The Effect of Chemical Vapor Infiltrated SiC Whiskers on the Change in the Pore Structure of a Porous SiC Body

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ABSTRACT

In this study, SiC whiskers were grown on a porous SiC diesel particulate filter for nanoparticle filtering. To grow the whiskers at the inner pore without closing the pores, we used chemical vapor infiltration with a solution source and a dilute. As the deposition time increased, the whiskers grew and formed a network structure. After 180 min of deposition, the mean diameter of the whiskers was 174 nm and the compressive strength was 58.4 MPa. The pores shrank from 10 μm to 0.4 μm and, because the whiskers filled the inner pores, the gradient of permeability decreased as the deposition time increased. However, by using the network structure of whiskers deposited for 120 min and 180 min, we obtained a diesel particulate filter with pores of 0.9 μm and 0.4 μm, respectively. Furthermore, the filter shows better permeability than a porous body with pores of 1 μm. In short, by filtering the nanoparticulate materials, the network structure of whiskers improves the strength, reduces the pore size and minimizes the permeability drop.

Key words: Silicon carbide, Whisker, Pore size, Permeability, Network structure

1. Introduction

A tmospheric pollution caused by particulate materials has recently caused serious problems such as lung disease, smog and reduced visibility. Because the particulate materials produced by diesel engines are a major source of atmospheric pollution, the development of a decontamination system has become an important issue.[1] Several porous ceramic filters have been developed for use in the decontamination system. Silicon carbide (SiC) filters, for instance, have useful properties that can be applied to a Diesel Particulate Filter (DPF): namely, low density, high mechanical strength, good thermal shock resistance, and high chemical tolerance.[2] However, the Health Effects Institute reported that the filtering efficiency of an SiC DPF is inadequate for removing nanoparticles that are smaller than 50 nm; furthermore, the institute reported that these unfiltered nanoparticles can cause serious pulmonary complaints.[3]

To improve the efficiency of filtering nanoparticles, we therefore endeavored to take advantage of the growth of the network structure inside the pores of the SiC DPF. First, we tried to grow the SiC whiskers into a network structure by using Chemical Vapor Infiltration (CVI) to stimulate a vapor-solid reaction.[4,5] After growing the whiskers, we confirmed the effect of the network structure by analyzing the changes in the microstructure, as well as the strength, the permeability, and the pore size distribution.

2. Experimental Procedure

To grow the whiskers, we used CVI in a horizontal hot-wall type of furnace: this process is a kind of low-pressure chemical vapor deposition.[6,7] In addition, to ensure that the whiskers grew inside the pores of the open-pored honeycomb body of the DPF (SD031, IBIDEN, Japan), which had a mean pore size of 10 μm and a porosity of 43%, we used methyltrichlorosilane (CH_3SiCl_3; MTS) (Acros Organics Co., USA) as a solution source and high purity H_2 as a diluted gas.[8]

After delivering the MTS to the DPF by bubbling the carrier gas (H_2), we diluted the MTS with the total H_2 gas-that is, with the sum of the diluted gas and the carrier gas. We then fixed the input gas ratio, which is defined as the total H_2 gas flow to the MTS source flow, at 30 (H_2 gas flow (750 sccm) : MTS gas flow (25 sccm)).[9]

The sample of whisker growth that we used for testing the compressive strength was a cubic centimeter, and the deposition time varied from 5 min to 180 min at a stationary pressure of 5 Torr under a fixed temperature of 1100°C. After the deposition, we used Scanning Electron Microscopy (SEM) (FESEM, Hitachi S-4200) to observe the microstructures, and we used a universal testing machine (H10K-C, Hounsfield Test Equipment Ltd., UK) to examine the compressive strength. We used a mercury porosimeter (AutoporeIII v3.02, Micromeritics Co., USA) to determine the

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pore size, and we used N_2 gas at 1 atm, under a temperature of 28°C, to examine the gas permeability. Finally, we sealed each side of the sample with an epoxy. The sealing enabled us to measure the gas permeability through the wall of the sample for real application.

