Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 1307–1312
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

A study of surface-coated SiC whiskers on carbon fiber substrates and their properties for diesel particulate filter applications

Yoo Youl Choi, Jun Gyu Kim, Kyu Min Lee, Hyun Chul Sohn, Doo Jin Choi *

Department of Materials Science and Engineering, Yonsei University, 262 Seongsanno, Sudaemun-Gu, Seoul, 120-749, Republic of Korea

Received 11 October 2010; received in revised form 25 October 2010; accepted 11 December 2010
Available online 22 January 2011

Abstract

β-Silicon carbide (β-SiC) whiskers were synthesized on carbon fiber substrates using a chemical vapor infiltration (CVI) vapor–solid (VS) growth mechanism. An additional SiC surface coating process was utilized after whisker deposition by controlling the input gas ratio of the source gas flow and changing the H_2 (hydrogen) diluent gas to N_2 (nitrogen) under the same deposition temperature of 1,300 °C. As the surface coating deposition time increased, whiskers thickness and spherical blunt tips which were seen at the top edge of the whiskers went thicker. Observing the microstructure of the resulting tips by transmission electron microscopy (TEM) revealed that uncoated whiskers showed few stacking faults, whereas surface-coated whiskers were completely filled with stacking faults. The effect of surface coating deposition time was also evaluated by measuring the properties of a filtration system. Specifically, as the surface coating deposition time increased, gas permeability decreased; however, even at 30 min, the gas permeability of the thickest surface coated whisker filters was five times higher than that of cordierite honeycomb, which is currently used in commercial diesel particulate filter (DPF) devices. A specimen that had been surface coated for more than 20 min almost completely maintained its prime line density under high-pressure (5 MPa) gas. Moreover, we confirmed that SiC surface coating on whiskers and carbon fiber substrates enhanced oxidation resistance and filtration efficiency.

Keywords: D. SiC; Carbon fiber; Diesel particulate filter; Surface-coated whisker

1. Introduction

Particulate matter (PM) is an important environmental air pollutant in terms of both human and ecological health [1,2]. For this reason, high filtration technologies that can reduce PM pollution are necessary. In this study, we propose a new filter structure consisting of surface-coated SiC whiskers grown on a carbon fiber substrate for diesel particulate filter (DPF) applications. Carbon fibers are light and have high strength and flexibility, and therefore their use can eliminate shape restrictions in manufacturing filter devices. As SiC is known for its excellent mechanical and physical properties [3], SiC whiskers can also be used at high temperatures, powers, and frequencies, as well as in severe environmental conditions. Therefore, we expect surface-coated SiC whiskers on a carbon fiber substrate to result in improved filtration properties for DPFs and other filter applications, including incinerators and electronic power stations.

SiC whiskers have been grown by several processes, including carbothermal reduction of silica [4], chemical reaction between silicon halides and CCl_4 [5], and CVD using metallic catalysts such as Ni or Fe [6]. In the present study, we grew SiC whiskers through a vapor–solid (VS) mechanism without catalysts by the chemical vapor infiltration (CVI) process [7]. To utilize these whiskers for filtration devices, the whiskers need to be arranged deeply inside the pores of a porous substrate. However, methods that use catalysts are not effective for prearranging the catalyst inside pores. Thus, the VS method has more advantages for filling micropores with whiskers. In addition, to maximize SiC whiskers utilize in filtration devices, additional SiC surface coatings can reinforce filter structure to improve both mechanical and chemical properties. The configuration of surface-coated SiC whiskers is depicted in Fig. 1. In this study, our goal was to investigate the morphological changes of surface-coated SiC whiskers on carbon fiber substrates using N_2 as the diluent gas. Moreover,

* Corresponding author. Tel.: +82 2 2123 2852; fax: +82 2 365 5882.
E-mail address: drchoidj@yonsei.ac.kr (D.J. Choi).

