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Formation of a Silicon Carbide Layer on Vapor Grown Carbon Nanofiber[®] by Sol-Gel and Carbothermal Reduction Techniques

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1. Introduction

Recent years have noted a growing interest in carbon nanofibre (CNF), due to its excellent chemical, physical, and mechanical properties (Jacobsen et al., 1995). Therefore, CNF has been used as composite reinforcement fibre within polymer and ceramic matrices in order to take advantage of these characteristics (Maensiri et al., 2007). Similar to this, vapor grown carbon nanofibre (VGCF[®]) is a highly crystalline CNF synthesized by the gas-phase method and exhibits excellent thermal conductivity, electrical conductivity, strength, sliding properties (lubricity), and restoring force (resiliency). Since the handling of VGCF is known to be easier compared to that of carbon nanotubes (CNT) in processes such as dispersion, VGCF has found widespread application. Despite this, the utilization of VGCF has been hindered by several issues, namely the problems of poor dispersibility and fibre aggregation which are attributed to strong van der Waals interactions (Sun et al., 2003).

Previously, single-walled carbon nanotubes (SWNT) have been solubilized through the use of polyvinyl pyrrolidone (PVP) as a surfactant, due to a wrapping effect (O'Connell et al., 2001; Asai et al., 2003). Thus, a similar possibility may arise for the dispersion of VGCF in polar solvents through the use of PVP. Apart from this technique, the present authors (Kita et al., 2010) have treated VGCF with an acid treatment (*i.e.*, mixture of sulfuric and nitric acids) in order to enhance dispersibility within polar solvents, with this effect being attributed to the formation of COO⁻ groups on the VGCF surface. Thus, the VGCF surface properties were found to be modified from hydrophobic to hydrophilic as a result of acid treatment.

Once the surface properties of VGCF have been changed to hydrophilic in nature, further opportunities may exist for modifying the VGCF surface using an accelerated solid-liquid reaction. For example, the extremely poor oxidation resistance of VGCF (due to the intrinsic oxidizing nature of carbon) may be enhanced when the surface of VGCF is covered with an oxidation resistant material. Silicon carbide (SiC) is a promising candidate for such a material

due to its excellent oxidation, corrosion and creep resistance (Raj, 1993). On the basis of such a background, the present work describes the enhancement of oxidation resistance, due to the surface coating of VGCF with SiC *via* the carbothermal reduction of a silica precursor/silica layer formed from tetraethyl orthosilicate (TEOS) using the sol-gel method.

2. Experimental procedures

Commercially available VGCF[®] was used as the starting powder (Showa Denko, Tokyo, Japan). Firstly, the coating conditions for the formation of silica precursor on the surface of VGCF were examined using TEOS, *i.e.*, (i) coating the VGCF surface following a surfactant treatment with polyvinylpyrrolidone (PVP; surfactant) and (ii) coating the VGCF surface following acid treatment in order to form carboxyl groups (COO⁻). The conditions for the coating of silica precursor on the surface of VGCF are shown in **Table 1**. Relating to the procedure for (i), VGCF (3 mg) was ultrasonically dispersed in 10 cm³ water containing 2 ~ 10 mg PVP, whereas the hydrolysis of 0.002 ~ 0.05 cm³ TEOS was conducted in the presence of 0.05 cm³ concentrated HCl stirred at room temperature for one week. In contrast to this, for procedure (ii) the VGCF (2 mg) was placed into a mixture of concentrated sulfuric acid (2.5 cm³) and 70% nitric acid (7.5 cm³) and ultrasonicated for 1 h. The mixture was then refluxed at 40°C for 5 to 30 h and finally washed with distilled water and filtered off. The resulting VGCF coated with silica precursor was further heated at a temperature between 1300 and 1500°C for 1 h in order to form SiC-coated VGCF.

Crystalline phases were identified using an X-ray diffractometer (XRD; Model RINT2000PC, Rigaku, Tokyo) with monochromatic CuK α radiation generated at 40 kV and 40 mA. The substitution groups on the surface of VGCF were investigated using a Fourier transform infrared (FT-IR) spectrometer (Model IR Prestige-21, Shimadzu, Kyoto) by means of the KBr method. The heat resistance of chemically-modified VGCF in air was examined by thermogravimetry (TG; Model Thermo Plus TG8120, Rigaku, Tokyo). The morphologies of chemically-modified VGCF were observed using a field-emission scanning electron microscope (FE-SEM; S-4500, Hitachi, Tokyo) at an accelerating voltage of 5 kV, after the specimen surface had been coated with Pt-Pd using an ion coater (Model E-1030, Hitachi, Tokyo) in order to avoid charging effects. Furthermore, the microstructure of chemically-modified VGCF was observed using a transmission electron microscope (JOEL 2011; JEOL, Tokyo, Japan) at an acceleration voltage of 200 kV.

