A study on the thermal stability of silicon carbide whiskers on growth temperature

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Silicon carbide whiskers have been widely studied since they are promising material for the reinforcement of various composite materials due to their outstanding mechanical and chemical properties, low density, good heat conductivity, and high thermal stability [1–3]. These whiskers have been produced by several processes such as carbothermal reduction of silica [4–6], reaction between silicon halides and CCl_4 [7], and chemical vapor deposition using a metallic catalyst such as Ni or Fe [8, 9]. Among these processes, carbothermal reduction and the chemical vapor deposition (CVD) methods have been widely used since they are amenable to mass-productive and are homogeneous, respectively. Our research group studied ceramic hot gas filter with modified inner pores using silicon carbide whiskers, which were grown by chemical vapor infiltration (CVI) method without any metallic catalyst. Thermal stability of the whiskers is one of the most important characteristics for applications in severe operation condition such as diesel particulate filters (DPF) or filters for incinerator and electronic power stations, etc. In this study, the property change of the whisker will be discussed using results from scanning electron microscopy (FESEM, Hitachi S-4200), high resolution transmission electron microscopy (HRTEM, JEM-4010), and specific surface area by the BET (ASAP 2010, Micromeritics Co., U.S.A.) method.

The Schematic diagram of the CVI system was shown in our previous paper [10]. In order to deposit on the inner pores, chemical vapor infiltration (CVI), was

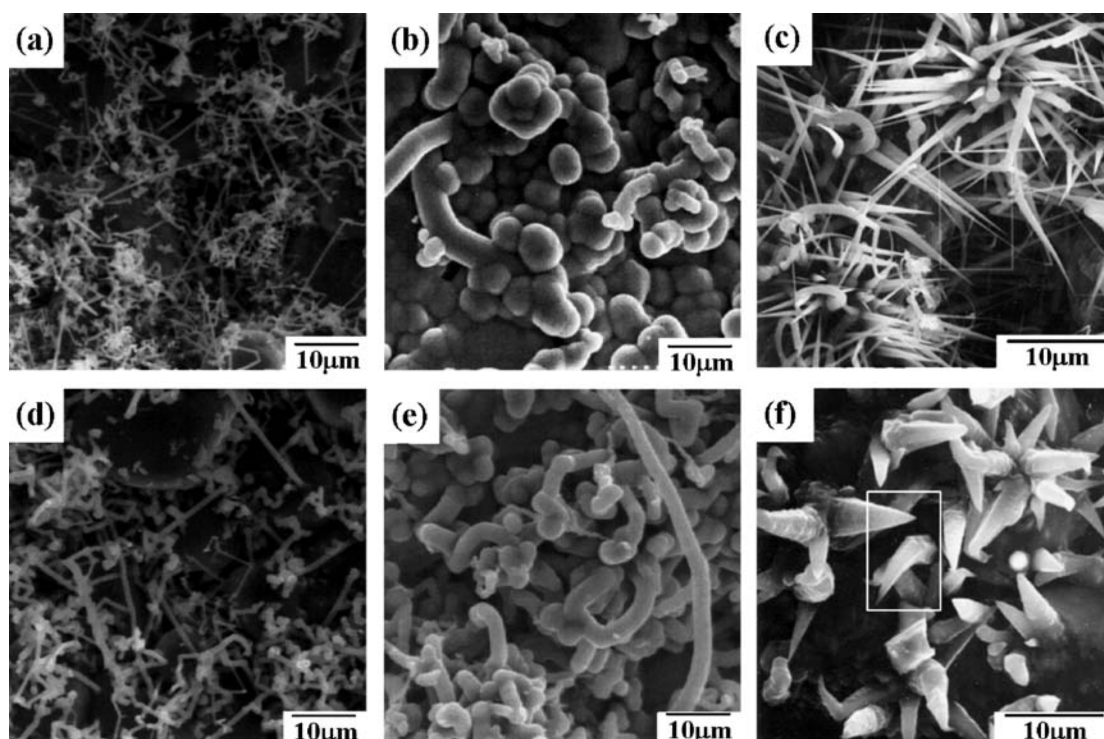

Figure 1 SEM images of whiskers which was grown at 1100 °C ((a) and (d)), 1200 °C ((b) and (e)), and 1300 °C ((c) and (f)). *Upper side* figures were as-deposited whiskers and *lower side* figures indicated the whiskers after annealing at 1100 °C for 100 hr.