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.12.016

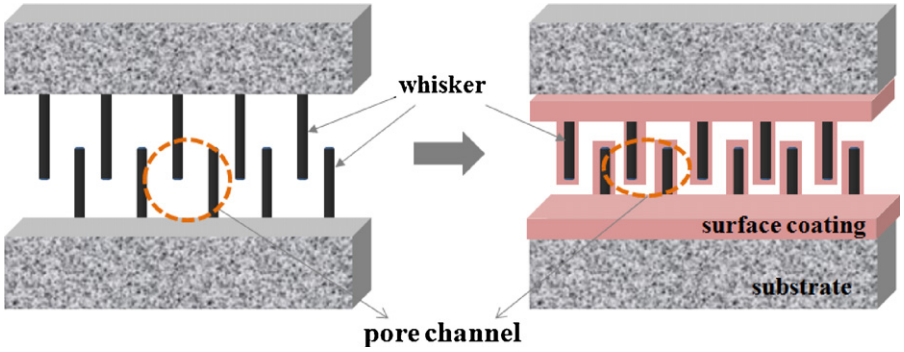

Fig. 1. Schematic showing the surface coatings on the carbon fiber substrates, demonstrating the effect of reduced pore size channels.

we evaluated filter properties of adhesion, gas permeability, oxidation resistance, and particle filtration efficiency for DPF applications.

2. Experimental

2.1. Filter fabrication

Whiskers and additional surface coatings were grown by the CVI process using low-pressure chemical vapor deposition (LPCVD) in a horizontal hot-wall furnace [7,8]. Carbon fiber (3327, Hankuk Carbon Co. LTD., Korea) was used as a substrate, which was cleaned with methyl alcohol and deionized (DI) water and then dried at 100 °C in a desiccator. A cordierite honeycomb (Honeycomb, Ceracomb, Korea) filter was used for comparison of gas permeability. Methyltrichlorosilane (CH_3SiCl_3, MTS, 99%, Aldrich) was used as the source, H_2 was used as the carrier gas, and N_2 or H_2 was used as the diluent gas. In this study, the applied input gas ratio, α, was defined as the ratio of the total diluent gas flow to the MTS source flow ($\alpha = H_2$ or N_2/MTS). The details of the deposition conditions are shown in Table 1.

2.2. Characterization methods

Morphology was characterized using scanning electron microscopy (SEM) (FESEM, FEI XL-30 FEG) and transmission electron microscopy (TEM) (JEM-2100 JEOL). The X-ray diffraction patterns of the whiskers were recorded with an advanced diffractometer (Rigaku Corporation, D/max 2200 V/PC) in the 2θ range of 30–80°.

Tests were performed to characterize whisker adhesion, gas permeability, oxidation resistance, and filtration efficiency. Whisker adhesion was evaluated by applying high pressure gas at room temperature. All specimens were fixed on an assembly frame, and a high gas pressure of 5 MPa of N_2 was applied. Line density was measured in order to define the growth density of whiskers in specific areas. Gas permeability was measured by injection of N_2 gas at a pressure from 5 kPa to 25 kPa at room temperature. The gas permeability flow rates of our surface-coated fabric filter (double-ply) and cordierite honeycomb filters were compared. Evaluation of oxidation resistance was performed by heating the specimens to temperatures ranging from 400 to 1,000 °C in air. The heating rate was 6 °C/min, and the temperature was held constant for 180 s at each step. The weight loss of each specimen was measured after the heating program.

Filtration efficiency was evaluated using DI water mixed with carbon black (Dae-Jung Chemicals, Korea). A dispersing agent was used to avoid agglomeration. Particles of carbon black were filtered from the solution, and the size distribution of particles that penetrated the specimen filter (double-ply) was measured with a relative particle size analyzer (Malvern-Mastersize 2000).

3. Results and discussion

3.1. Morphological characteristics

Fig. 2 shows the morphologies of SiC whiskers deposited on the carbon fiber substrate, as well as the additional SiC surface coatings deposited, for different deposition times. We observed the progress of whisker blunting by the additional surface coating process. Fig. 2(a) shows that each whisker has a sharp edge at the top end, which can form only by the VS whisker growth mechanism without the use of a catalyst. Most studies use the vapor–liquid–solid (VLS) method for synthesizing SiC whiskers; however, this VLS method necessarily results in

Table 1
Deposition conditions for SiC whiskers and surface coatings.

