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Stacking faults in silicon carbide whiskers

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Abstract

Stacking faults in SiC whiskers grown by three different growth mechanisms; vapor–solid (VS), two-stage growth (TS) and vapor–liquid–solid (VLS) mechanism in the carbothermal reduction system were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The content of stacking faults in SiC whiskers increased with decreasing the diameter of whiskers, i.e. the small diameter whiskers (<1 μm) grown by the VS, TS and VLS mechanisms have heavy stacking faults whereas the large diameter whiskers (>2 μm) grown by the VLS mechanism have little stacking faults. Heavy stacking faults of small diameter whiskers were probably due to the high specific lateral surface area of small diameter whiskers.

Keywords: B. Whiskers; D. Silicon carbide; Stacking faults

1. Introduction

SiC whiskers are an effective material for the reinforcement of various composite materials, due mainly to their superb mechanical properties [1–3]. At the present time, the preferred synthesis method for the SiC whiskers is carbothermal reduction of silica [4,5]. SiC whiskers are grown by the three different growth mechanisms in carbothermal reduction; vapor–solid (VS) mechanism [6,7], two-stage growth (TS) mechanism [8,9] and vapor–liquid–solid (VLS) mechanism [10–13], (hereafter, the grown whiskers are designated by VSSCW, TSSCW and VLSSCW, respectively). The VSSCW is grown by the direct accommodation of silicon and carbon atoms to the growth plane from the silicon- and carbon-carrying vapors. The TSSCW is grown in the raw materials containing metal impurities such as rice-hulls. The impurities form discrete liquid droplets on the growth plane. The droplets are quickly covered with vapor species because of their high accommodation coefficient and act as nucleation sites for the whisker growth. It results in axial growth of whiskers (first stage), and, then in lateral thickening (second stage). In the two-stage growth process, radial dislocations are typically formed. The VLSSCW is grown by dissolving silicon- and carbon-carrying vapors in the liquid droplets. The liquid droplets are formed by melting of metallic catalysts that are usually intentionally added. The dissolved silicon and carbon atoms diffuse across the droplet, and precipitate at the growth plane as SiC.

Stacking faults are usually found in SiC whiskers and affect various properties of whiskers [14–16]. The stacking faults in the VSSCW and TSSCW have been studied well in previous studies [6–9]. However, the stacking faults in the VLSSCW have been briefly referred in the literature [6,11,12,17]. In this study, the VSSCW, TSSCW and VLSSCW were grown by carbothermal reduction. The stacking faults in these whiskers were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) with the aim of ascertain the important factor to the formation of stacking faults.

2. Experimental procedures

The system for the growing of SiC whiskers consisted of substrate and boats in an alumina tube reactor. The graphite boats containing carbon (carbon black, N220, Lucky Continental Co. Ltd., Seoul, Korea)-silica (Aerosil 200, Degussa Corp., NJ, USA) mixtures were placed at the left-hand end of the tube reactor at the beginning of each run. The substrate on which SiC whiskers grew was placed at the hot zone. Argon gas was introduced

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Table 1
Growth conditions and characteristics of SiC whiskers

Designee	Growth site	Growth mechanism	Reaction conditions				Diameter (μm)	Relative intensity ($I_{33.6°}/I_{41.4°}$)
			T (°C)	t (h)	SiO generation rate ($cm^3\ min^{-1}$)	Catalyst		
VSSCW	Substrate	Vapor–solid	1450	5	9	None	< 0.2	2.83
TSSCW	Rice-hulls	Vapor–solid two-stage	1450	5	–	Impurities	< 0.6	1.01
VLSSCW	Substrate	Vapor–liquid–solid	1450	5	9	Fe (5 μm)	2–10	0.11