3. Results and Discussion

The SEM images in Fig. 1 show how the whiskers grew inside the pores of the DPF in relation to the deposition time. Fig. 1(a) shows the initial growth of the whiskers after
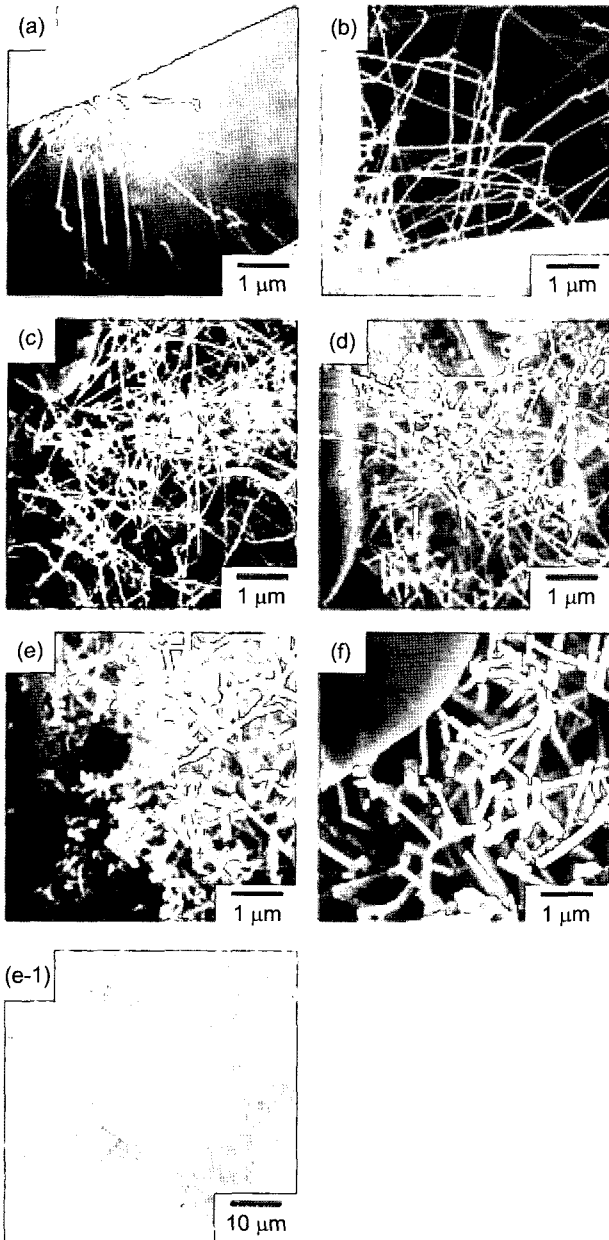

Fig. 1. A SEM image of whiskers grown inside the pores with varied deposition times of (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min, (e) 120 min (high magnification), (e-1) 120 min (low magnification), and (f) 180 min (T_{dep} = 1100°C, α = 30).

5 min of deposition. As the deposition time increased, the whiskers grew more densely and, after more than 30 min of deposition, as shown in Fig. 1(c), (d), (e), and (f), they filled a large part of the pores. Fig. 1(e-1), which is a low magnification image of Fig. 1(e), shows the actual growth of the whiskers inside the pores.

Fig. 2 shows that the width of whiskers increased as the deposition time increased and that the mean diameter of the whiskers increased remarkably after more than 60 min of deposition. When the deposition time increased from 60 min to 120 min, the mean diameter of the whiskers increased from 64 nm to 112 nm (175%); and, at 180 min, the whiskers showed the highest mean diameter of 174 nm. Generally, as the deposition time increases, the amount of supplied reactant gas increases and the width of the whiskers increases.[10]

Fig. 3 plots the compressive strength of the DPF after the growth of the whiskers. We measured the compressive strength (dotted line) in order to examine how the mechanical property improved as a result of the whiskers. As the
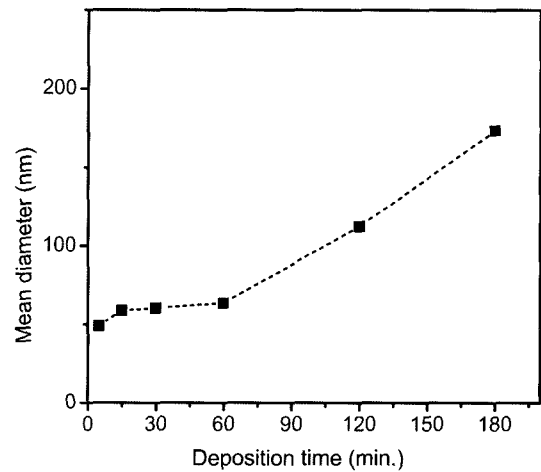