3. Results and discussion

3.1 Coating of silica precursor on the surface of VGCF

Prior to carbothermal reduction to form a SiC layer, conditions necessary for the coating of silica precursor on the surface of VGCF using TEOS were examined, *i.e.*, (i) coating of silica precursor following the modification of surface properties from hydrophobic to hydrophilic using PVP as a surfactant, and (ii) coating of silica precursor following an acid treatment to form carboxyl groups at 30°C for 48 h. Details for these procedures will be discussed in this section.

3.1.1 Utilization of PVP for the coating of silica precursor on the surface of VGCF

Firstly, the surfactant (PVP) was utilized not only for the dispersion of VGCF in the polar solvent but also for the interaction with TEOS. To this end, PVP was placed into the VGCF-

dispersed and TEOS-hydrolyzed solutions in order to homogeneously coat the surface of VGCF. The experimental conditions were chosen on the basis of research previously reported (Asai et al., 2003). The expected mechanisms concerning the interaction of PVP with water and TEOS in these solutions are shown in **Fig. 1**. The site of $O^{\delta-}$ in Equal layout interacts with $H^{\delta+}$ sites in water (H-O-H) (Fig. 1(b-1)) and $-OH^{\delta+}$ in the TEOS (Fig. 1(b-2)). Thus PVP is expected to aid dispersion of the VGCF in H_2O and TEOS in HCl solution due to the wrapping effect on the VGCF.

On the basis of experimental conditions listed in Table 1, VGCF (3 mg) was dispersed in a H_2O solution containing 2 to 10 mg PVP, whereas the amounts of TEOS, PVP and HCl were fixed at 0.05 cm^3 , 50 mg and 0.05 cm^3 , respectively (Sample Nos. 1 to 3). Typical FE-SEM micrographs of VGCF/silica precursor are shown in **Fig. 2**. Spherical particles with diameters of 5 ~ 10 μm , as well as acicular particles, were found to be present in the powder (Fig. 2(a)), with no significant coating of material noted on the surface of the acicular particles (Fig. 2(b)). The spherical and acicular particles were ascribed to be silica precursor and VGCF, respectively, and indicate the difficulty in homogeneous coating the surface of VGCF using PVP as a surfactant. It is suggested that the spherical particles of silica precursor were formed as a result of: (i) the formation of PVP micelle due to the excess amount over that for the surrounding of VGCF, and (ii) nuclei formation and subsequent growth of silica precursor entrapped by the PVP micelle (Wang et al., 2008; Woo et al., 2010; Duque et al., 2008).

Sample No.	VGCF-dispersed solution			TEOS-hydrolyzed solution		
	VGCF	PVP	H ₂ O	TEOS	PVP	HCl
	mg	mg	cm ³	cm ³	mg	cm ³
1	3	2	10	0.05	50	0.05
2	3	5	10	0.05	50	0.05
3	3	10	10	0.05	50	0.05
4	3	2	10	0.05	1	0.05
5	3	5	10	0.05	1	0.05
6	3	10	10	0.05	1	0.05
7	3	2	10	0.02	1	0.05
8	3	5	10	0.02	1	0.05
9	3	10	10	0.02	1	0.05
10	3	10	10	0.015	1	0.05
11	3	10	10	0.010	1	0.05
12	3	10	10	0.005	1	0.05
13	3	10	10	0.002	1	0.05

Table 1. Experimental conditions for the dispersion of VGCF in the presence of PVP (VGCF-dispersed solution) and for the hydrolysis of TEOS (TEOS-hydrolyzed solution).

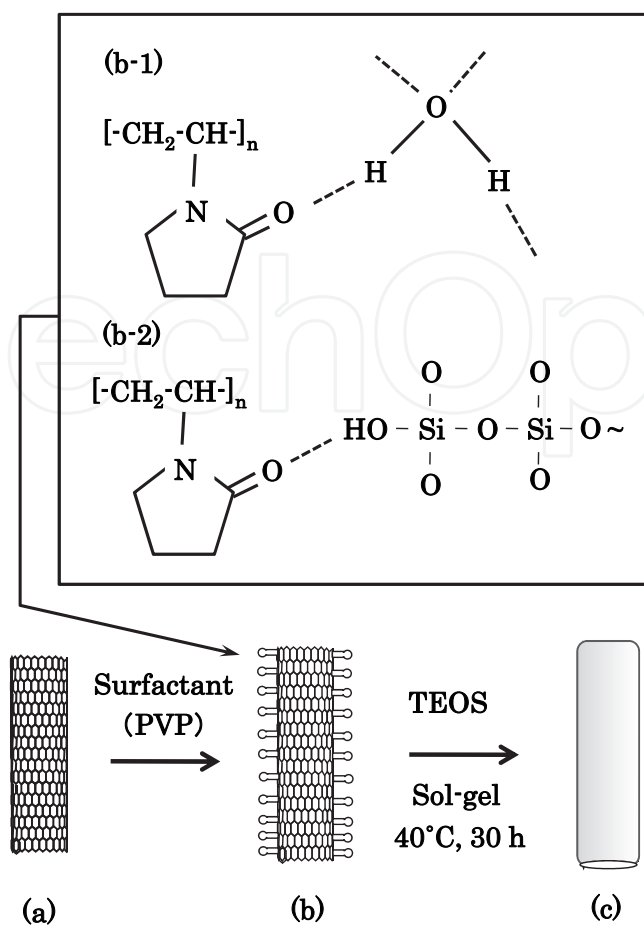


Fig. 1. Schematic diagram of the coating by silica precursor.