Section	Diluent gas species	Input gas ratio (α)	Pressure (Pa)	Temperature (°C)	Deposition time (min)
Whiskers	H_2	50	533	1300	60
Surface coatings	N_2	10	533	1300	10
					20
					30

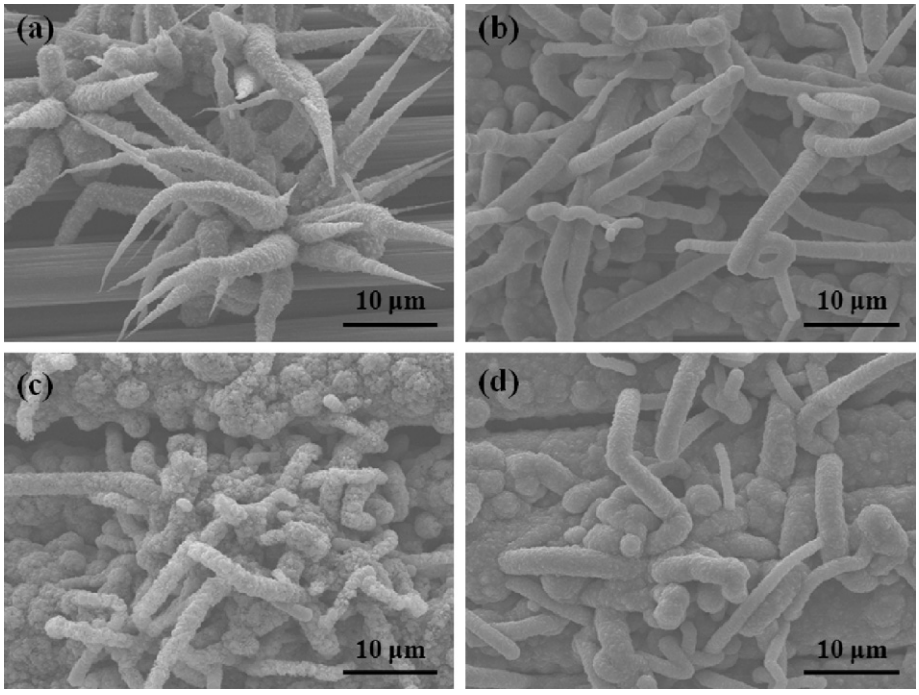

Fig. 2. Morphology of SiC whiskers deposited on carbon fibers with additional SiC surface coatings for various deposition times: (a) uncoated whiskers, (b) whiskers coated for 10 min, (c) whiskers coated for 20 min, and (d) whiskers coated for 30 min.

spherical tips that are a result of the use of metallic catalysts [9,10]. Thus, our uncoated whisker growth can be explained by the use of the VS deposition mechanism. For specimens surface-coated for 10 min, 20 min and 30 min in Fig. 2(b)–(d), spherical blunt tips were seen at the top edge of the whiskers and these tips went thicker as the surface-coated deposition time increased. These tips are clearly depicted in Fig. 3 which is subscribed latter in this paper. For the specimen surface-coated for 30 min at Fig. 2(d), we noted whiskers that partially stick together and form a mass cluster. This cluster can make the whiskers lose their individual and structural string properties, leading to functional performance reduction in filtration devices.

Our observations of the carbon fiber substrate were focused on the surface state and the space between carbon fibers with respect to increasing surface coating deposition time. Fig. 2 shows the progress of carbon fiber gap space reduced by the additional surface coating process. In addition, the specimen

