, caused by irregular growth direction, increased the compressive strength because the whiskers bound the empty space of cordierite body. The mechanical strength also increased with the additional SiC film coating (B). The compressive strength of the specimen in (A) that was deposited for 60 min was remarkably high (60 MPa). Also, the mechanical strength of the specimen in (B), on which was deposited additional film coating, was remarkably high (82 MPa) when compared to the bare substrate (24 MPa). Our method has improved the low compressive strength of the porous cordierite. Figure 4 shows the pore size distribution measured by a mercury porosimeter. The pore size distribution tended to decrease after growing whiskers (A) and the additional film coating (B). The mean pore size of the bare cordierite substrate was 4.4 µm and decreased to 2.6 µm after growing whiskers (A), and 2.1 µm after growing the additional film coating (B). It is assumed that the networked structures were formed during whisker growth in the open pore structure of the cordierite substrate and that the networked structure reduced pore size. These networked whiskers deposited in- and outside pores and the decrease in the mean pore size are expected to enhance an efficiency of filtering diesel particulates materials. Figure 5 shows the results of the N_2 gas permeability measurements used to examine the rate of decrease in permeability as mean pore size decreased. Permeability decreased after growing whiskers (A) and the additional film coating (B) since the SiC whiskers and additional film filled the inner pores. Figure 6 shows the permeability change caused by the whiskers and additional

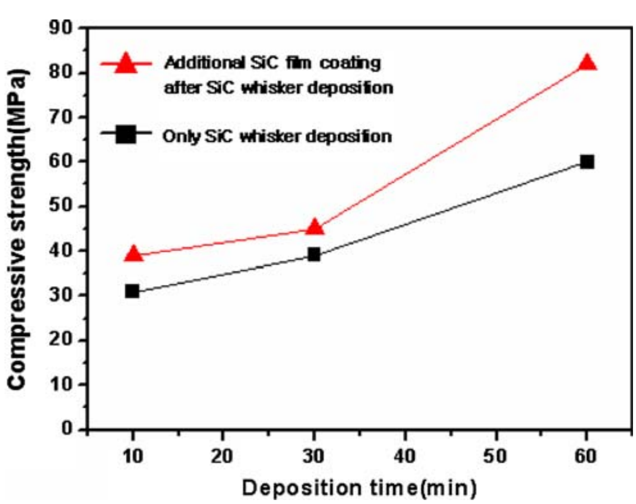

Fig. 3 Plots of compressive strength of the cordierite body after growing whiskers (A) and an additional film coating (B) after whisker deposition (T_{dep} = 1200 °C, for α = 100)

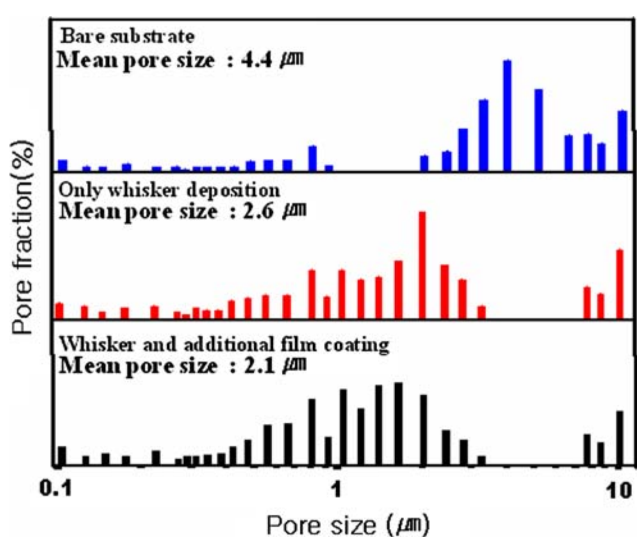

Fig. 4 Pore size distribution measured by mercury porosimeter in bare substrate, substrate with whiskers (A), and substrate with additional film coating (B) (T_{dep} = 1200 °C, α = 100, T_{dep} = 30 min)