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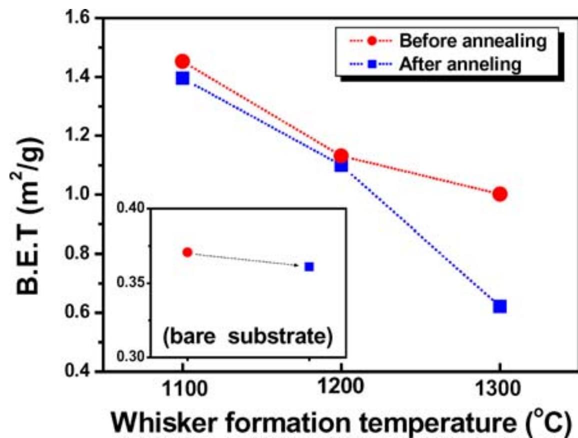

Figure 2 Variation of specific surface area before and after annealing with different growth temperature; *inner box* indicated the variation of specific surface area of substrate itself before and after annealing.

used as a deposition method [11]. Gaseous reactants infiltrate into the preform and are deposited on the SiC substrate during the CVI process. Porous silicon carbide (SD031, IBIDEN Co., Japan), which was designed for DPF, was used as substrate; it had uniform open pore size of about 10 μm. Methyltrichlorosilane (CH_3SiCl_3, MTS, Acros Organics Co., U.S.A) was chosen as the source of SiC since it produces stoichiometric silicon carbide more readily than other precursors. Hydrogen was used as both a carrier gas and as a dilution gas. The input gas ratio of diluent plus carrier gas to MTS, $P_{(\text{diluent+carrier})}/P_{(\text{MTS})}$, was defined as the character of 'α'. In this study, all the input gas ratios were fixed as 30 and silicon carbide whiskers were grown at 1100, 1200, and 1300 °C. Then the samples after whisker growth were annealed at 1100 °C for 100 h under a normal air atmosphere and naturally cooled down to the room temperature.

In this study, we focused on how temperature variations of whisker formation affected thermal stability after annealing. Fig. 1 shows the SEM images of fractural surface. The upper images show the as-deposited whiskers and the lower images the whiskers after annealing at 1100 °C for 100 hr. As you see, the morphologies of the as-grown whiskers are different from each other. This topic will be discussed later. Comparing Fig. 1(a) and (b) with (d) and (e), shows that the change in the shape of the whisker before and after annealing is slight. However, in case of whisker formed at 1300 °C (Fig. 1(c) and (f)), the variation of morphology such as length and diameter of whisker is significant. After annealing, the whiskers were shorter and thicker. The BET data is shown in Fig. 2 and is in consistent with the result of SEM. When whisker was grown at 1300 °C, the specific surface area was drastically decreased due to the decrease of the aspect ratio (the ratio of length to diameter of whisker). It seemed that the whisker was thermally evaporated and then some of them were re-deposited during the annealing process. From the fact that this phenomenon appeared in only one case, it could be inferred that there are some factors which cause thermal etching. The factor can be mainly explained in terms of the deposition rate. The higher the growth temperature, the faster is the deposition rate [12]. Particularly over 1250 °C, deposition rate of