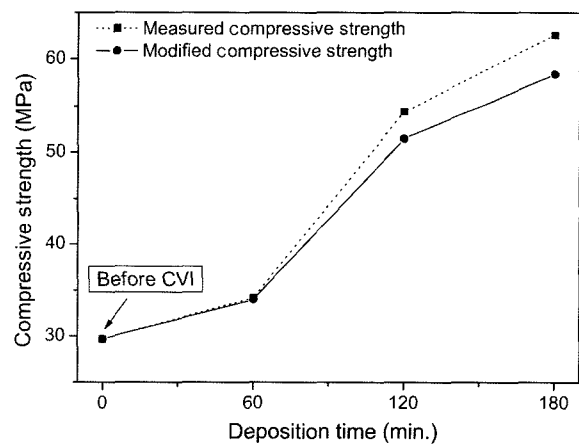**Fig. 2.** The mean whisker diameter with deposition times (T_{dep} = 1100°C, α = 30).

Fig. 3. The compressive strength with deposition times (T_{dep} = 1100°C, α = 30).

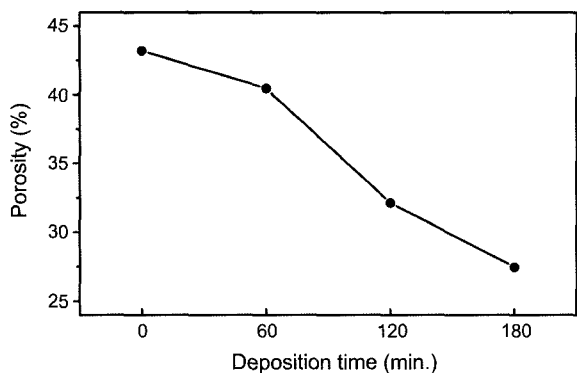**Fig. 4.** The porosity with deposition times $(T_{dep} = 1100°C,$ $\alpha = 30)$.

deposition time increased, the strength of the whiskered DPF became high; and, after more than 60 min of deposition, the compressive strength of the whiskered DPF increased remarkably.

As shown in Fig. 4, the increase in deposition time led to a drop in the porosity of the DPF, from 43% to 28%. If the pores have the same shape, the compressive strength generally decreases exponentially as the porosity of porous materials increases.[11] Given the strength effect of porosity, we modified the compressive strength of the DPF from 34.0 MPa to 58.4 MPa as the deposition time increased from 60 min to 180 min; the modification is shown in Fig. 3 (solid line). When we increased the deposition time from 60 min to 120 min, the compressive strength of the whiskered DPF increased remarkably from 34.0 MPa to 51.5 MPa (151%). The compressive strength of the whiskered DPF, which was deposited for 180 min, reached a maximum strength of 58.4 MPa, representing a 197% increase over a bare DPF.

The sintering effect might have affected the increase in compressive strength because the whiskering process was done at a relatively high temperature. However, the compressive strength remained unchanged after we heated the bare DPF at 1100°C for 180 min without growing whiskers. We deduced therefore that the increase in the strength of the whiskered DPF was not due to the sintering of the bare DPF.

Our results show a similar increasing tendency for the mean diameter of the whiskers; the results also show that the compressive strength increases as the deposition time increases. The whiskers inside the pores seem to increase the mechanical strength of the DPF. As other studies have reported,[12,13] the mechanical strength increases as a result of SiC film deposition of a few nanometers before the whiskers grow; when the SiC whiskers grow, they then increase the strength as the deposition time increases. Our results confirm the results of other studies and, as shown in Figs. 2 and 3, we can reasonably deduce that the whiskers are the main cause of the increase in mechanical strength after more than 120 min of deposition.

We focused on effectively forming a network structure in

the whiskers in order to filter nanoparticle materials. Thus, we had to ensure that the whiskers grew sufficiently inside the pores and that they improved the mechanical properties of the DPF. We therefore chose whisker deposition periods of 120 min and 180 min, and we measured the pore size distribution of the samples.

Fig. 5 shows that the space between the growing whiskers acts as a pore for gas permeability. The results show that the peak points of the pore size distribution tend to become smaller as the deposition time increases. The mean pore size is 0.9 μm for the sample deposited for 120 min and 0.4 μm for the sample deposited for 180 min.

