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Properties of a carbon woven fabric filter grown SiC whisker by chemical vapor infiltration

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Abstract β-silicon carbide whiskers were synthesized on a carbon fabric using a vapor–solid (VS) mechanism. The morphologies of the SiC deposits changed as deposition time increased. Pore size distribution and mean pore size of the fabric filter was reduced by whisker growth. A particle-trapping test was conducted to examine the efficiency of the filter. Then, the size of the particles infiltrated within the filter was analyzed. The maximum increase rate of the particle trap rate was 136.6% by whisker growth. The fine particles ranged from 550 to 800 nm and could be trapped by forming whiskers on the carbon filaments of the fabric filter. The carbon fabric filter's gas permeability is 6 times higher than conventional honeycomb filters.

Introduction

Environmental pollution is one of the most important topics in modern industry [1]. For this reason, filtering technologies have been widely studied by many research groups [2, 3]. Among these filtering technologies, diesel particulate filters (DPF), made of ceramic materials, have been developed to eliminate particulate matter from diesel vehicles. Commercially available diesel particulate filters (DPF) produced today are made from cordierite and silicon carbide [2]. However, these types of filters are very expensive and generate high pressure drops. They also have limitations in capturing nano-sized particulate matter [2, 3]. Metal filters and pellet filters have been studied as possible solutions. However, the corrosion of the metal at high temperatures, and the high production costs of these filters make these options less desirable. Also it is generally known that the pellet filter is heavier and generates higher backpressures than monolith filters [3]. In this study, we suggest SiC whiskers on carbon woven fabric as a substrate for filter applications. Previous studies have shown that SiC whiskers can be used for field emissions [4] and improving mechanical properties of ceramic materials [5]. In our case, we propose that SiC whiskers grown on carbon woven fabric substrate will enhance filter efficiency by reducing the pressure drop, and trapping small particulate matter.

Whiskers have been produced by several processes such as the carbothermal reduction of silica [6, 7], reactions between silicon halides and CCl_4 [8], and chemical vapor deposition using a metallic catalyst like Ni or Fe [9]. Among these processes, chemical vapor deposition (CVD) methods have been widely used because they can form homogeneous whiskers. The present study grew SiC whiskers through a vapor–solid (VS) mechanism using the chemical vapor infiltration (CVI) process. We analyzed the properties of the fabric filter, including change in mean pore size, efficiency of the particle trap, and gas permeability. The carbon woven fabric substrate is flexible, which eliminates shape restrictions in filter manufacturing. Also, the use of a fabric substrate can decrease the likelihood of a brittle fracture, which is one of the problems with conventional ceramic filters. Therefore, we expect that these carbon woven fabric filter grown whiskers can be applied to various filter applications, including DPF (diesel particulate filter).

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Experimental procedure

The whiskers were grown by the CVI process using low pressure chemical vapor deposition (LPCVD) in a horizontal hot-wall furnace [10, 11]. Carbon woven fabric (3327, Hankuk Carbon Co. LTD, Korea) with a filament diameter of 8 μm was used as a substrate. The substrate was cleaned using methyl alcohol and DI water for 1 min each, and then dried at 100 °C in a dry oven. For the comparison of gas permeability a cordierite honeycomb (Honeycomb, Ceracomb, Korea) filter was used. Methyltrichlorosilane (CH_3SiCl_3, MTS, Acros Organics Co., USA) was used as a source and hydrogen (H_2) gas was used as the dilute and carrier gas. The MTS source was bubbled at a temperature of 0 °C. 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 ($\alpha = H_2/MTS$) [2]. SiC whiskers were deposited at an input gas ratio of 50 and the total deposition pressure was fixed at 4 Torr. The deposition temperature was 1300 °C and the deposition time was 10 to 60 min. After the deposition of whiskers, the morphologies were characterized using scanning electron microscopy (SEM) (FESEM, JOEL JSM-6700F) and the phase of the whiskers was examined by X-ray diffraction (XRD) (Regaku. Co. D/Max rint 2000). Pore size distribution of the woven fabric was analyzed using capillary flow porometry (CFP-1100-A, PMI, USA) and the mean pore size was calculated. A particle trap test was performed using DI water mixed with carbon black (DaeJung Chemicals, Korea) and a dispersing agent to avoid agglomeration. Particles of carbon black were filtered from the solution, and the weights of the filter before and after the trap test were compared. The size distribution of the particles that passed through the filter was measured with laser scattering (ELS-z, Otsuka Electronics Co., Japan). The gas permeability was measured with an injection of N_2 gas at a pressure of 1 atmosphere, 28 °C.