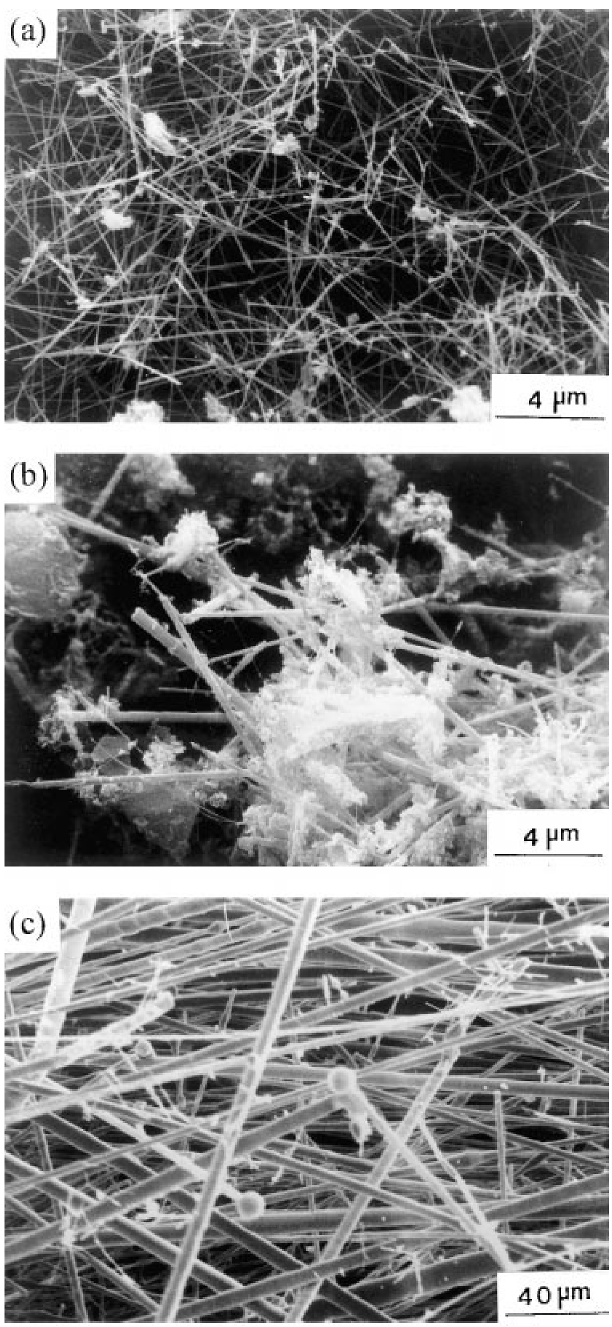

Fig. 1. Representative microstructure of SiC whiskers: (a) VSSCW, (b) TSSCW and (c) VLSSCW.

to maintain an inert atmosphere during the heat-up period. At the reaction temperature (1450°C), the process gas (hydrogen) was introduced at the rate of 191 $cm^3\ min^{-1}$ and the graphite boats were pushed forward into the hot zone at a predetermined rate of 0.25 g batch min^{-1}. At this set-up, the SiO generation rate from batch was fixed to ~9 $cm^3\ min^{-1}$. The VSSCW was grown on the high-purity graphite substrate (NP60, PF Grade, Toshiba

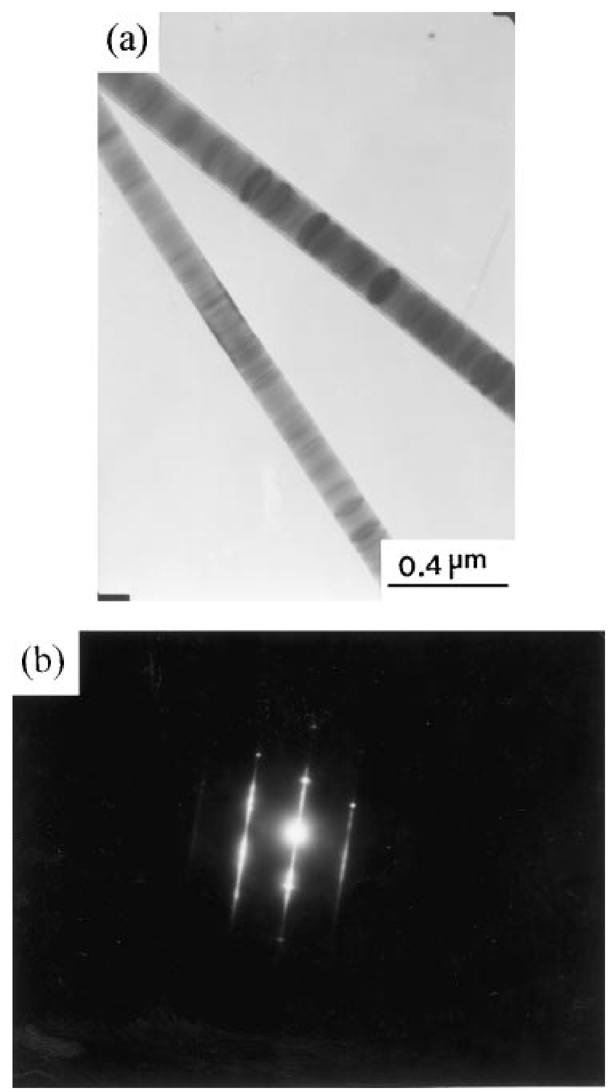

Fig. 2. (a) BF image and (b) SAD pattern of the VSSCW.