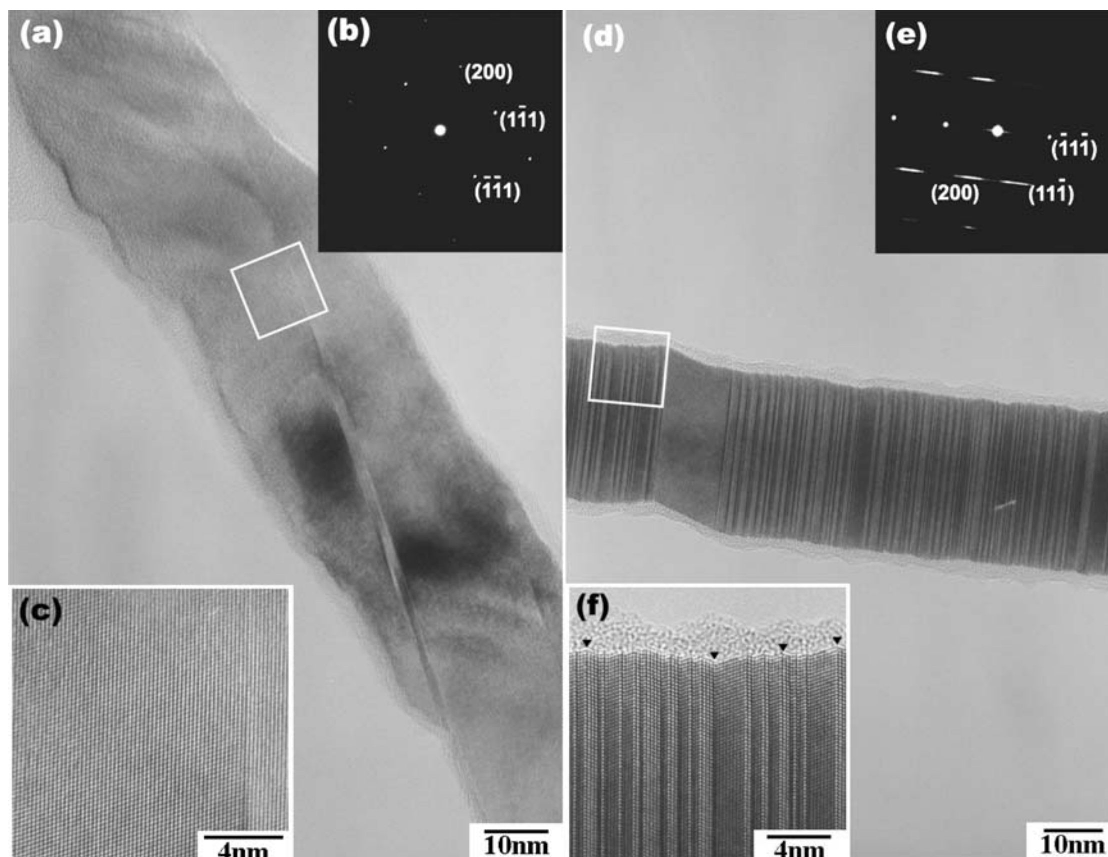

Figure 3 BF images and SAD patterns of whiskers which was grown at the 1100 °C ((a), (b), and (c)) and 1300 °C ((d), (e), and (f)); (a) and (d) BF images, (b) and (e) SAD patterns, and (c) and (f) magnified BF image of selected area.

TABLE I The intensity ratios of the XRD peak at 33.6 ° and 41.4 ° (2θ) as different whisker growth temperature

Whisker growth temperature (°C)	Annealing temperature (°C)	Annealing time (h)	X value	
			Before annealing	After annealing
1100			1.21	1.09
1200	1100	100	1.35	1.29
1300			1.98	1.90

silicon carbide was significantly increased [12]. As a result of the rapid growth rate, whiskers may have a more imperfect crystal structure, i.e., include many defects like stacking faults. To make an analysis of the amount of stacking faults, X-ray diffraction measurements of the whiskers were conducted using CuKα radiation. The intensities of the peaks at 33.6 ° and 41.4 ° (2θ)were measured, and their intensity ratio was calculated using the following equation: [13]

$$X = \frac{33.6^\circ \text{ peak intensity}}{41.4^\circ \text{ peak intensity}}$$

It is well known that a larger X value indicates a higher density of stacking faults in β-SiC [14]. In Table I the X values are listed. The XRD results indicated that there are heavy stacking faults in the whiskers formed at 1300 °C. These stacking faults provide higher energy sites which enable thermal evaporation at a relatively low temperature (1100 °C).

The bright field (BF) image in Fig. 3(d) and (e) and the selected area diffraction pattern (SAD) in Fig. 3(f) of the whiskers grown at 1300 °C showed heavy stacking faults along the entire whisker length, which was evidenced by the contrast bands in the BF image and streaks in the SAD pattern. Especially, many microtwins (indicated as '▼') and stacking faults were clearly observed in Fig. 3(f). However we scarcely find any evidences of stacking faults in Fig. 4(a), (b), and (c), which are the images of whiskers formed at 1100 °C. The observations of stacking faults by TEM support the results of XRD analysis.

In summary, the whiskers formed at over 1300 °C were heavily faulted due to the rapid growth rate. The stacking faults, as defects, reduce the activation energy for evaporation, so that evaporation occurred in spite of the relatively low temperature of annealing of 1100 °C. Therefore, in order to guarantee a thermal stability, whisker should be grown at a low temperature in order to avoid the formation of high density stacking faults.

Acknowledgments

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