- a. As-received VGCF
- b. VGCF coated with PVP (b-1) Interaction with water (b-2) Interaction with TEOS
- c. VGCF coated with silica precursor

Since the amount of PVP was considered to be slightly in excess of that required for the optimal coating of VGCF, the amount of PVP in the TEOS-hydrolyzed solution was reduced from 50 to 1 mg, and the conditions to homogeneously coat the surface of VGCF were examined (Sample Nos. 4 to 6). Typical FE-SEM micrographs of VGCF/silica precursor are shown in **Fig. 3**. It was noted that spherical particles with diameters of 5 ~ 10 μm , as well as acicular particles, were present in the powder (Fig. 3(a)), although no significant coating of material was observed on the surface of the acicular particles (Fig. 3(b)). As already mentioned, the spherical and acicular particles were believed to be silica precursor and VGCF, respectively, and further reinforce the difficulty in homogeneous coating the surface of VGCF using PVP as a surfactant.

Since little effect on the coating of silica precursor was apparent from the decrease in the amount of PVP, the amount of TEOS in the TEOS-hydrolyzed solution was reduced from 0.05 to 0.02 cm^3 , with the conditions required to homogeneously coat the surface of VGCF being examined (Sample Nos. 7 to 9). Typical FE-SEM micrographs of VGCF/silica precursor have been shown in **Fig. 4**. Spherical particles with diameters of 5 ~ 10 μm , as well as acicular particles, were found to be present in the powder, and the number of spherical particles became small (Fig. 4(a)).

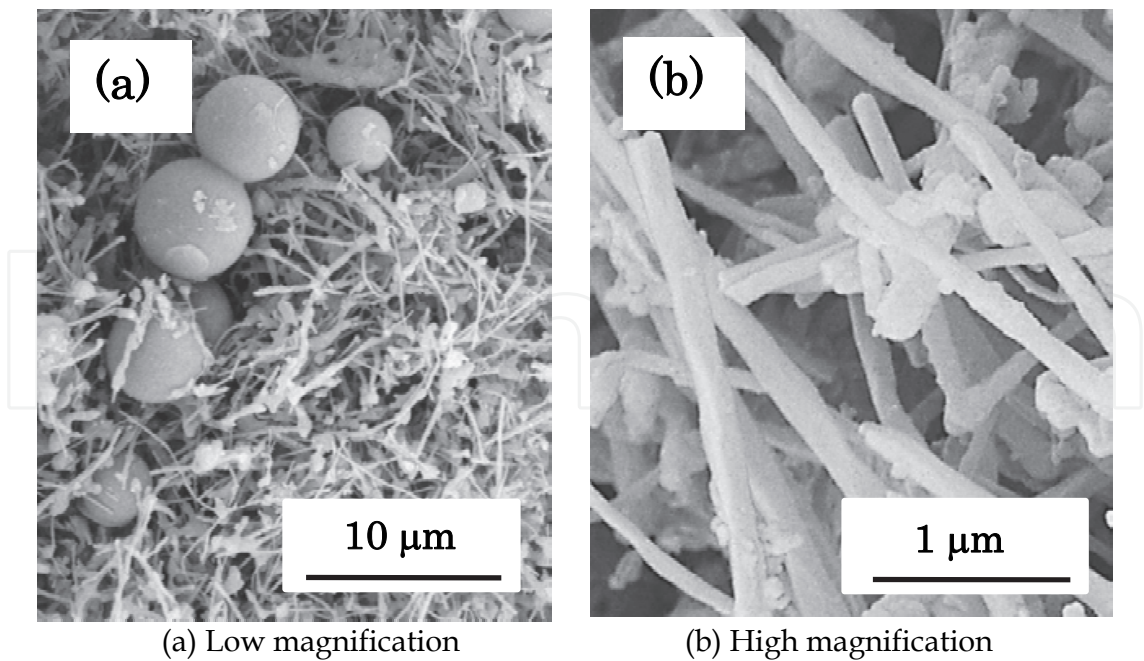


Fig. 2. Typical FE-SEM micrographs of VGVF and silica precursor formed by hydrolyzing TEOS at 40°C for 30 h (Sample No. 3).