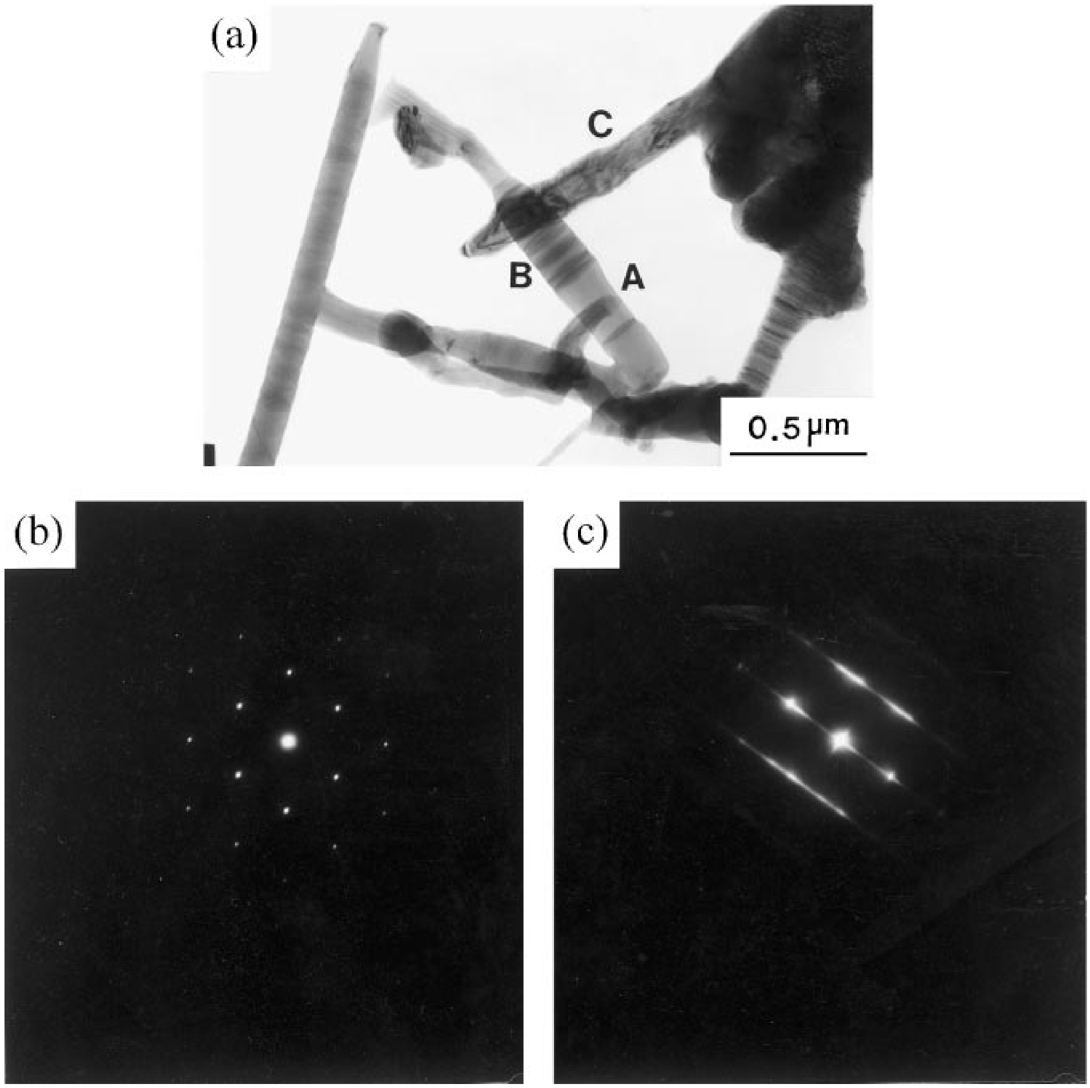

Fig. 3. BF image and SAD patterns of the TSSCW; (a) BF image, (b) SAD pattern of the section A, and (c) SAD pattern of the section B.

