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A study of the chemical vapor deposited silicon carbide whisker growth and whisker-containing composite coating

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Many researchers have studied silicon carbide due to its excellent mechanical and chemical properties. Silicon carbide whiskers are important for reinforcement of CMC composites. However, metallic catalyst, which is necessary for the growth of whiskers, can cause degradation of their properties. Thus, we made silicon carbide whiskers without using a metallic catalyst. Whiskers were obtained with an input gas ratio of above 20, and their diameter decreased as the input gas ratio increased. We also deposited whisker-containing coatings based on these conditions by using nitrogen as a dilutant gas. The coatings obtained showed pebble-like structures, and their morphologies differ according to the whiskers grown under the coating layer.

Key words: silicon carbide, whisker, CVD, coating.

Introduction

Silicon carbide is an important material for potential applications in photoelectronics, high temperature semiconducting devices, hard wear resistant coatings and protective barriers for corrosion or thermal oxidation. All these applications are due to its unique properties such as wide band gap, high electron mobility, high thermal conductivity and high melting point. Thus, many researchers have studied this material for various applications.

Silicon carbide whiskers have been the subject of research for various applications because they are an effective material for the reinforcement of various composite materials due to their superb mechanical properties [1, 2]. Whiskers have been produced by several processes such as carbothermal reduction of silica [3-5], reaction between silicon halides and CCl_4 [6], and chemical vapor deposition using a metallic catalyst such as Ni or Fe [7, 8]. Among these, the carbothermal reduction and chemical vapor deposition methods have been widely used. However, whiskers, which were fabricated by the former process, did not show homogeneous properties. Moreover, in order to synthesize whisker by chemical vapor deposition, an additional process of forming the metallic catalyst is needed. In addition, the metallic catalyst that exists at the tip of the whisker acts as an impurity. This causes degradation in mechanical properties. To prevent this, another additional process is required to remove these catalysts. Considering all of these problems, we have made silicon carbide whisker without using a metallic catalyst. And based on those growth conditions, we deposited whisker-containing composite coating as well.

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Experimental Details

Figure 1 shows a schematic diagram of LPCVD system, which was used in this experiment. Silicon carbide whiskers and the whisker-containing coatings were grown in a hot-wall type horizontal CVD reactor, which has a double-tube structure to prevent turbulent flow. Methyltrichlorosilane (CH_3SiCl_3, MTS) was used as a precursor. Since it has silicon and carbon in a same mole ratio, it is easier to obtain stoichiometric silicon carbide than with other precursors. High purity hydrogen was used as a carrier gas and as a dilutant gas. Nitrogen was also used as a dilutant gas to deposit whisker-containing coatings. The carrier gas and dilutant gas flow rates were controlled by a Mass Flow Controller. The source gas flow rate was controlled by adjusting the bubbler pressure and equilibrium vapor pressure of the MTS. All the depositions, whiskering and coating were performed on Isotropic Graphite Substrates (Tokai Carbon Co., G347, Japan). Graphite substrates were polished with SiC papers. Details of the deposition conditions are in Table 1.

Deposition rates were measured by comparing the weight changes before and after the depositions. The crystalline phase was confirmed with X-ray diffractometry (XRD) at a wavelength of 1.5418 Å (using CuK_α radiation). Microstructures of deposits were examined with scanning electron microscopy (SEM, Hitachi S-2700/FESEM, Hitachi S-4200).