Results and discussion

Figure 1 shows the microstructures of the SiC whisker as a function of deposition time. Figure 1a and d is the result of 10-min deposition. A number of pebble-shaped deposits and a whisker are observed on the carbon fabric substrate. It is thought that this is the initial stage in which nucleation occurred during the growth of the whisker. In this study, we synthesized the SiC whisker using a VS mechanism. In the case of one VLS mechanism, it takes 8 min to complete nucleation stage for SiC whisker growth [12]. This is faster than our result which has shown no whisker growth stage until 10 min. We guess that metal catalyst activated the reaction in the VLS mechanism, explaining why the quick nucleation occurred. An axial-growth of a whisker where reactants were deposited at the nucleation site as the deposition time increased to 30 min is shown in Fig. 1b and e. Both the diameter and length of the whisker increased at 60-min deposition in Fig. 1c and f. The diameter and length of the whisker grown at 10, 30, 60 min was 470 nm, 1 μm, 1.6 μm and 1 μm, 7 μm, 10 μm, respectively. The exact mechanisms responsible for vapor–solid growth have not been completely elucidated yet [13]. However, it is well-known that the degree of supersaturation determines growth morphology. A low supersaturation is required for one-dimensional nanostructure growth (such as a whisker, nanorod, and nanowire), whereas a medium supersaturation supports bulk crystal growth [14]. Lee et al. [15] reported that SiC film was deposited at a low input gas ratio, which is considered less than 10. In this study, the input gas ratio was 50. So we believe that the highly diluted source gas in this study lead to low supersaturation, resulting in the one-dimensional structure made as shown in Fig. 1b and c. In our previous report [16], a whisker with a cone-like structure was observed at the high deposition temperature of 1300 °C. In this study, the deposition temperature was also 1300 °C and the whisker maintained a cone-like structure as shown in Fig. 1e and f. Like Park et al. [16], these whiskers grown at high temperatures have many defects such as stacking faults due to its rapid growth rate. Also, it is reported that in the VS mechanism, the radial growth of whiskers might be induced by micro facets, which are formed by microtwins [17]. Thus, we guess that irregular radial growth on the surface of the whisker as shown in Fig. 1f occurred due to the many defects which were produced during the proceeding of axial growth of the whisker from the nucleation stage as shown in Fig. 1d and e. XRD confirmed that the whisker was β-silicon carbide.

Figures 2 and 3 show the changes in pore size distribution and mean pore size, respectively, as whiskers grow on the substrate. The fraction of small pores increased as deposition time increased as shown in Fig. 2. This is due to the growth of whiskers on the carbon filament of the fabric filter. The increase in diameter and length of the whisker as deposition time increased is consistent with this result. The fabric filter without deposition has an approximate mean pore size of about 19 μm as shown in Fig. 3. The mean pore size decreased to 18, 11, and 10 μm as deposition time increased to 10, 30, and 60 min, respectively. We assume that the cone-like whisker contributes to a decrease in mean pore size due to the axial growth of the whisker after more than 30 min of deposition. In the case of 10 min of deposition, the pebble-shaped deposits have a weak effect on the decrease in mean pore size.

Figure 4 shows the trapping rate of the fabric filter using carbon black particles as the deposition time increased and the number of filters increased. In the case of single-ply,

