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Chemical vapor infiltration (CVI) SiC whisker on carbon woven fabric for filter applications

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β-silicon carbide whiskers have been synthesized on a carbon fabric by a vapor–solid (VS) mechanism using the Chemical Vapor Infiltration (CVI) process. Optimum processing conditions for SiC whisker growth were determined by mapping of SiC deposition behavior. SiC was deposited on a carbon fabric substrate as a film or whiskers, depending on processing conditions. The mean diameter and line density of the whiskers was the highest at an input gas ratio of 50. As temperature increases, the mean diameter of the whiskers increased and the line density of whiskers decreased. In the optimum processing conditions, whiskers grew uniformly with high growth density and formed a networking structure between each of the carbon filaments resulting in a structure suitable for filter applications.

Key-words : Silicon carbide, Whisker, Vapor–solid mechanism, Carbon fabric, Mapping, Networking structure, Filter

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1. Introduction

In modern industry, environmental pollution has been one of the most important topics.[1] For this reason, filtering technologies have been widely studied by many research groups in order to reduce pollution. In this study, we suggested carbon woven fabric as a substrate for filter applications. Carbon woven fabric substrate is flexible, which eliminates shape restrictions in filter manufacturing. Also, using fabric substrate can avoid a brittle fracture, which is one of the problems in conventional ceramic filters. Therefore, we expect SiC whiskers to be grown on the carbon woven fabric substrate, improving filtering properties for applications in diesel particulate filters (DPF), and filters for incinerators, electronic power stations, etc.

Silicon carbide whiskers have been widely researched since they are effective materials for the reinforcement of various composite materials due to their outstanding mechanical and chemical properties.[2),3)] Whiskers have been produced by several processes such as carbothermal reduction of silica,[4),5)] reaction between silicon halides and CCl_4,[6)] and chemical vapor deposition using a metallic catalyst like Ni or Fe.[7)] Among these processes, chemical vapor deposition (CVD) methods have been widely used because they result in homogeneous whiskers.

In this study, we tried to form pore sizes in the carbon woven fabric smaller by growing SiC whiskers through a vapor–solid (VS) mechanism using the Chemical Vapor Infiltration (CVI) process. The effects of input gas ratio and deposition temperature were examined with respect to their impact on control of whisker mean diameter and growth density.

2. Experimental procedure

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)] Carbon woven fabric (Hankuk Carbon Co., LTD.) with a filament diameter of 8 μm was used as a substrate. Round substrates with radii of

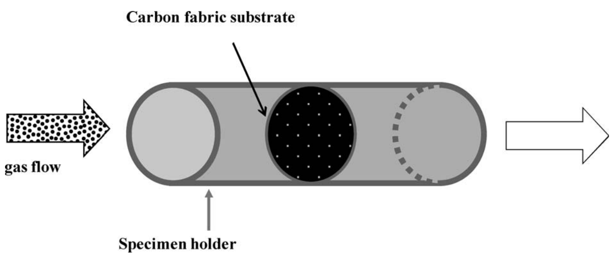

Fig. 1. Schematic diagram of substrate and specimen holder.

1.5 cm were used and the substrate was held by a specimen holder vertically to the gas flow in the furnace as shown in **Fig. 1**. Substrates were cleaned using methyl alcohol and DI water for 1 min, and then dried at 100°C in a dry oven. Methyltrichlorosilane (CH_3SiCl_3, MTS, Acros Organics Co., USA) was used as a source and hydrogen (H_2) gas was used as the dilution 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).[10)] SiC whiskers were deposited at an input gas ratio range from 10 to 70 and the total pressure was fixed at 667 Pa. The deposition temperature was varied from 1100°C to 1300°C and the deposition time was 60 min. After the deposition process, the morphologies of the whiskers were characterized by scanning electron microscopy (SEM; FESEM, JOEL Ltd., JSM–6700F). The composition and phase of the whiskers were examined by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD; Regaku Co., D/Max rint2000). Line density was measured to define the growth density of whiskers at various deposition conditions. Details of line density measurements were described in our previous report.[10)]

3. Results and discussion

The deposition of SiC on the carbon fabric was classified into four different behaviors including film deposition (■), low growth density of the whiskers (△), medium growth density of

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whiskers (●), and high growth density of the whiskers (★), as shown in **Fig. 2**. Figure 2(a) (1200°C, α = 10) shows a SEM image of the diameter increase in each filament of carbon fabric as SiC films are wrapping the filament of the fabric. Figure 2(b) (1150°C, α = 30) shows the SEM image of low whisker growth density on the carbon fabric, where few whiskers were grown. At medium whisker growth density as shown in Fig. 2(c) (1200°C, α = 30), whiskers wrap around the filament of the carbon fabric but not whole area of the fabric. High whisker growth density also occurred, where whiskers were deposited on the whole area of the fabric as shown in Fig. 2(d) (1200°C, α = 50).