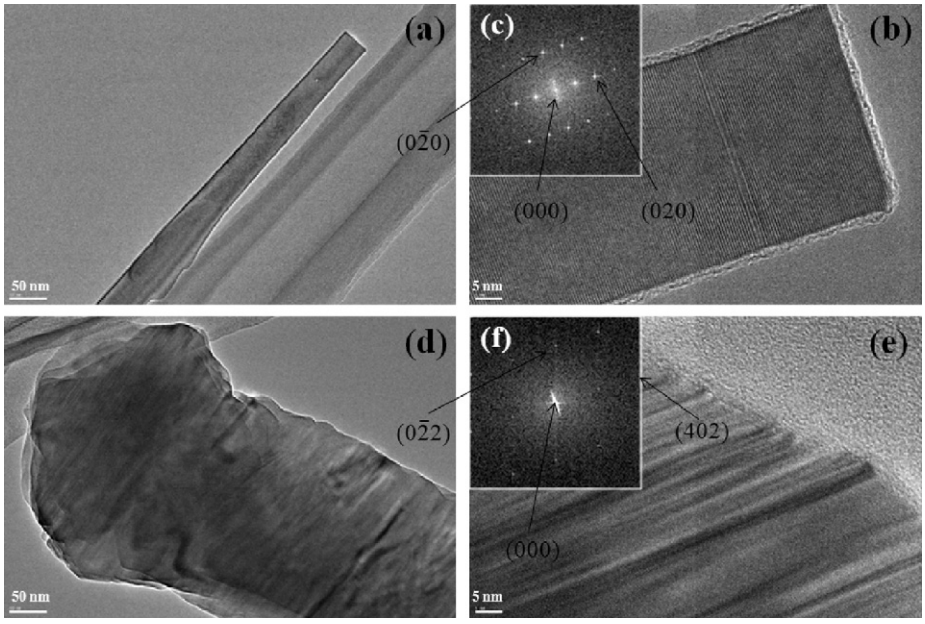

Fig. 3. Microstructures of β-SiC whiskers: (a) TEM image of an uncoated whisker, (b) high-resolution TEM image of the whisker in (a), (c) FFT pattern of a whisker (a), (d) TEM image of a 20 min coated whisker, (e) high-resolution TEM image of the whisker in (d), and (f) FFT pattern of a whisker (d).

that was surface coated for 10 min exhibited partial SiC coatings on the carbon fiber substrate, while the specimen that was surface coated for over 20 min exhibited complete SiC coatings on the carbon fiber substrate. To synthesize a fine coating layer, inside carbon fiber filaments must be surface coated like the outside of the carbon fiber substrate. In our research, we chose N_2 for the diluent gas to deposit surface coatings on carbon fiber substrates. According to Lee et al. [11], the use of N_2 as a diluent gas produces a lower reactant depletion effect than H_2. This means that N_2 gas can push source gas molecules such that they reach more deeply inside carbon fiber space than when H_2 is used, and the difference can be explained by differences in the molecular weights of N_2 and H_2. Therefore, we expected that using N_2 as the diluent gas would produce a more uniformed surface coating process. Moreover, N_2 was expected to result in whisker diameter growth as opposed to whisker elongation. In our study, this was confirmed by comparing the sizes of uncoated and surface coated whiskers, which showed almost no differences in vertical length but did exhibit increased thickness.

Fig. 3 shows the TEM microstructures of the top ends of the uncoated whiskers and 20 min coated whiskers. In Fig. 3(a), in which the whiskers were not coated, a slim edge of the top end of whisker is visible. However, Fig. 3(d) shows that the additional surface coating made the whisker edges thicker and more spherical. This could be explained by the potential energy difference in which the top edge of the whisker had more dangling bonds that possess higher dipole moments and more unstable surface energy. Therefore during the deposition process, heterogeneous reactant atoms may have preferred to move toward the unstable position at the end of whisker, leading to the round tips. In addition, we observed stacking faults of the top ends of the uncoated whiskers and 20 min coated whiskers. While Fig. 3(b) has a few examples of these stacking faults, Fig. 3(e) shows a tip completely filled with stacking faults. Thus, we concluded that the additional SiC surface coating and SiC whiskers are inhomogeneous. This stacking fault difference can be explained by the diluent gas, which was changed from H_2 to N_2. Specifically, as N_2 decomposed to a single nitrogen atom, a small amount of interstitial nitrogen may have increased the stress on a material, leading to disorder on and around the interstitial site. In support of this observation, other studies have indicated that heavy nitrogen doping favors the formation of stacking faults in SiC [12]. The diffraction (FFT) pattern of Fig. 3(c) and Fig. 3(f) was taken at the electron beam direction of [0 0 1], [–1 2 2], respectively, and the pattern showed that both SiC whiskers and SiC surface coating were highly crystalline within FCC structures.