Ceramics Co. Ltd., Tokyo, Japan) which was treated with boiling hydrochloric acid (37%) for 4 h. The VLSSCW was grown on the high-purity graphite substrate with uniform coating of catalyst. Fe powder with a size of 5 μm was used as catalyst. When control of the size of catalyst was needed, $Fe(OH)_3$ was precipitated on the substrate by using $Fe(NO_3)\cdot 9H_2O$ and NH_4OH (Junsei Chemical Co., Tokyo, Japan). During reaction, the $Fe(OH)_3$ precipitates converted to Fe. The TSSCW was grown by carbothermal reduction of rice-hulls in the boat. Chemical analysis of the rice-hulls showed that they contained 2.6 wt% of various metal impurities such as Fe, Ni, Mg, Mn, Na, Ca, and K. The whisker growth process was described in an earlier work [13].

Upon completing the reaction, the collected VSSCW, TSSCW and VLSSCW were observed by scanning electron microscopy (SEM, S-4100, Hitachi, Japan). The stacking faults in the whiskers were characterized by XRD (RINT/DMAX-2000, Rigaku, Japan) and TEM (CM30, Philips, Netherlands). The intensity ratios of the XRD peak of whiskers at 33.6 and 41.4° (2θ) ($I_{33.6^\circ}/I_{41.4^\circ}$) were used to compare the stacking faults content in the whiskers [18]. The whiskers for TEM were prepared in two ways: (1) thin whiskers were dispersed in isopropyl alcohol and a droplet of the suspension was deposited onto a perforated carbon film that was supported on a 3 mm Cu grid; and (2) thick whiskers were consolidated into a Si_3N_4 matrix composites. The thin foils for TEM were prepared by the standard procedures of cutting, grinding, dimpling, and argon-ion-beam thinning followed by carbon coating.

3. Results and discussion

Table 1 summarizes the growth conditions and characteristics of whiskers. Fig. 1 shows the microstructures of whiskers. Very thin VSSCW with the diameter less