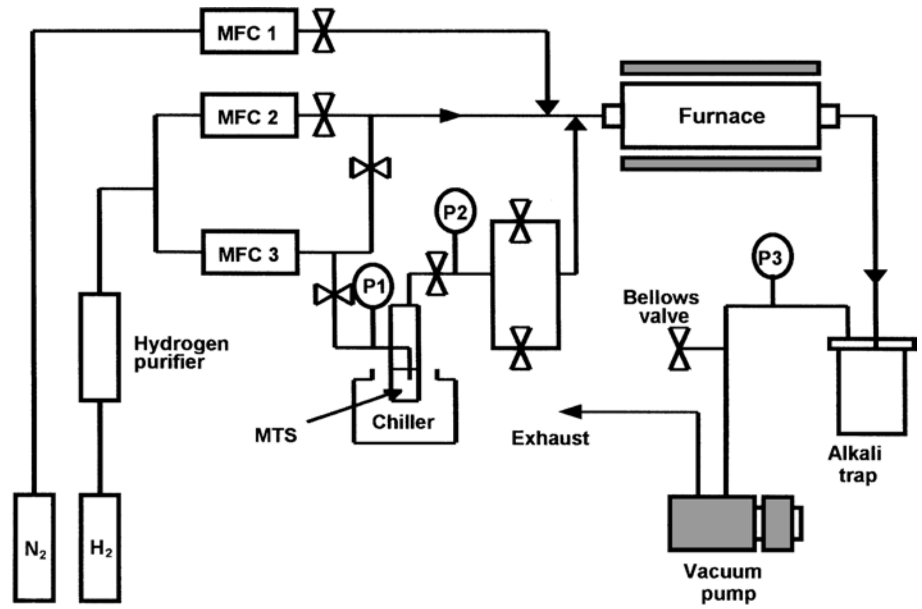

Fig. 1. The schematic diagram of CVD-SiC System.

Table 1. The details of the deposition conditions for whisker growth and the composite coating

Input gas ratio	Dilutant gas	Temperature (°C)	MTS flow rate (sccm)	Dilutant gas + Carrier gas flow rate (sccm)
10	H_2	1100	25	250
20	H_2	1100	25	500
30	H_2	1100	25	750
40	H_2	1100	25	1000
20/20	H_2/N_2	1100	25/25	500/500
30/20	H_2/N_2	1100	25/25	750/500

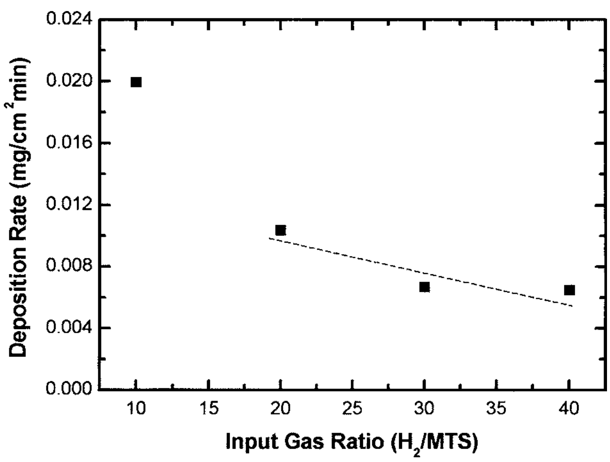

Fig. 2. The variation of the deposition rate as a function of input gas ratio.

Result and Discussion

Figure 2 shows the variation of the deposition rates as a function of input gas ratio. As input gas ratio increased, the deposition rates decreased. And there is a little difference in the decreasing behavior below an input gas ratio of 20 and above an input gas ratio of 20. This difference seems to be caused by differences in deposition mechanisms. This will be discussed later.

Figures 3 are SEM images of deposits. As we mentioned above, their morphologies looked quite different. When the input gas ratio was 10, a film with a pebble-like structure was deposited. But when the input gas ratio was over 20, a whisker shaped deposit was obtained. Also, there are some differences between Fig. 3(b) and Figs. 3(c), (d). In Fig. 3(b), lateral growth occurred in addition to axial growth. But in Figs. 3(c), (d), axial growth seems to be a predominant growth mechanism. We are suggesting that an input gas ratio of 20 is an intermediate area between film deposition and whisker growth. Whiskers that were grown by this process differ from those that were grown by the other processes [3-8]. The later usually have metal impurities on their tips. And in a case of the vapor-solid mechanism, the whisker diameter changed periodically, but this whisker type is unusual [9]. As shown in Fig. 4, the average whisker diameter decreased as the input gas ratio increased. Measured diameters were 0.94 μm, 0.44 μm, 0.39 μm when input gas ratios were 20, 30, 40, respectively.

By using hydrogen and nitrogen as dilutant gases, whisker-containing coatings were made at input gas ratios equal to 20 and 30. It was confirmed that both coatings are composed of silicon carbide in Fig. 5. Figures 6 shows surface and cross-sectional views of whisker-containing coatings. We can see two-layers, one is the whisker-containing coating and the other is a normal silicon carbide coating were successfully