Based on these four classifications of deposition behaviors, we made a map of SiC deposition as a function of process conditions, as shown in **Fig. 3**. At an α (input gas ratio) of 50, the growth density of the whiskers is relatively high in the deposition temperature range from 1200°C to 1300°C. On the other hand, a delamination phenomenon was observed for all specimens deposited at 1250°C and 1300°C. For these conditions, the whiskers could be easily separated from substrate although they had medium and high growth density. We believe that the delamination occurred due to differences in the thermal expansion coefficient between carbon fabric substrate and silicon carbide whisker during cooling down after the experimental process.

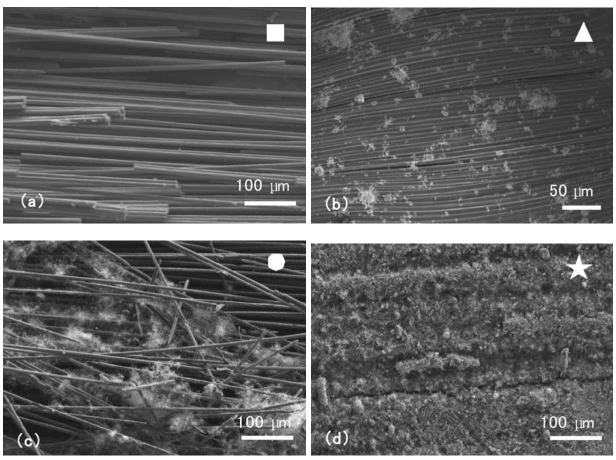

Fig. 2. Classification of SiC deposition behavior on carbon fabric: (a) film, (b) low growth density of whisker, (c) medium growth density of whisker, (d) high growth density of whisker.

Figure 4 shows SEM images of changes in microstructure with varying process conditions. Figures 4(a, b, c, and d) correspond with the vertical rectangle in Fig. 3: α values of 10, 30, 50, 70 at 1200°C. A SiC film of about 1.5 μm was observed with the canning effect (Fig. 4(a), inset)[11),12)] only at an α of 10. The canning phenomenon is caused by the different reaction rates in the deposition reaction and the mass transport reaction of the reactant gases.[12)] As α increases, whiskers grew instead of the film, as shown in Fig. 4(b). As in a previous study by Ahn and Choi,[8)] deposition rate increases as α decreases, so that the deposition mechanism changes, especially for α values less than 10. Thus, it is assumed that, in this study, the deposition rate increases rapidly for α values between 10 and 30, so that a mechanism for whisker growth changes to a mechanism for film deposition at 1200°C. As α increases to 50 and 70 from 30, whisker growth in a broad area was observed as shown in Fig. 4(c) and Fig. 4(d). Considering that the substrate is placed in the specimen holder as shown in Fig. 1, we assume that the reactant gas can reach a broad area of the surface of the substrate due to a high quantity of total gas flow rate at α values of 50 and 70, i.e., 510 and 710 sccm (standard cubic centimeters per minute), respectively. Thus it seems that at an α value of 30, whiskers grew gathered together as shown in Fig. 4(b) due to a low quantity of total gas flow, 310 sccm. Figures 4(e, f, g, and h) correspond with the horizontal rectangle in Fig. 3 with deposition temperatures of 1150, 1200, 1250, 1300°C at an α of 50. As deposition temperature increases beyond 1200°C, the whiskers grew with a high growth density as shown in Fig. 4(f, g, and h). Further, increases in the length and diameter of the whiskers were observed at 1250, 1300°C, as shown in Fig. 4(g) and Fig. 4(h), respectively. The tendency of mean diameter to increase as temperature increases can be explained by the increase in the rate of the decomposition reaction of MTS and an increase in the diffusivity of reactants on the surface of substrate. Further, we assume that nucleation is relatively more dominant than growth at 1200°C, while growth is relatively more dominant than nucleation at 1250 and 1300°C due to an increase in diffusivity at relatively higher temperatures. Also, it is reported that in the VS mechanism, the axial growth of whiskers occurs where screw dislocations exist at the tip of the whisker because those dislocations act as accommodation sites for the atoms to attach.[13)] Radial growth might be induced by micro facets, which were formed by microtwins.[14)] From these explanations, we infer that a rapid deposition reaction caused by high temperature (more than 1250°C) leads to occur-