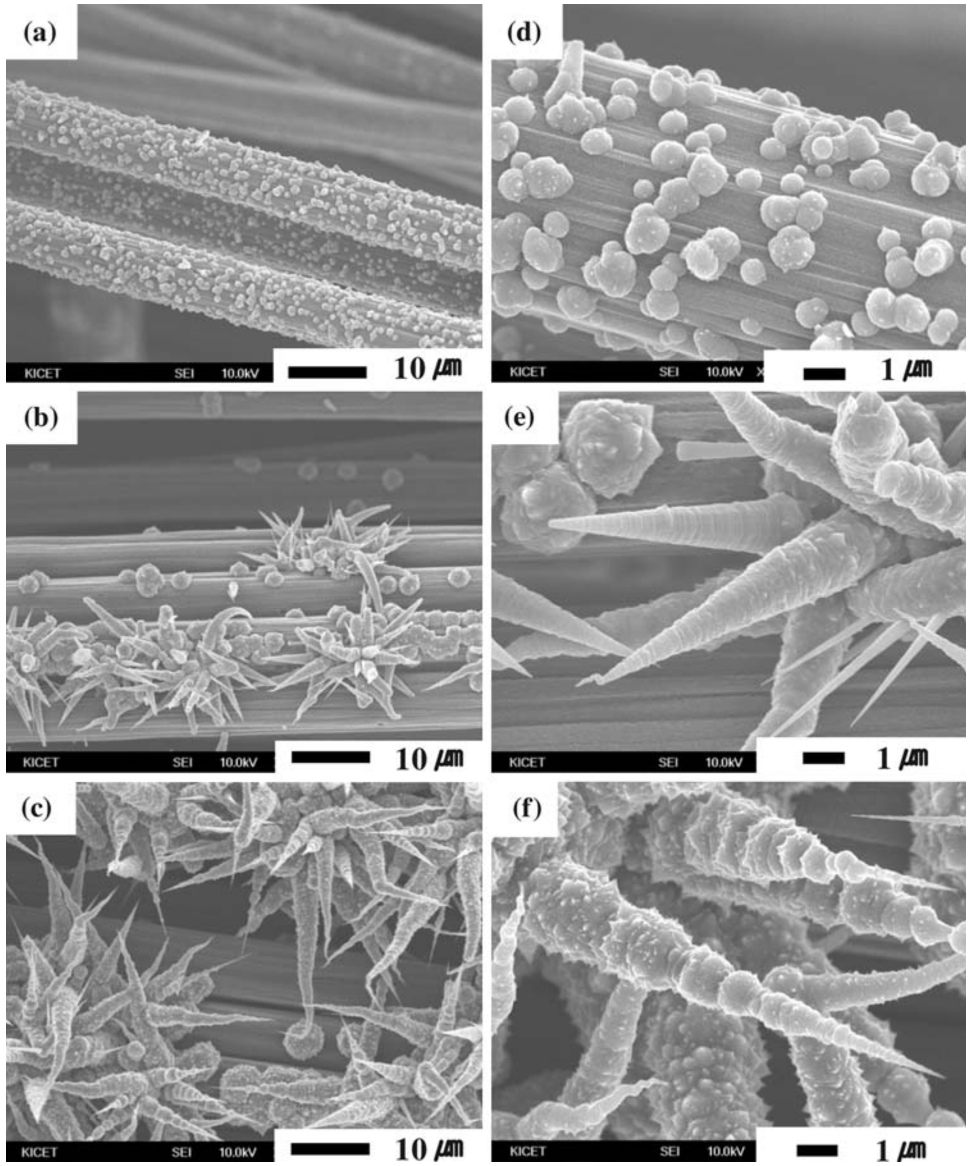

Fig. 1 SEM images of the SiC whisker on the carbon filament as deposition time increases **a** 10 min, **b** 30 min, **c** 60 min, and **d–f** are magnified images of **a–c**, respectively (1300 °C, 4 Torr, $\alpha = 50$)

the trapping rate of the bare substrate was 2.9%. And the filter at 10, 30, and 60 min of deposition was 11.9%, 23.7%, and 28.8%, respectively. In the case of the double-ply filter, the trapping rate of bare substrate was 30.6%. And filter with 10, 30, and 60 min deposition was 59.5%, 68.8%, and 72.4%, respectively. Deposition time dependency of the trapping rate is consistent with the results of microstructures, pore size distribution, and mean pore size as shown in Figs. 1, 2, and 3, respectively. The double-ply filter, especially, shows a drastic increase in particle trapping rate. Construction of the woven fabric is planar consisting of 3,000 filaments warping and cross filling each other. There are holes located at the edge of the crossing point that warps and fills and its length and width are 325 and 485 µm, respectively. The dimension of the holes occupies 4.5% of the total area of the filter. The holes are located every 1.4 mm in the horizontal direction and 1.5 mm in the vertical direction at regular intervals on the fabric. While the particles infiltrate the fabric filter, these particles tend to infiltrate the holes because the size of a hole is much larger than the pore of the filter. In the case of the double-ply filter, this phenomenon can be minimized because holes on the one filter are blocked by the other filter. The increased rate of the particle trap rate using the double-ply filter with 10, 30, and 60 min deposition time was 94.4%, 124.8%, and 136.6% compared with the bare substrate.