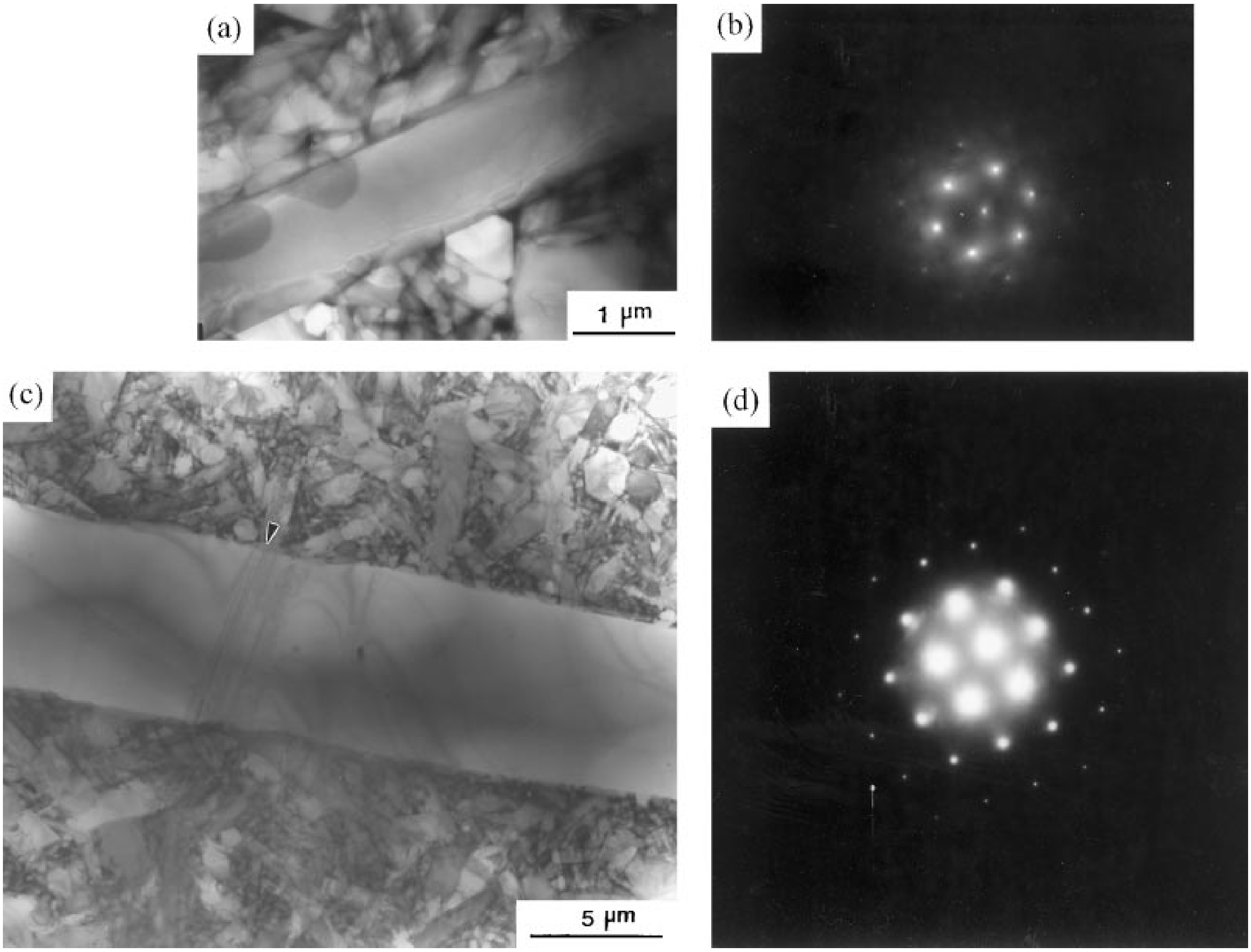

Fig. 4. BF images [(a) and (c)], and SAD patterns [(b) and (d)] of the VLSSCW.

than 0.2 μm were grown on the substrate [Fig. 1 (a)]. SiC whiskers grown in the rice-hulls batch were observed in a wide variation of the diameters within the range of less that 0.6 μm [Fig. 1(b)]. It may be due to the gradual decrease of the SiO generation rate with time in the rice-hulls batch. Generally, the diameter of SiC whiskers is decreased with increasing SiO generation rate [10]. The VLSSCW that was grown by using the Fe powder was thick with the diameters of 2–8 μm [Fig. 1(c)]. Liquid droplets at the end of the whiskers, which are typical for the VLS mechanism [6,10–13,17], were found in the VLSSCW. All whiskers in this study were identified as cubic 3C SiC (β-phase) by XRD. The intensity ratio of the XRD peak at 33.6 and 41.4°, $I_{33.6}$°/$I_{41.4}$°, of the VSSCW, TSSCW and VLSSCW were 2.83, 1.01 and 0.11, respectively (Table 1). The intensity ratio increased with contents of stacking faults [7,17]. The XRD results indicated that there are heavy stacking faults in the VSSCW and little stacking faults in the VLSSCW.

The bright field (BF) image [Fig. 2(a)] and selected area diffraction (SAD) pattern [Fig. 2(b)] of the VSSCW 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. Fig. 3 shows the BF image and SAD patterns of SiC whiskers grown in the rice-hulls batch. Some whiskers showed alternating section without stacking faults [marked A in Fig. 3(a)] and with heavy stacking faults [marked B in Fig. 3(a)]. The SAD patterns of sections A and B also showed, respectively, no stacking faults and heavy stacking faults [Fig. 3(b) and (c)]. It was inferred that these whiskers are the VSSCW [6]. The other whiskers showed Moire patterns [marked C in Fig. 3 (a)], which was the evidence of the presence of dislocations and stacking faults in the whiskers [14]. Therefore, it is believed that the VSSCW and TSSCW were simultaneously grown in the rice-hulls. Fig. 4 shows the BF images and SAD patterns of VLSSCW. The VLSSCW with a diameter of about 2 μm showed no contrast band in the BF image [Fig. 4(a)] and streaks in the SAD pattern [Fig. 4(b)]. Other VLSSCW with a diameter of about 7 μm showed contrast bands in the narrow region indicated by the arrow in Fig. 4(c) that indicates the existence of stacking faults. However, no streak appeared in the SAD pattern [Fig. 4(d)], which may result from the low density of stacking faults. It was confirmed that the consolidation process for the preparation of TEM sample did not induce the annihilation of stacking faults in SiC whiskers. The observations of stacking faults by using TEM support the results of XRD analysis. Heavy stacking faults were found in the VSSCW that show the high intensity ratio of 2.83. However, little stacking faults were found in the VLSSCW that show the low intensity ratio of 0.11.