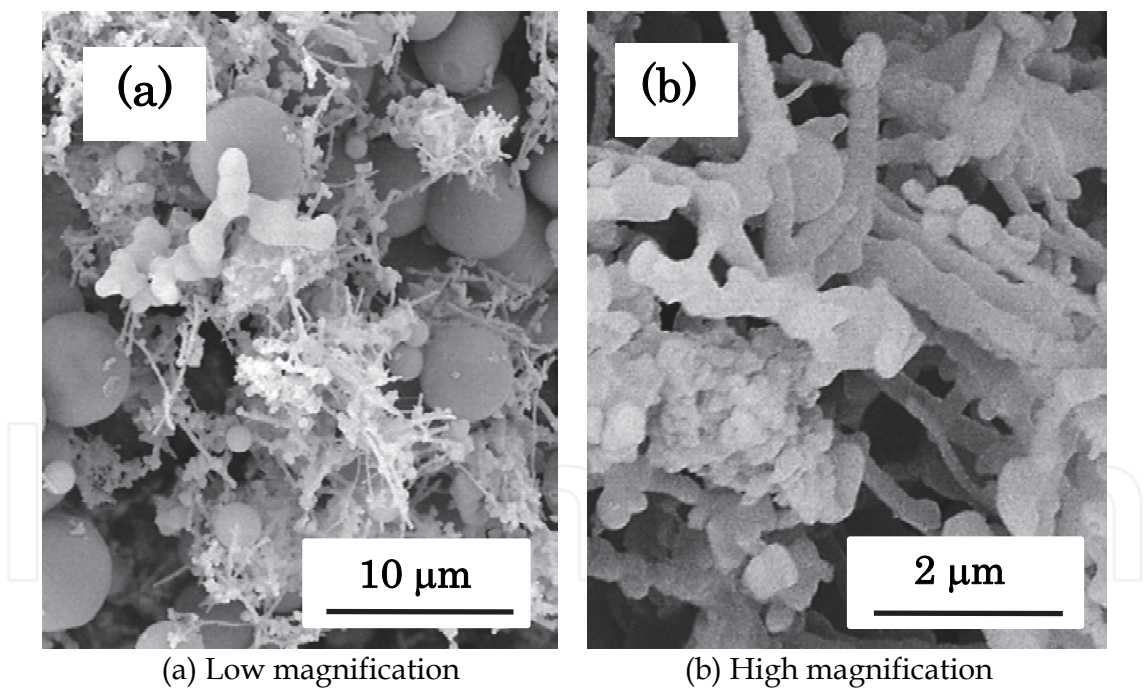


Fig. 3. Typical FE-SEM micrographs of VGVF and silica precursor formed by hydrolyzing TEOS at 40°C for 30 h (Sample No. 6).

Furthermore, the surface of VGCF was partly coated by a layer of material (Fig. 4(b); see the arrow mark). As has already been mentioned, the spherical and acicular particles were believed to be silica precursor and VGCF, respectively, and thus the presence of a partly-coated silica precursor on the surface of VGCF indicates the possibility of homogeneous coating the surface of VGCF. Following this, the amount of TEOS was further reduced from

0.015 to 0.002 cm³ in order to homogeneously coat the surface of VGCF with the results being shown in Fig. 5. According to the low magnification FE-SEM micrographs in this figure, spherical particles with diameters of approximately 1 ~ 3 μm, as well as acicular particles, were present in the powder, but the number of spherical particles was small (TEOS amount: 0.015 cm³). The number of spherical particles was reduced as the amount of TEOS was reduced from 0.010 to 0.002 cm³. According to the higher magnification FE-SEM micrographs in Fig. 5, no significant coating of TEOS was observed on the surface of the VGCF.