We employed XRD to compare the phases of the whiskers using H_2 or N_2 as the diluent gas with different deposition times. Previously, XRD patterns of SiC whisker-containing composite coatings deposited at 1,100 °C using H_2 and N_2 as diluent gas have been reported [7]. In this study, we focused on whiskers deposited at 1,300 °C with surface coating only using N_2 as the diluent gas and carbon fibers as the substrate. Fig. 4 shows the XRD patterns of uncoated and 20 min surface-coated

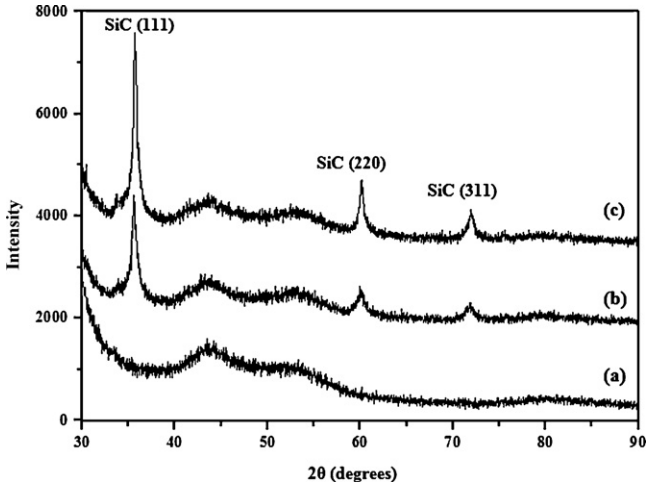

Fig. 4. XRD patterns of whiskers and surface-coated whiskers (T_{dep} = 1,300 °C): (a) bare carbon fiber substrate, (b) whiskers grown at α = 50 with H_2 dilution gas, and (c) additional surface coating grown on the whiskers at α = 10 with N_2 dilution gas for 20 min.

whiskers. Except for the carbon fiber peaks, peaks around 2θ values of SiC (1 1 1), SiC (2 2 0), and SiC (3 1 1) were all observed. This result indicates that both specimens were composed entirely of cubic β-SiC [13]. Although the specimen in Fig. 4(b) was deposited with N_2 as the diluent gas instead of H_2, the XRD pattern showed no difference of β-SiC phase peaks at (1 1 1), (2 2 0), and (3 1 1). In addition, the specimen in Fig. 4(c) shows higher intensities than the specimen in Fig. 4(b). As shown in Fig. 3, the whisker and surface coating were both confirmed to have high crystalline structure, the difference in intensity of which can be explained by the enlarged area of the surface-coated whiskers, which increased the possibility of diffraction regions.

3.2. Mechanical and chemical property tests

Fig. 5 shows the plots of line density changes of whiskers, evaluating the adhesion preservation under a high-pressure

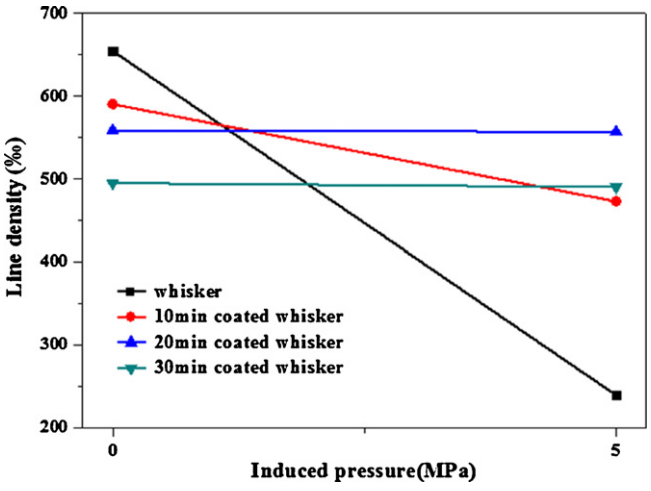

Fig. 5. Plots of line density change of whiskers evaluating adhesion preservation under a high-pressure (5 MPa) injected N_2 gas.