The results shown in Table 1 and TEM observations indicate that the contents of stacking faults relate to the diameter of whiskers, i.e. heavy stacking faults are found with decreasing diameters. According to the axial next nearest-neighbor Ising (ANNNI) model [6,19], SiC whiskers with stacking faults have a lower energy than SiC whiskers without stacking faults. Furthermore, formation of stacking faults promotes {111} facets, which have much lower surface energy than {211} or {110} facets, at the lateral surface and reduce the total surface energy of whiskers [6]. The lateral surfaces of a whisker without stacking faults are usually parallel to {211} or {110}. Therefore, with regard to energetic consideration, formation of stacking faults during the growth of SiC whiskers is favorable due to the contribution of the stacking faults themselves and {111} facets at the lateral surface to the formation energy of SiC whiskers. The specific lateral surface area of whiskers becomes relatively large when the whisker diameter is small. In this case, the contribution of surface energy to the formation energy of SiC whisker becomes large. It may enhance the formation of stacking faults to reduce the contribution of lateral surface energy. Wang et al. reported that the more stacking faults were found in the relatively small diameter VSSCW ($\sim$0.2 μm) [6].

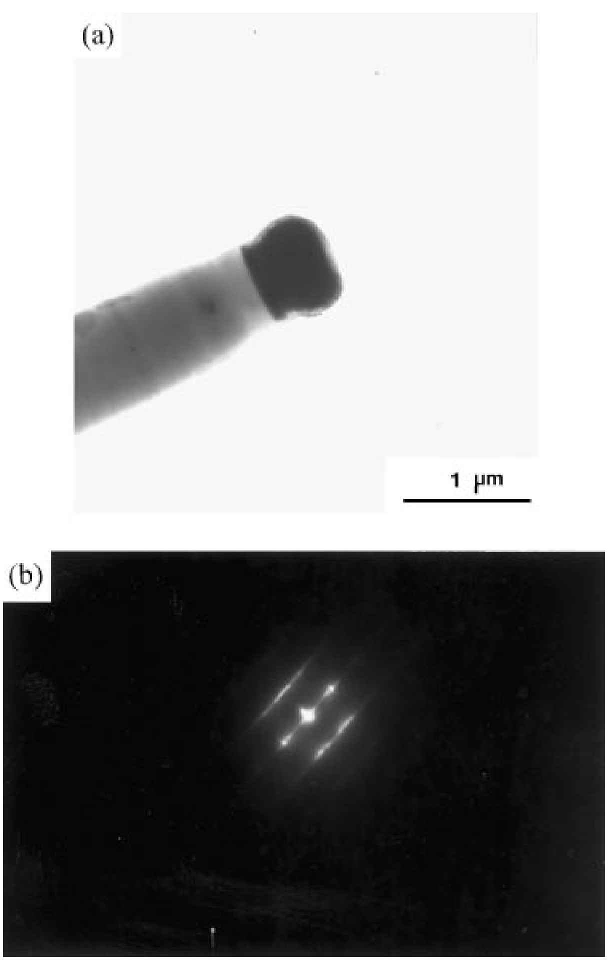

Fig. 5. (a) BF image and (b) SAD pattern of the small diameter VLSSCW.

It was documented that the growth of SiC whiskers through the liquid phase (i.e. the VLS mechanism) is a more near-equilibrium process than the growth of SiC through the vapor phase (i.e. the VS or TS mechanism) [17], and that the near-equilibrium process may suppress the formation of stacking faults during the growth of SiC whiskers. Fig. 5 shows the BF image and SAD patterns of the small diameter VLSSCW (< 1 μm) that was grown by using the $Fe(OH)_3$ precipitates. As shown in Fig. 5(a), the liquid droplets at the end of whisker were found in the VLSSCW. It shows the contrast bands originating from the stacking faults which was also evidenced by SAD pattern [Fig. 5(b)]. The result indicates that heavy stacking faults can also be formed in the VLSSCW when the diameter is small and, consequently, the specific lateral surface area of whiskers becomes large.