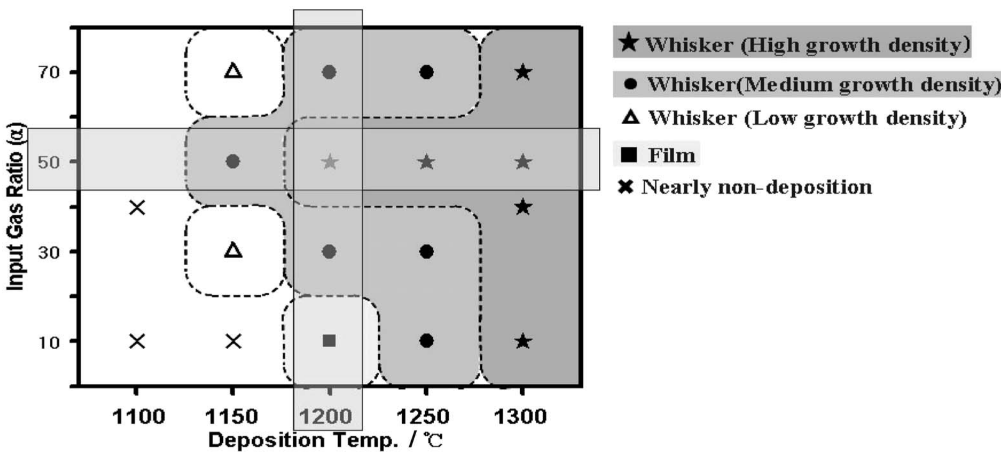

Fig. 3. Map of SiC deposition behavior on carbon woven fabric as a function of processing conditions (P_{dep} = 667 Pa, T_{dep} = 1 h).

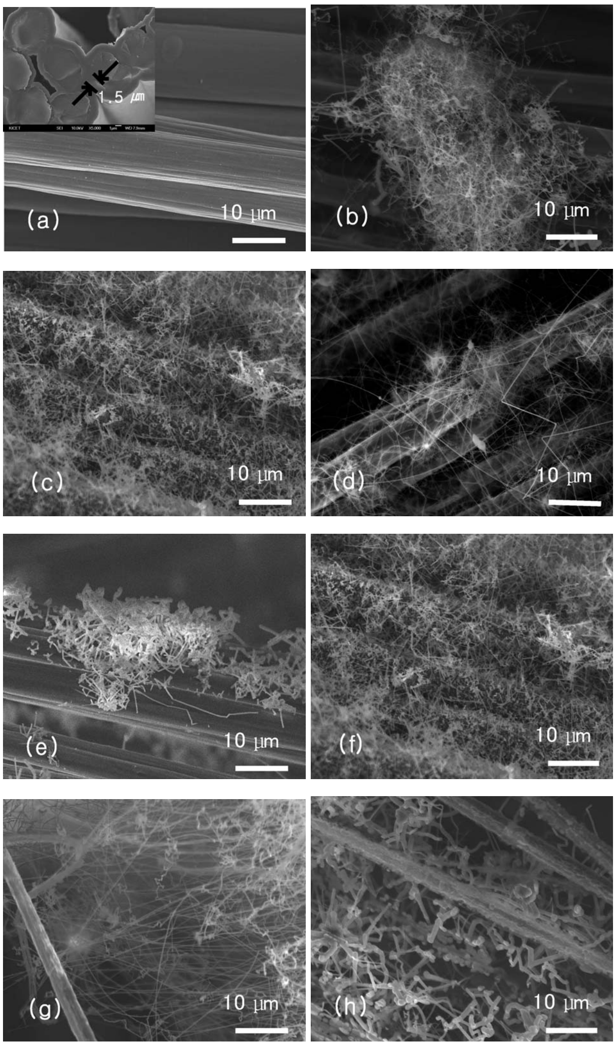

Fig. 4. SEM images of the SiC film and whiskers with varying input gas ratios, (a) $\alpha = 10$, (b) $\alpha = 30$, (c) $\alpha = 50$ and (d) $\alpha = 70$ at fixed temperature of 1200°C and with varying processing temperatures, (e) 1150°C, (f) 1200°C, (g) 1250°C and (h) 1300°C at fixed α of 50.

rence of more defects in a whisker, and these defects accelerate axial and radial growth of the whisker.