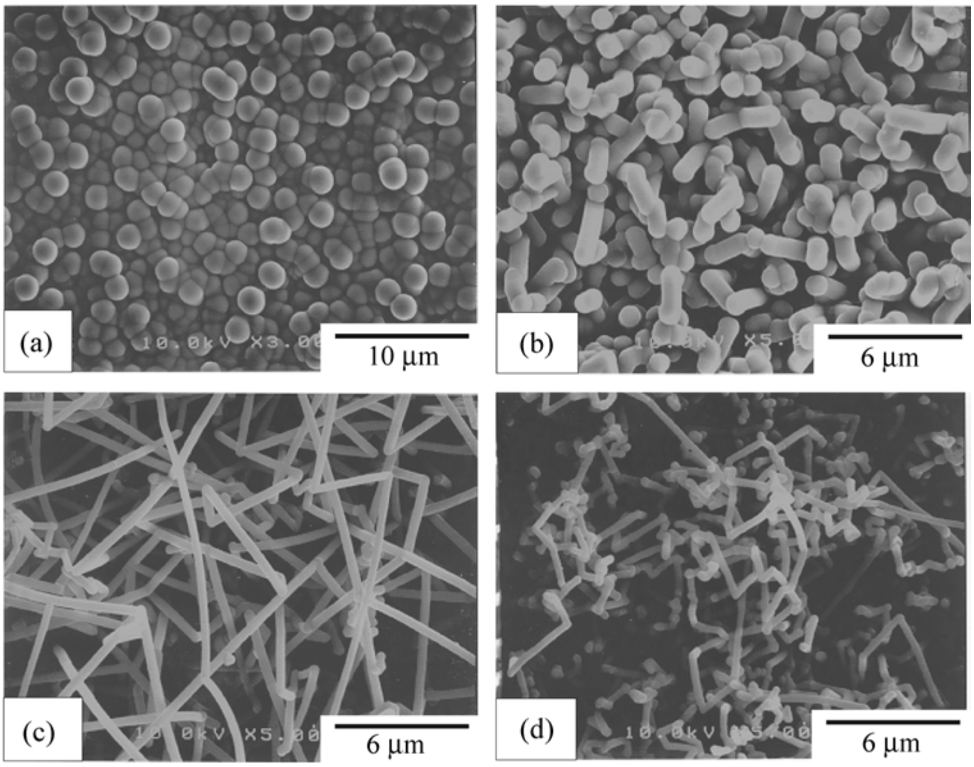

Fig. 3. SEM images of the deposits which were produced at different input gas ratios, (a) α=10, (b) α=20, (c) α=30 and (d) α=40.

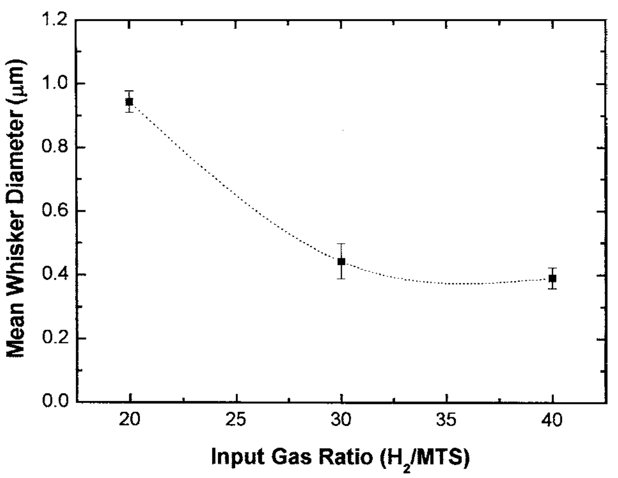

Fig. 4. The effect of input gas ratio on the changes of mean whisker diameter.