(5 MPa) N_2 gas. First, the whisker line densities before gas injection were compared. The line density of the specimen with uncoated whiskers was the highest, with a value of 650‰. However, as the surface coating deposition time increased, the whisker line density decreased. These decrements were related to the line density criterion that is achieved for whiskers or substrates. Specifically, as shown previously in this study, diameter growth with surface coating on the whiskers is preferred to elongation, so the root part of the whisker grew thicker and more attached to the surface-coated carbon fiber substrate body. Thus, the bottom bodies of the whiskers, which were mixed with the fiber substrates, were excluded in the line density measurement. Unlike the line density before gas injection, the tendency after gas injection was toward greater variability. The line density of uncoated whiskers decreased by 400‰, but a specimen that had been surface-coated for more than 20 min maintained its prime line density almost completely. Based on these results, we concluded that the additional surface coating enlarged the interface area between whiskers and carbon fiber substrates, and that this enlarged area stabilized the structure under high-pressure gas conditions.

Fig. 6 shows the gas permeabilities of specimens coated for different deposition times. As the additional surface coating time increased, the gas permeability decreased. Although the specimen that had been surface-coated for 30 min had the worst gas permeability of any of our samples, the filter had a gas permeability five times higher than cordierite honeycomb, which is currently used commercially. This indicates that, even when the pores are reduced by additional surface coatings, it does not significantly influence gas permeability.

Fig. 7 shows the oxidation resistances of specimens prepared using different surface coating deposition times. First, the bare substrate showed rapid oxidation around 600 °C. The filter with uncoated whiskers showed about a 100 °C higher oxidation temperature, demonstrating increased oxidation resistance, as compared to the bare substrate. Further, filters that had been coated for more than 20 min showed rapid oxidation around

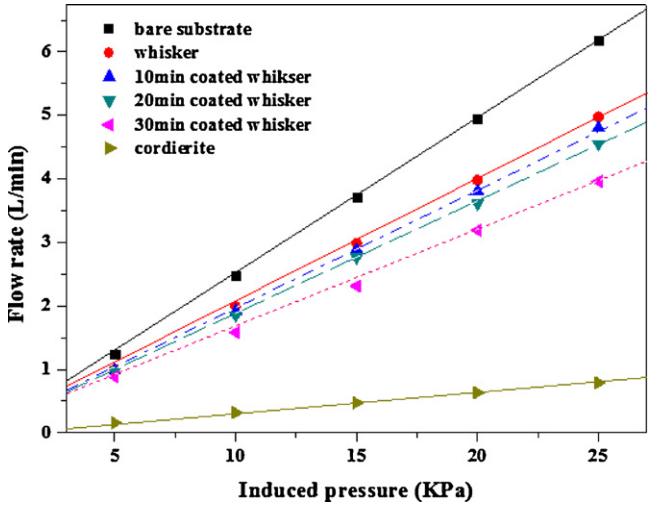

Fig. 6. Gas permeability of surface-coated filters for different SiC surface coating deposition times. A cordierite honeycomb filter and a bare fabric filter are shown for comparison purposes [injected gas: N_2].

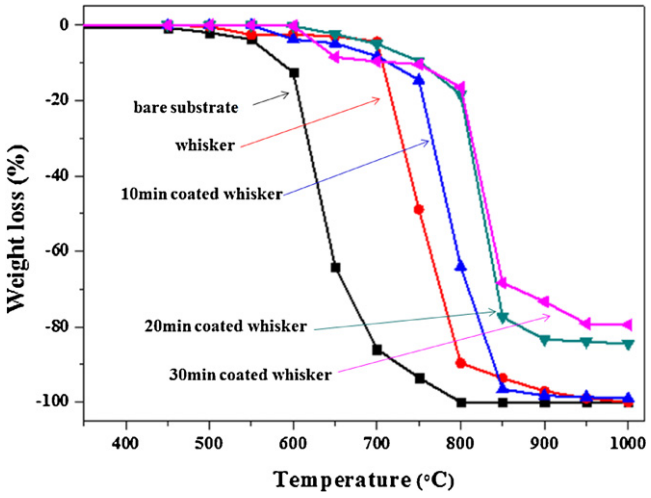

Fig. 7. Thermal resistance of surface-coated filters for different SiC surface coating deposition times [heating rate = 6 °C/min with the temperature held for 3 min at each step].