Figure 5 shows the number distribution of particles that infiltrated the fabric filters. The size of the distributed carbon black particles range from 650 nm to 6 µm. The number distribution of 1.8 µm particles is the highest. In the case of the bare substrate, the distributed particles range

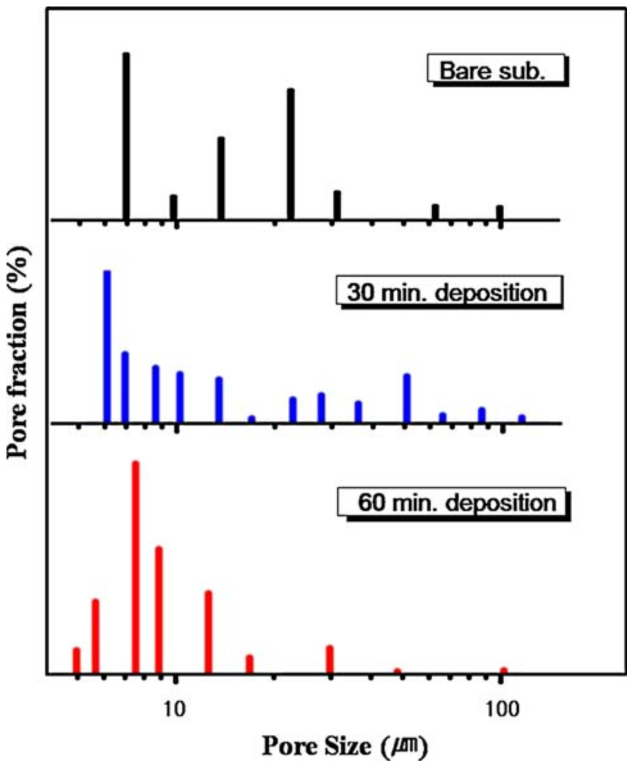

Fig. 2 Changes in pore size distribution during whisker growth for 30 and 60 min

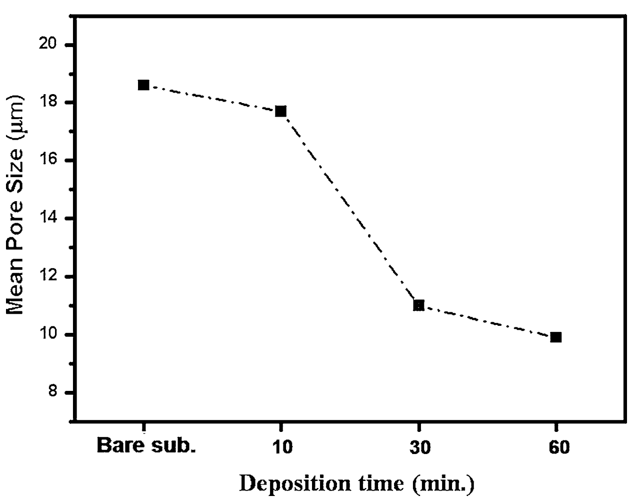

Fig. 3 Changes in mean pore size as deposition time increases

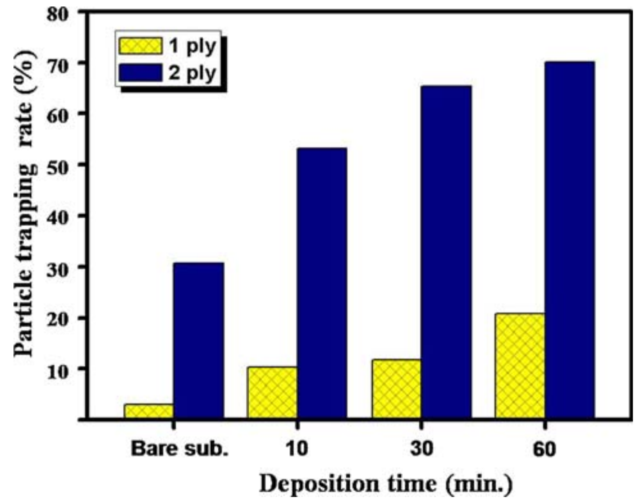

Fig. 4 Particle trapping rate as deposition time increases and the number of filters increase

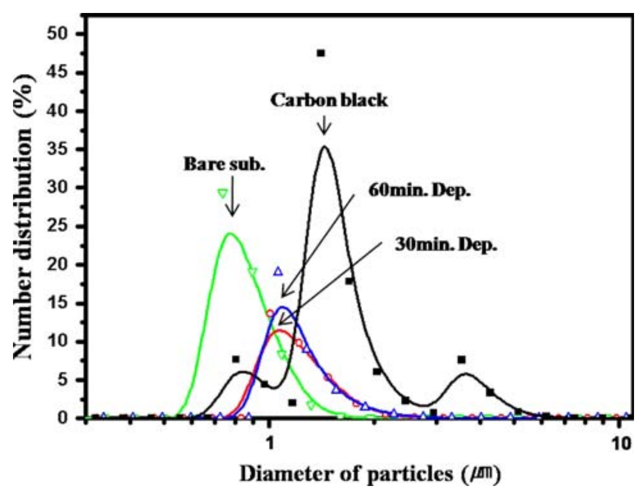

Fig. 5 Number distribution of infiltrated particles through the filter without deposition, and through the filter with 30 and 60 min of deposition