Figure 5(a) shows the change in line density and diameter of whiskers as a function of input gas ratio. In accordance with the findings of Lim et al.,[15] an increase in the input gas ratio causes a decrease in whisker mean diameter due to a decrease in the excessive free carbon in the SiC whisker. This is explained by the fact that the excessive free carbon produces higher surface energy sites.[15] Ahn and Choi[8] also reported that an increase in the input gas ratio causes a decrease in whisker mean diameter. In this study, the mean diameter and line density decrease as either α increases or decreases from an α value of 50 as shown in Fig. 5(a). We assume that this difference of input gas ratio dependency is caused by the shape of susceptor (the specimen holder). In this study, the woven fabric substrate was held vertically to a gas flow using a cylinder shaped specimen holder as shown in Fig. 1. Thus, the quantity of reactant gas affects the velocity of the reactant gas infiltrating the substrate because, for small quantities of gas, it is easy to infiltrate the carbon fabric. With a decrease in α from 50 to 30, the decrease in line density and whisker diameter seem to be caused by a decrease in resi-

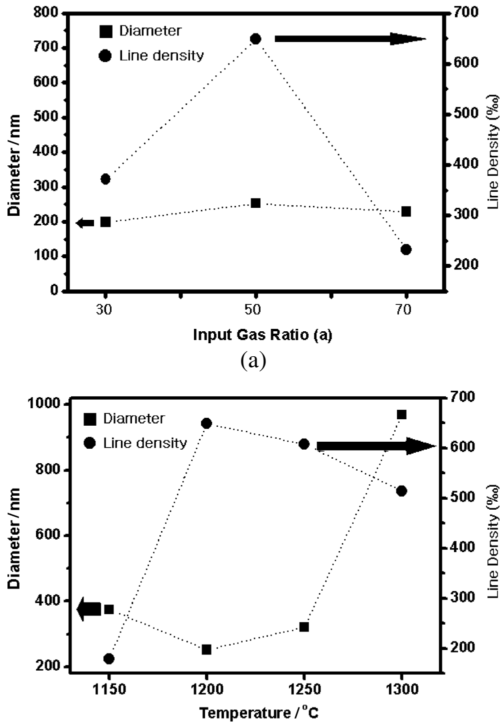

Fig. 5. Change in whisker mean diameter and line density as (a) a function of input gas ratio and (b) as a function of temperature.

dence time of the reactant gas due to a small amount of total gas flow. On the other hand, for an increase of α from 50 to 70, the line density and diameter of whisker decrease seem to be caused by a decrease in the MTS concentration due to highly diluted reactant gas at α of 70 (α = H_2/MTS). Figure 5(b) shows the change in line density and whisker diameter as a function of temperature. We believe that at 1150°C, it is still hard for nucleation and subsequent SiC whisker growth to occur due to the high activation energy at relatively low deposition temperatures. Gathered growth and the slightly larger diameter of the whiskers at 1150°C, as shown in Fig. 4(e) and Fig. 5(b), seem to be caused by the fact that nucleation cannot occur easily at 1150°C. However once the nucleation and growth begin, the whisker grew continuously at that growth site. The mean diameter of whiskers grown at 1200, 1250, and 1300°C were 252, 321, 969 nm, while line density was 649, 608, 514‰, respectively, as shown in Fig. 5(b). Line density decreases as temperature increases beyond 1200°C. The reason for this can be explained in that nucleation is relatively dominant at 1200°C, as we assumed above, so that much whiskers with short lengths and small diameters occupy the largest dimension of fabric per unit area as shown in Fig. 4(f).

X-ray diffraction (XRD) confirmed that the whisker and film were β-silicon carbide. Energy dispersive spectroscopy analysis verifies that SiC film (1200°C, α of 10) and SiC whiskers (1200°C, α of 50) deposited on carbon fabric consist of C–57%, Si–43% and C–70%, Si–22%, O–8%, respectively.

4. Conclusion

Silicon carbide whiskers were grown on a carbon woven fabric substrate by a vapor–solid (VS) mechanism using the CVI process. The effect of temperature and input gas ratio was examined by mapping the deposition behavior of silicon carbide. The input gas ratio has an optimum value as α of 50 for high growth density of the whiskers. As deposition temperature increases, whiskers grew uniformly with an increase in mean diameter. However delamination occurs at temperatures above 1250°C. Thus, the optimum conditions for SiC whisker growth are thought to be 1200°C and α of 50. At optimum processing conditions, the mean whisker diameter was 252 nm and whiskers formed a networking structure between each filament of the carbon fabric substrate. It is expected that this microstructure will give great advantages for filter applications due to its high surface area and networking structure. Also, the results of this study will aid in controlling the microstructure of whiskers including diameter, growth density, and distribution of growth as variables change.

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