800 °C, indicating that the additional surface coating, deposited for more than 20 min, improved the oxidation resistance temperature by up to 200 °C, as compared to the bare substrate filter. However, the oxidation behavior of our surface-coated filter, when compared with that of other studies of SiC coating [14], was lower than expected. This could be attributable to a mismatch between the SiC coating and the carbon fiber substrate. According to Cheng et al. [15], such mismatches can produce cracks at temperatures below the deposition temperature, opening channels of oxygen diffusion. Thus, as the burning temperature increased, surface cracks on the coating layer were partially revealed, which provided an oxygen path to the carbon substrate to burn.

For the filtration efficiency test, carbon black particles that had passed through our specimen trap filter were measured by a relative particle size analyzer. Fig. 8(a) shows the relative distribution curves of the carbon black particles sizes after filtration. The distribution curve of dispersed carbon black was wide, ranging from 0.32 μm to 17.38 μm. These particles were then filtered by the bare substrate, and the particle sizes decreased slightly from 0.32 μm to 6.61 μm. This indicates that particles larger than 6.61 μm were captured by the gap between the carbon fibers substrate. For a specimen with uncoated whiskers, particles larger than 0.72 μm were partially detected, which is shown in the left part of the graph curve. The 20 min surface-coated filter, which was shown to be more efficient than any other specimen in previous field trials, also showed higher filtration efficiency, as heavy particles larger than 1.10 μm were partially detected. Arrows in Fig. 8(b) indicate the trapped minimum particle sizes of each specimen filter. The 20 min surface-coated filter showed the best filtration efficiency in trapping small particles compared with the other filter specimens. Although almost all of the particles were trapped by the filter, 1-μm sized particles were still found, which may have happened because large, heavy particles reach the filter more quickly than smaller particles. As the filter possesses relatively large pores, several heavy particles that

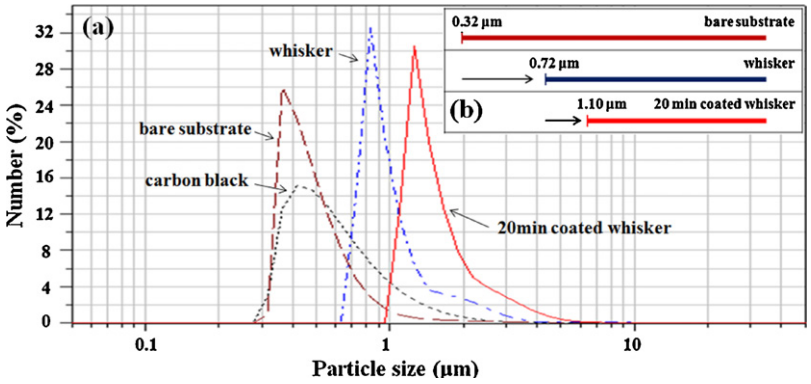

Fig. 8. (a) Relative size distribution of infiltrated particles through a carbon fiber filter without surface deposition, and filters with uncoated whiskers and whiskers coated for 20 min. (b) Arrows indicate the trapped minimum particle sizes of each specimen filter.

reach the filter first can initially penetrate; however, after these pores are closed more particles are captured, thereby eliminating paths by which small particles can penetrate. Since this type of measurement uses relative statistics, these few penetrated particles were detected and are expressed in the graphs. Therefore, our data showed that the surface coating resulted in improved filtration efficiency compared to uncoated whiskers.

4. Conclusions

SiC whiskers and additional SiC surface coatings were produced by LPCVD with a surface coating process following whisker deposition at the same deposition temperature of 1,300 °C. Surface coating was performed by controlling the input gas ratio of the source gas flow and changing the diluent gas from H_2 to N_2. We observed the changes of whisker and carbon fibers, and as surface coating deposition time increased, the spherical blunt tips became thicker at the top edge of the whiskers. Through observation of the TEM images of the tips, we found that the uncoated whiskers showed few stacking faults, whereas the surface-coated whiskers were completely filled with stacking faults. The effects of surface coating deposition time were evaluated by measuring the properties of the filtration system. As the surface coating deposition time increased, the filters showed improved adhesion, oxidation resistance, and filtration efficiency. In this study, a specimen that had been surface coated for 20 min demonstrated the best blend of properties. The addition of surface coatings on whiskers not only reduced the sizes of the pore channels, but also resulted in high gas permeability for use in filtration devices. In conclusion, in the present study we have proposed a new filtration device that involves a simpler structure, lighter weight, lower cost, and improved mechanical properties, compared to DPF devices currently used in industrial applications.