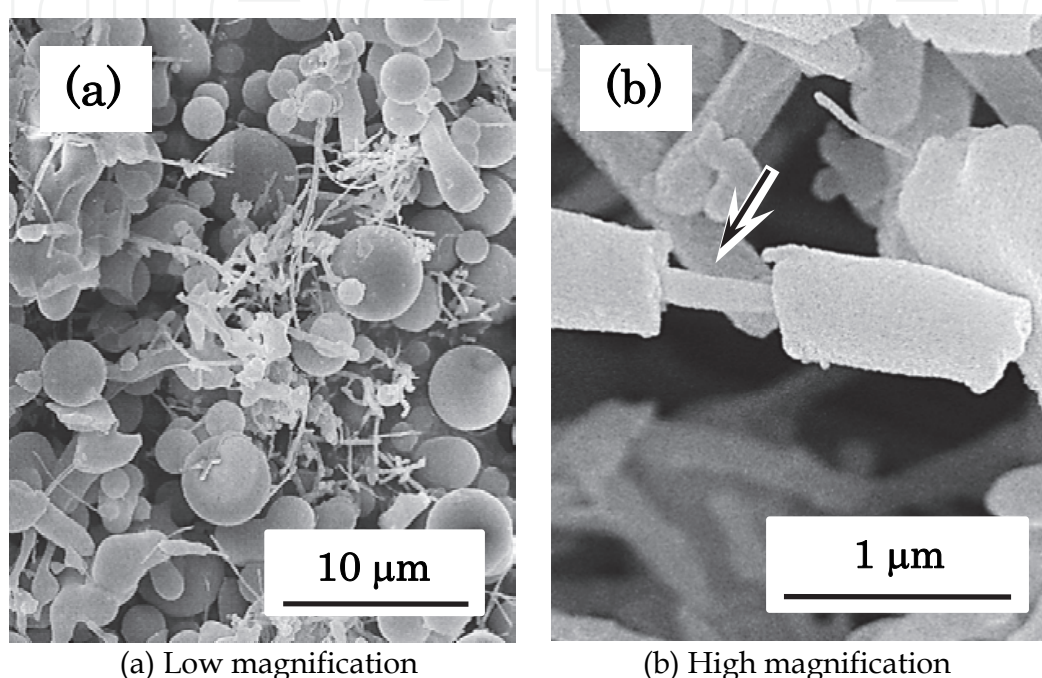


Fig. 4. Typical FE-SEM micrographs of VGCF and silica precursor formed by hydrolyzing TEOS at 40°C for 30 h (Sample No. 9).

Arrow mark in Fig. 4(b) indicates evidence of coating of silica precursor on the surface of VGCF.

In contrast to previous work (Asai et al., 2003) that suggested the silica precursor to have been successfully covered with SWNT, the application of a homogeneous coating on the surface of VGCF could not be achieved in the present research. The diameter of the VGCF (mean diameter: 150 nm) is approximately 15 times that of SWNT (mean diameter: 10 nm). Due to the significant difference in diameter between SWNT and VGCF, it seems to be possible for PVP to wrap the SWNT (*i.e.*, smaller diameter) but be difficult for PVP to wrap the VGCF (*i.e.*, larger diameter) (O'Connell et al., 2001). In the present case, therefore, it is concluded that the PVP may be significantly easier to form as spherical particles rather than as a layer on the surface of VGCF.

3.1.2 Acid treatment for the coating of silica precursor on the surface of VGCF

As shown in Section 3.1.1, the homogeneous coating of silica precursor could not be achieved using PVP. The authors therefore consider that the VGCF surface properties need to be modified from hydrophobic to hydrophilic in order to allow interaction between the VGCF and TEOS. In light of this, the authors planned to form carboxyl (*i.e.*, hydrophilic)

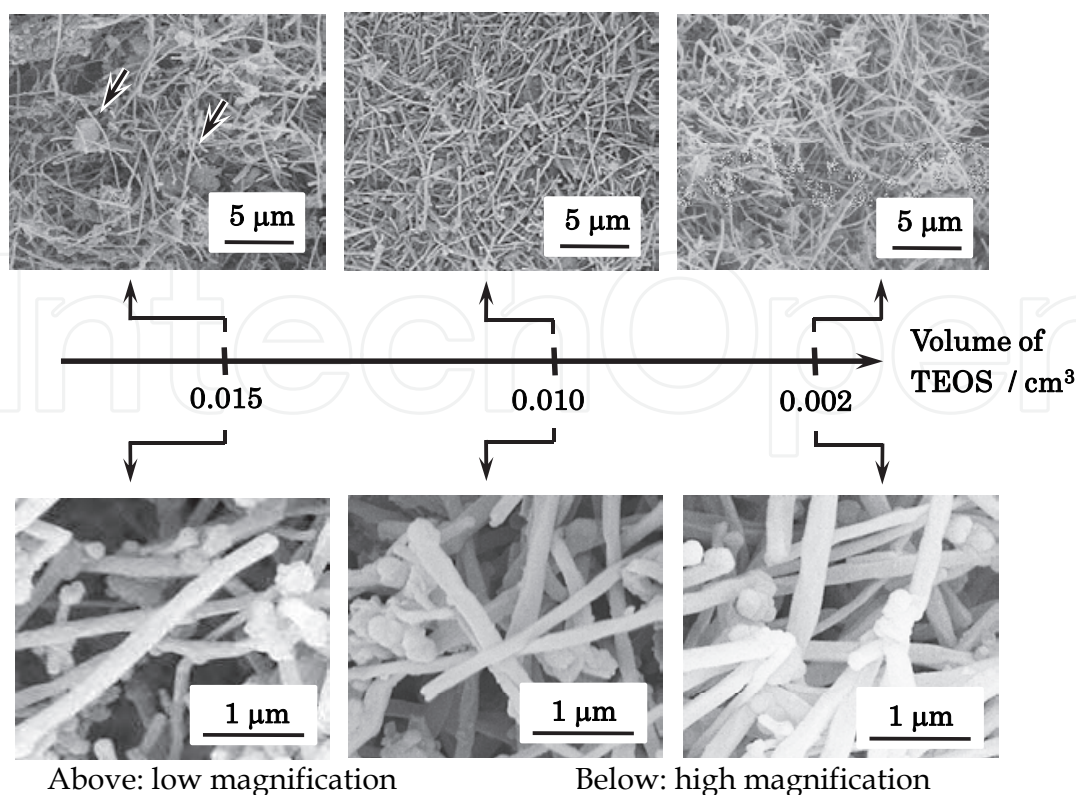


Fig. 5. Typical FE-SEM micrographs of VGCF and silica precursor formed by hydrolyzing TEOS at 40°C for 30 h (Sample Nos. 10 to 12).