from 550 nm to 1.7 μm and the number distribution of 700 nm particles is the highest. For the bare substrate filter, we can see particles ranging from 1.7 to 6 μm were trapped and do not appear on its curve (Fig. 5). But particles smaller than 1.7 μm infiltrated through the pores of bare filter. For the fabric filter with whiskers grown at 30 and 60 min, the trapped particles range from 800 nm to 2.5 μm. Unlike those of the bare substrate filter, particles smaller than 800 nm do not appear on the whisker-deposited curves. This means particles smaller than 800 nm have been trapped by whiskers growth on fabric filter. Thus, we can say that filters with whiskers deposited can trap smaller particles than the bare substrate filter. Particles larger than 2 μm can be trapped by both a filter with whisker growth and a filter without a whisker. These results can be explained by the microstructure of the whisker as shown in Fig. 1. The bare substrate is composed of carbon filaments of 8-μm diameter and has a cylinder-like structure. But the diameter of the whisker halfway up the total length is 1 and 1.6 μm at 30 and 60 min of deposition, respectively. The cone-like structure of the whisker is such that the tip of the whisker is very sharp, as shown in Fig. 1e and f. Also, these whiskers form very small pore channels because of the cone shaped whisker

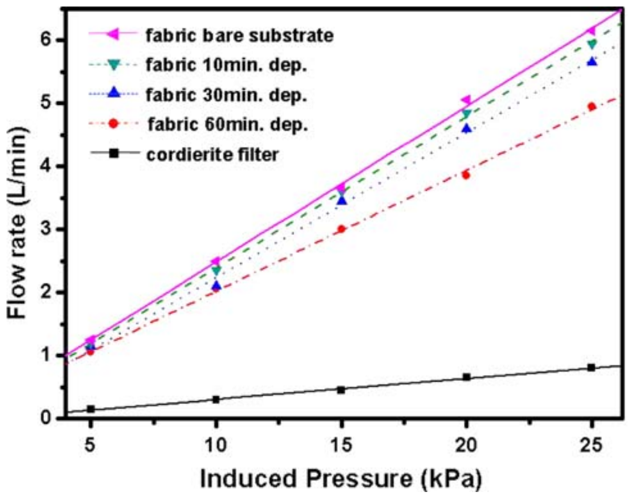

Fig. 6 Comparison of gas permeability between the cordierite honeycomb filter and the fabric filters (double-ply)

growth. These microstructural differences result in the trapping of finer particles by whisker growth on the fabric filter. From the results shown in Figs. 4 and 5, we can conclude that a higher quantity of particles, including smaller sized particles, can be trapped by whisker growth on the fabric filter.

Pressure drop is one of the problems with conventional diesel particulate filters [3]. Figure 6 shows the comparison of gas permeability between conventional cordierite filters and the double-ply of carbon fabric filters, which demonstrates a high particle trapping rate. We defined gas permeability as the slope of the graph in Fig. 6. The decreased rate in gas permeability of the fabric filter as deposition time increased to 10, 30, and 60 min was 3%, 8.2%, and 20.4%, respectively, compared with the bare substrate. Although the fabric filter at 60 min of deposition shows the highest decreased rate of gas permeability, 20.4%, compared with the bare substrate, its gas permeability is 6 times higher than the conventional cordierite honeycomb filter.

Conclusion

Silicon carbide whiskers were grown on a carbon woven fabric substrate by a vapor–solid (VS) mechanism using the CVI process. The morphology of the deposits was a pebble-shaped structure at 10 min of deposition, then one-dimensional growth proceeded as deposition time increased. The fraction of small pores increased as deposition time increased. Also, the mean pore size decreased to 18, 11, and 10 μm as deposition time increased, at 10, 30, and 60 min, respectively. A higher quantity of smaller sized particles was trapped by whisker growth. The highest increase in the particle trap rate was 136.6% at 60 min of deposition of the double-ply fabric filter. Also this specimen's gas permeability is 6 times higher than conventional honeycomb cordierite filters. We expect that this fabric filter, with its high gas permeability and enhanced trap rate by whisker growth, has great potential for application in the reduction of emissions from diesel vehicles.

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