Acknowledgment

This work is the outcome of a Manpower Development Program for Energy & Resources supported by the Ministry of Knowledge and Economy (MKE).

References

[1] F. Saint-Georges, G. Garcon, F. Escande, P. Shirali, et al., Role of air pollution particulate matter (PM2.5) in the occurrence of loss of heterozygosity in multiple critical regions of 3p chromosome in human epithelial lung cells (L132), Toxicol. Lett. 187 (2009) 172–179.
[2] N. Bai, M. Khazaei, S. Eeden, I. Laher, The pharmacology of particulate matter air pollution-induced cardiovascular dysfunction, Pharmacol. Ther. 113 (2007) 16–29.
[3] D. Jianxin, Z. Jinlong, L. Yousheng, S. Wenlong, Microstructure and mechanical properties of hot-pressed SiC/(W, Ti)C ceramic composites, Ceram. Int. 34 (2008) 1361–1366.
[4] N.K. Sharma, W.S. Williams, A. Zangvil, Formation and structure of silicon carbide whiskers from Rice Hulls, J. Am. Ceram. Soc. 67 (1984) 715–720.
[5] N. Sedaka, K. Ajiri, Influence of vapor-phase composition on morphology of SiC single crystals, J. Am. Ceram. Soc. 55 (1972) 540.
[6] J.V. Milewski, F.D. Gac, J.J. Petrovic, S.R. Skaggs, Growth of beta-silicon carbide whiskers by the VLS process, J. Mater. Sci. 20 (1985) 1160–1166.
[7] H.S. Ahn, D.J. Choi, Fabrication of silicon carbide whiskers and whisker-containing composite coatings without using a metallic catalyst, Surf. Coat. Technol. 154 (2002) 276–281.
[8] G.E. Youngblood, D.J. Senor, R.H. Jones, S. Graham, The transverse thermal conductivity of 2D-SiCf/SiC composites, Compos. Sci. Technol. 62 (2002) 1127–1139.
[9] I.C. Leu, Y.M. Lu, M.H. Hon, Factors determining the diameter of silicon carbide whiskers prepared by chemical vapor deposition, Mater. Chem. Phys. 56 (1998) 256–261.
[10] H.J. Choi, J.G. Lee, Stacking faults in silicon carbide whiskers, Ceram. Int. 26 (2000) 7–12.
[11] Y.J. Lee, D.J. Choi, S.S. Kim, H.L. Lee, H.D. Kim, Comparison of diluent gas effect on the growth behavior of horizontal CVD SiC with analytical and experimental data, Surf. Coat. Technol. 177–178 (2004) 415–419.
[12] K. Irmscher, M. Albrecht, M. Rossberg, H.J. Rost, D. Siche, G. Wagner, Formation and properties of stacking faults in nitrogen-doped 4H-SiC, Physica B 376–377 (2006) 338–341.
[13] G. Amirthan, A. Udayakumar, V.V. Bhanu Prasad, M. Balasubramanian, Properties of Si/SiC ceramic composite subjected to chemical vapour infiltration, Ceram. Int. 35 (2009) 2601–2607.
[14] X. Yang, Y.H. Zou, Q.Z. Huang, Z.A. Su, X. Chang, M.Y. Zhang, Y. Xiao, Improved oxidation resistance of chemical vapor reaction SiC coating modified with silica for carbon/carbon composites, J. Cent. South Univ. Technol. 17 (2010) 1–6.
[15] L. Cheng, Y. Xu, L. Zhang, X. Yin, Effect of coating defects on oxidation behavior of three dimensional C/SiC composites from room temperature to 1500 °C, J. Mater. Sci. 37 (2002) 5339–5344.