groups and followed by the formation of silica precursor on the surface of VGCF, using TEOS. Work previously carried out on VGCF had included an acid treatment at 50°C for 24 h (Kita et al., 2010). In this work the temperature for the acid treatment of VGCF was reduced to 30°C in order to prevent damage to the VGCF surface, as this would negatively influence any additional modification to the VGCF surface that would be carried out using TEOS. Photographs indicating dispersion states of as-received and acid-treated VGCF in a polar solvent (acetone) are presented in Fig. 6, together with the FE-SEM micrographs. The as-received VGCF was seen to be sedimented to the bottom of the sample bottle whereas the acid-treated VGCF was still dispersed within the acetone after standing for 24 h. FE-SEM micrographs of VGCF showed that no marked difference in particle appearance was observed before and after the acid treatment. Since the VGCF could be dispersed in the polar solvent, the functional groups bonded to the surface of VGCF were examined using FT-IR spectroscopy. Typical FT-IR spectra of as-received and acid-treated VGCFs are shown in Fig. 7. In both cases, the absorption peaks appeared at 1550 and 1350 cm^{-1} , respectively. The absorption peaks at 1550 and 1350 cm^{-1} were both assigned to the COO- stretching vibration (Kubota et al., 2005), both of which are known to be typical modes of the carboxyl group. This fact demonstrates that carboxyl groups may be formed on the surface of VGCF as a result of the acid treatment. The imbalanced charge of H^+ in the carboxyl group ($-\text{COOH}$) may thus interact with that of the carbonyl group ($> \text{C} = \text{O}$) in the acetone, thereby making possible the dispersion of acid-treated VGCF in acetone.

Previously, the oxidation of SWNT to form carboxyl groups has been examined by Zhang *et al.* (Zhang et al., 2003), who considered the reaction to comprise of three steps as follows: (i) an initial attack on the original existing active sites such as the $-\text{CH}_2$, $-\text{CH}$ groups and

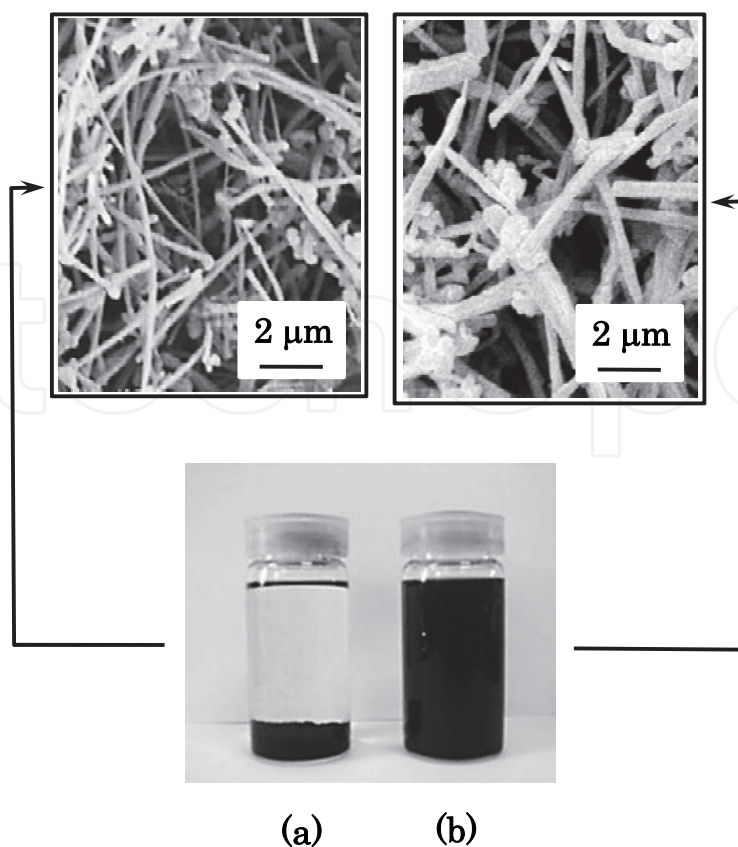
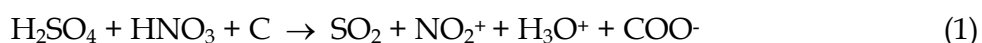


Fig. 6. FT-IR spectra of (a) as-received VGCF and (b) VGCF acid-treated at 30°C for 48 h.

heptatomic rings, (ii) electrophilic addition at hexatomic-hexatomic boundaries, generating active sites or new defects (defect-generating step), and (iii) the breaking of the graphene structure around the generated active sites (defect-consuming step). The acid treatment, due to the presence of sulfuric acid, effectively produces electrophilic groups such as NO_2^+ , which contribute to forming $-\text{COOH}$ groups as follows:



Since the surface of VGCF could be modified to be hydrophilic through the formation of carboxyl groups, the conditions for the hydrolysis of TEOS were further conducted in order to coat the silica precursor on the surface of VGCF. In this case the heat-treatment temperature was fixed at 40°C whereas the time was changed from 5 to 30 h. Typical XRD patterns are shown in **Fig. 8**, together with FE-SEM micrographs. The crystalline phase detected by XRD was only carbon (JCPDS-ICDD Card, No. 41-1487) with the intensity of the carbon peaks increasing with hydrolysis time from 5 to 15 h but then being reduced upon further hydrolysis time to 30 h. Also of note was the broad XRD background in the 2θ range of 20 to 30°. According to the FE-SEM micrographs, the VGCF surface was increasingly covered with material as the TEOS hydrolysis time increased from 5 to 15 h at 40°C (Fig. 8(a) → (b); see the part enclosed with the square). On further increasing the hydrolysis time to 30 h, however, the VGCF became stuck together to form agglomerates.