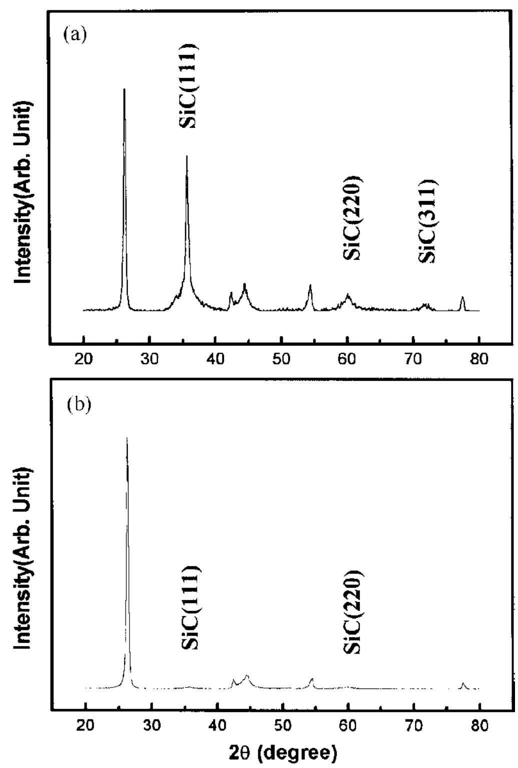

Fig. 5. XRD patterns of whisker-contained coating which were deposited at 1100ºC, (a) whisker was grown at α=20 with H_2 dilutant gas, coated at α=20 with N_2 dilutant gas and (b) whisker was grown at α=30 with H_2 dilutant gas, coated at α=20 with N_2 dilutant gas.

deposited. Both coatings have pebble-like structures. However, the coating that was deposited after growing whiskers at an input gas ratio of 20 has larger grains than that was formed at an input gas ratio of 30. Usually, deposited films are affected by substrates characteristics, such as morphologies, lattice constant, and thermal expansion coefficient, etc. Thus, the difference of grain size seems to result from the difference the diameters of the whiskers grown before depositing silicon carbide coating.

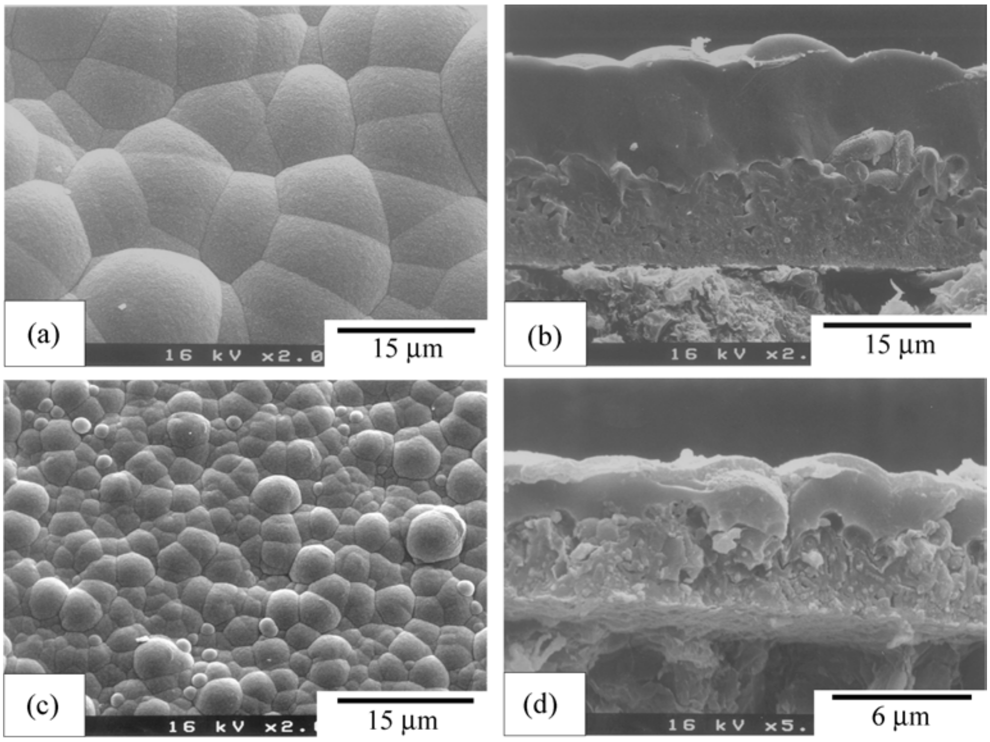

Fig. 6. Surface and cross-sectional SEM images of whisker-containing coatings, (a) whisker was grown at α=20 with H_2 dilutant gas, coated at α=20 with N_2 dilutant gas and (b) whisker was grown at α=30 with H_2 dilutant gas, coated at α=20 with N_2 dilutant gas.

Conclusions

We have successfully grown silicon carbide whiskers and the whisker-containing coatings without using a metallic catalyst. Whiskers started to appear when the input gas ratio was over 20. Whisker diameters were 0.94 μm, 0.44 μm, and 0.39 μm respectively, and decreased as the input gas ratio increased. Whisker-containing coatings were deposited by using nitrogen as a dilutant gas. They showed pebble-like structures and different grain sizes according to the whiskers that were contained in the lower section of the coatings.

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