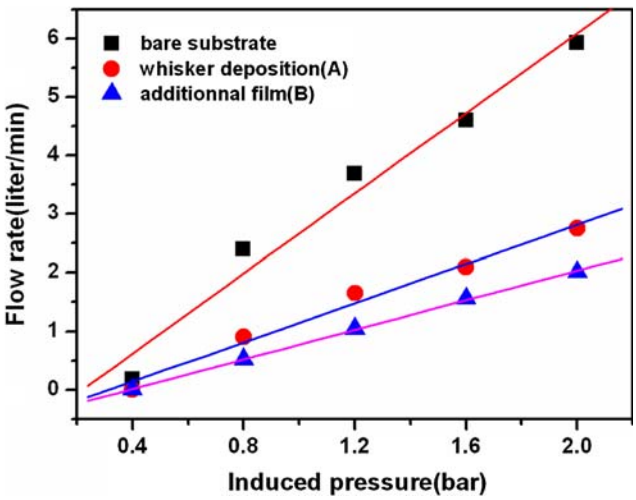

Fig. 5 Nitrogen gas permeability with bare, whiskers deposition (A) and additional film coating (B) substrate (T_{dep} = 1200 °C, α = 100, T_{dep} = 30 min)

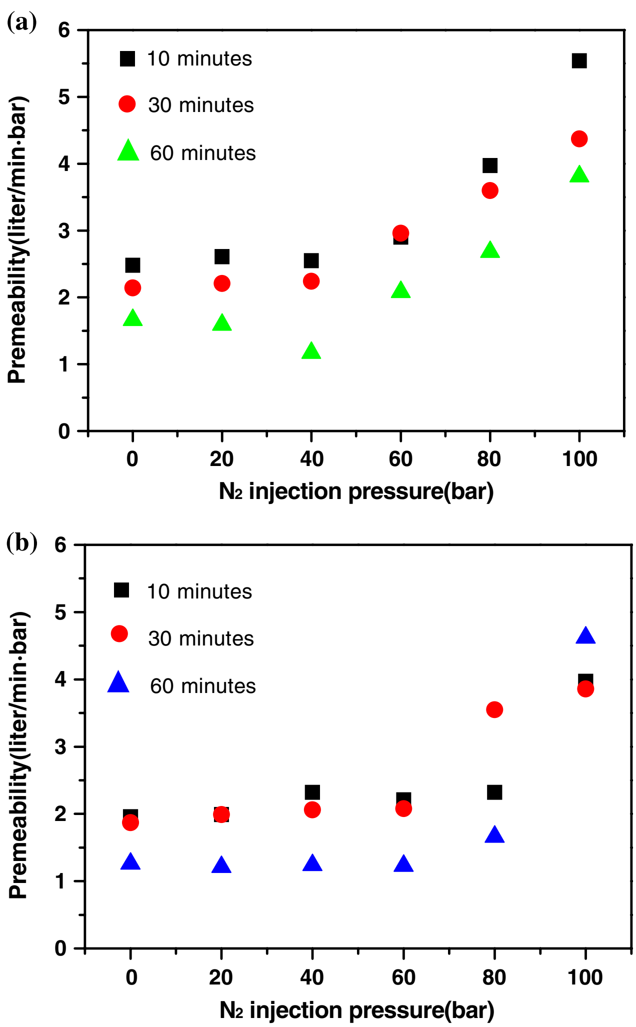

Fig. 6 The plots of permeability change with (**a**) growing whiskers (A) and (**b**) additional film coating (B) after N_2 gas injection of various pressure from 0 bar to 100 bar (T_{dep} = 1200 °C, for α = 100)

film coating after an N_2 gas injection at pressures ranging from 0 bar to 100 bar. This permeability change can be attributed to the separation of whiskers from the cordierite substrate. The permeability increased above pressures of 60 bar in the whiskered substrate (A) and 80 bar in the substrate with the additional film coating (B). The difference in pressures at which the permeability increased was caused by improved adhesion strength between the whiskers and substrate allowed by the additional film coating (B). Consequently, the separation of the whiskers from the substrate may be minimized by the film coating (B). The maximum pressure of the exhaust gas is known to be 70 bar in an actual diesel engine, so the additional film coating (B) after the whisker deposition could be applied to an actual engine.

Conclusion

Using the CVI process, SiC whiskers were grown in open pore structures of a cordierite body to maximize filtering efficiency. The mean diameter of the whiskers (A) increased with deposition time. The compressive strength of the substrate (A) that was deposited for 60 min was remarkably high at a value of 60 MPa. The substrate with the additional film (B) had a remarkably high compressive strength at 82 MPa as compared to the bare substrate (24 MPa). The pore size distribution showed a trend toward decreasing size after whisker growth (A) and additional film coating (B). The permeability increased above pressures of 60 bar in the whiskered substrate (A) and above 80 bar in the substrate with the additional film coating (B). Therefore, an additional SiC film coating (B) after the growth of SiC whiskers improves compression strength, adhesion between whiskers and substrate, and filtering efficiency by reducing pore size. This method improves the cordierite substrate's feasibility for use as a nano-particle filter in diesel automobiles.

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