The broad XRD background for VGCF in the 2θ range of 2 to 30° following hydrolysis of TEOS (see Fig. 8) indicates the presence of amorphous material with this being further investigated using FT-IR as shown in **Fig. 9**. The FT-IR spectra were found to contain

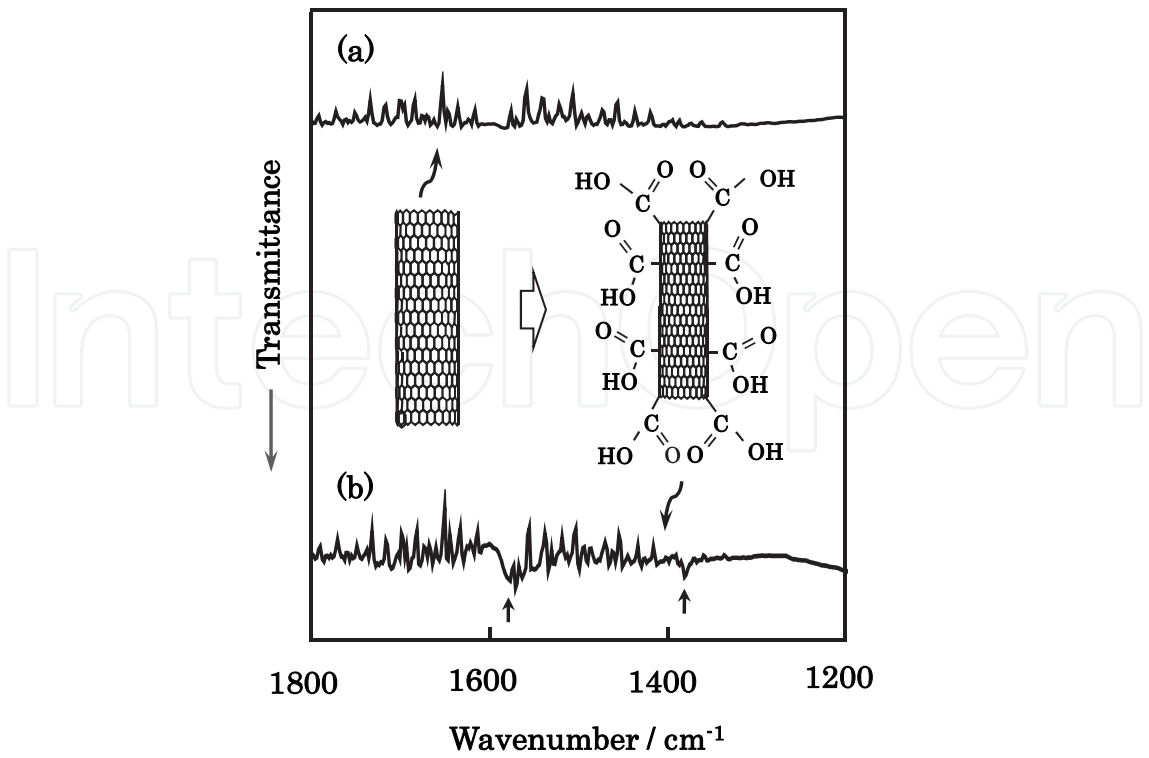


Fig. 7. Typical appearance and FT-IR micrographs of (a) as-received VGCF and (b) VGCF acid-treated at 30°C for 48 h.