4. Summary

Stacking faults in SiC whiskers grown by three different growth mechanisms in the carbothermal reduction system were investigated. The content of stacking faults, characterized by XRD and TEM, increased with a decrease in the diameter of whisker. The increasing specific lateral surface area of whiskers with decreasing diameter may enhance the formation of stacking faults in SiC whiskers.

References

[1] G.C. Wei, P.F. Becher, Development of SiC-whisker-reinforced ceramics, Am. Ceram. Soc. Bull. 64 (1985) 298–304.
[2] P.D. Shalek, J.J. Petrovic, G.F. Hurley, F.D. Gac, Hot pressed SiC whisker/Si_3N_4 matrix composites, Am. Ceram. Soc. Bull. 65 (1986) 351–356.
[3] R. Lundberg, L. Kahlman, R. Pompe, R. Carlsson, R. Warren, SiC-whisker-reinforced Si_3N_4 composites, Am. Ceram. Soc. Bull. 66 (1987) 330–333.
[4] P.A. Janeway, ART: reinforcing tomorrow technology, Ceram Ind. (1992) 42–44.
[5] J.M. Schoenung, The economics of silicon carbide whisker fabrication, Ceram. Eng. Sci. Proc. 12 (1991) 1943–1951.

[6] L. Wang, H. Wada, L.F. Allard, Synthesis and characterisation of SiC whiskers, J. Mat. Res. 7 (1992) 148–163.
[7] W.-S. Seo, K. Koumoto, Stacking faults in β-SiC formed during carbothermal reduction of SiO_2, J. Am. Ceram. Soc. 79 (1996) 1777–1782.
[8] S.R. Nutt, Microstructural and growth model for rice-hull-derived SiC whiskers, J. Am. Ceram. Soc. 71 (1988) 149–156.
[9] K.M. Knowels, M.V. Ravichandran, Structure analysis of inclusions in β-silicon carbide whiskers grown from rice hulls, J. Am. Ceram. Soc. 80 (1997) 1165–1173.
[10] J.V. Milevski, F.D. Gag, J.J. Petrovic, S.R. Skaggs, Growth of beta-silicon carbide whiskers by the VLS process, J. Mat. Sci. 20 (1985) 1160–1166.
[11] H. Wang, Y. Berta, G.S. Fischman, Microstructure of silicon carbide whiskers synthesized by carbothermal reduction of silicon nitride, J. Am. Ceram. Soc. 75 (1992) 1080–1084.
[12] R.D. Jong, R.A. McCauley, Growth of twinned β-silicon carbide whiskers by the vapor-liquid-solid process, J. Am. Ceram. Soc. 70 (1987) C-338–C-341.
[13] H.J. Choi, J.G. Lee, Continuous synthesis of silicon carbide whiskers, J. Mat. Sci. 30 (1995) 1982–1986.
[14] M.E. Brito, Y. Bando, M. Mitomo, S. Saito, Microstructural features of sintered Si_3N_4/SiC-whiskers composites: mechanical integrity whiskers, J. Mat. Sci. 29 (1994) 250–254.
[15] L.M. Russel, K.Y. Donaldson, D.P.H. Hasselman, N.D. Corin, J.J. Petrovic, J.F. Rhodes, Effect of vapor-liquid-solid and vapor-solid silicon carbide whiskers on the effective thermal diffusivity/conductivity of silicon nitride matrix composites, J. Am. Ceram. Soc. 74 (1991) 874–877.
[16] D.P.H. Hasselman, K.Y. Donaldson, J.R. Thomas Jr, J.J. Brennan, Thermal conductivity of vapor-liquid-solid and vapor-solid silicon carbide whisker-reinforced lithium aluminosilicate glass-ceramic composities, J. Am. Ceram. Soc. 79 (1996) 742–748.
[17] W.-S. Seo, K. Koumoto, Effects of boron, carbon, and iron content on the stacking fault formation during synthesis of β-SiC particles in the system SiO_2-C-H_2, J. Am. Ceram. Soc. 81 (1998) 1255–1261.
[18] H. Takayama, N. Sutoh, N. Murakawa, Quantitative analysis of stacking faults in the structure of SiC by X-ray powder profile refinement method, J. Ceram. Soc. Jpn 96 (1988) 1003–1011.
[19] C. Cheng, R.J. Needs, V. Heine, Inter-layer interactions and the origin of SiC polytypes, J. Phys. C 21 (1988) 1049–1063.