Fig. 6, which shows the ratio of the N_2 gas flow rate to the induced pressure, enables us to examine the permeability of gas. The plots show relative permeability of each sample, and the higher slope of the fitted line means better permeability. In general, as the pore size decreases, the gas per-
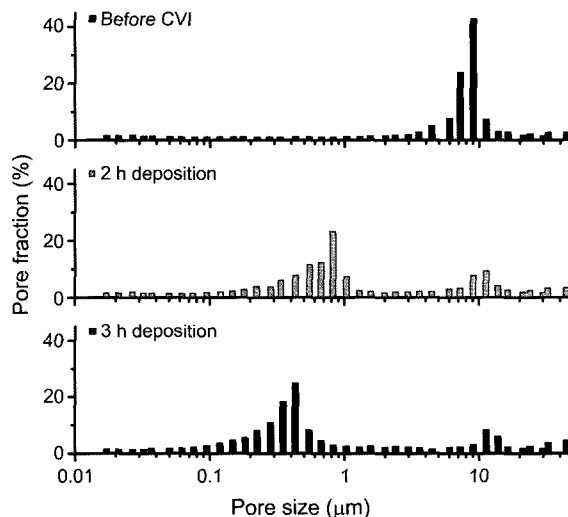

Fig. 5. Effective pore size distribution as measured by a mercury porosimeter with deposition times $(T_{dep} = 1100°C,$ $\alpha = 30)$.
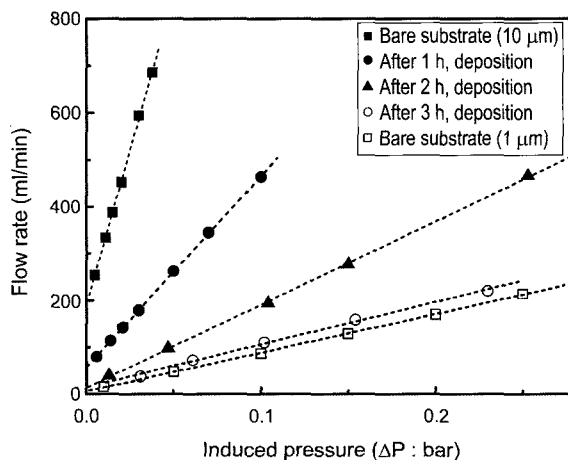

Fig. 6. The nitrogen gas flow rate with deposition times $(T_{dep} = 1100°C, \alpha = 30)$.

meability decreases. Although the growing whiskers don't generate pores, the network structure of the whiskers diminishes the space in the pores. Our results show that, because the whiskers filled the inside of the pores, as shown in Fig. 1, the gas permeability drops considerably as the deposition time increases.

The relation between the permeability and the pore size is the most important factor for evaluating the filtering efficiency. As shown in Fig. 5, when the whiskers grew for a deposition time of 120 min, the pore size was 0.9 μm; and when they grew for a deposition time of 180 min, the pore size was 0.4 μm. Moreover, as shown in Fig. 6, the slope of the permeability plots of the whiskered DFA is higher than that of the bare porous filter with a pore size of 1 μm. This means that use of whisker growth to control the pore size is an effective method of improving the relation between the gas permeability and the pore size. Accordingly, this process of forming a network structure in the growing whiskers inside the pores of a DPF might be useful for filtering nano-particle materials.

4. Conclusions

Using CVI, we grew SiC whiskers in an SiC DPF to improve the filtering efficiency. A network structure was formed in the growing whiskers inside the pores of the DPF, and the density of the whiskers increased after more than 30 min of deposition. The mean diameter of the whiskers was 112 nm after 120 min of deposition and 174 nm after 180 min of deposition. As the deposition time increased, the strength of the whiskered DPF increased, mainly due to the network structure of the whiskers after more than 120 min of deposition; in addition, the compressive strength increased remarkably from 29.7 MPa to 58.4 MPa after 180 min of deposition. The effective pore size and the permeability both decreased as the deposition time increased because the whiskers filled the inside of the pores. However, the whiskered DPF, which had pore sizes of 0.9 μm after 120 min of deposition and 0.4 μm after 180 min of deposition, showed better permeability than a porous filter with a pore size of 1 μm. Accordingly, a filter with a network structure of SiC whiskers has great potential for filtering nano-particle materials; furthermore, this type of filter can have improve mechanical strength because it reduces the pore size and minimizes the permeability drop.

Acknowledgment

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