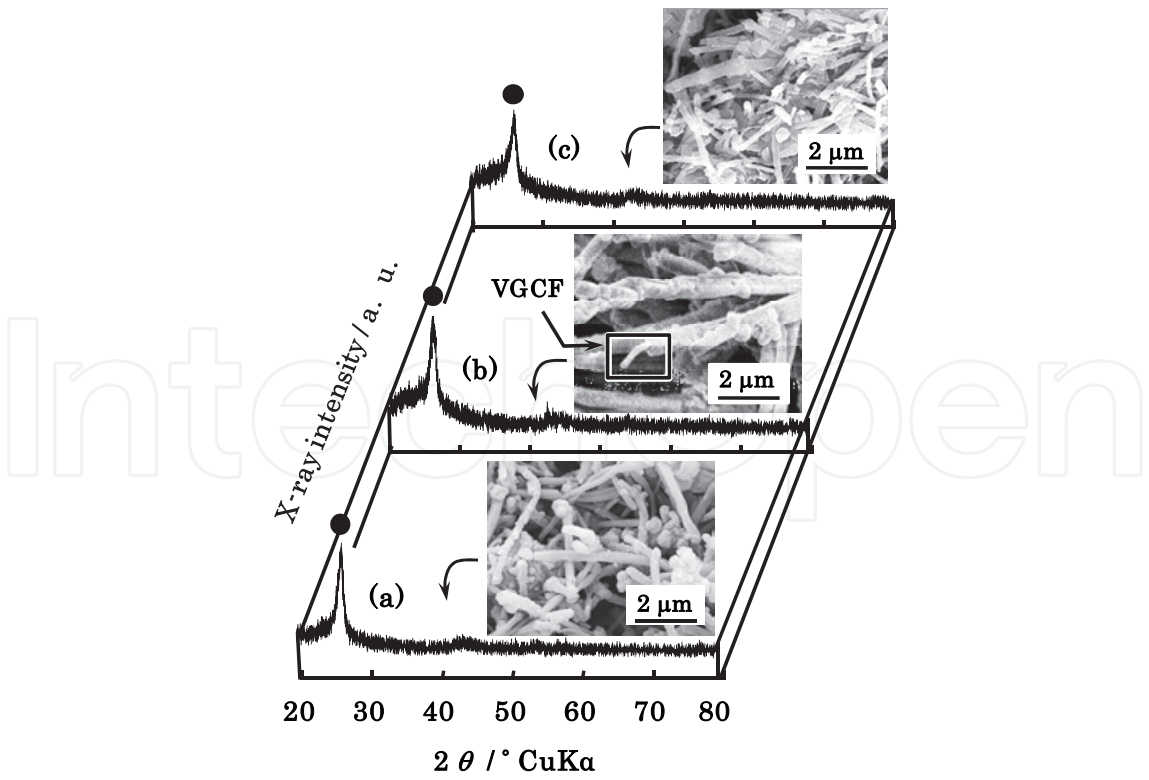


Fig. 8. Typical XRD patterns of VGCF coated with silica precursor at (a) 40°C for 5 h, (b) 40°C for 15 h, and (c) 40°C for 30 h after acid treatment at 30°C for 48 h. ●: C.

absorption peaks at 1200 (shoulder), 1047 and 947 cm^{-1} with the intensities of these absorption peaks increasing with hydrolysis time from 5 to 30 h. The absorption peaks at 1200 (shoulder) and 1047 cm^{-1} were assigned to Si-O-Si bonding, whereas the absorption peak at 947 cm^{-1} may be assigned to Si-CH₃ bonding (Navamathavan et al., 2008). Since the intensity of the absorption peak at 1047 cm^{-1} increased with hydrolysis time from 5 to 15 h, the bonding of Si-O-Si was concluded to have been enhanced with hydrolysis time. This fact indicates that the starting TEOS may be changed into silica *via* a silica precursor with increasing hydrolysis time.

Further to the results mentioned above, the formation of agglomerates following hydrolysis of TEOS at 40°C for 30 h indicates that an excess of silica precursor over the optimum amount required for the coating of VGCF contributes to unwanted adhesion between the VGCFs. An increased amount of silica precursor on the VGCF surface was also confirmed by the XRD patterns which indicated the X-ray intensity of carbon to have been reduced with increasing hydrolysis time of TEOS from 15 to 30 h. On the basis of these results, the optimum condition for hydrolysis of TEOS was determined to be 40°C for 15 h, with this being expected to result in homogeneous coating of silica precursor on the surface of VGCF.

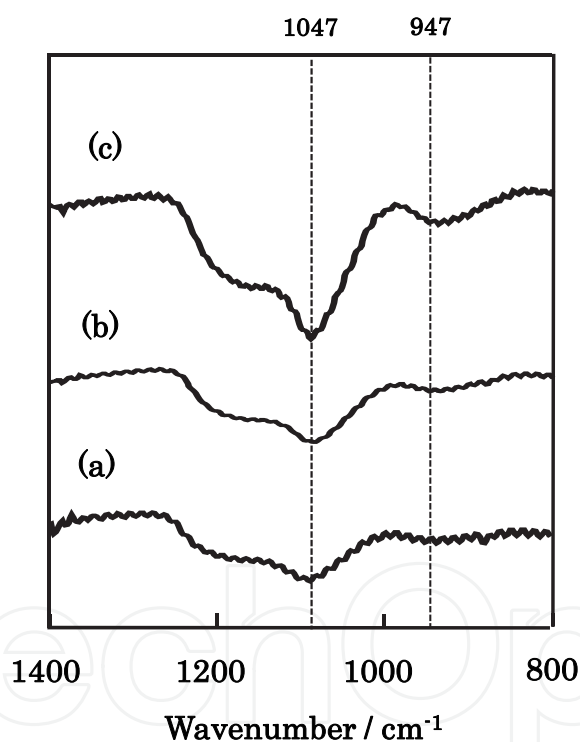


Fig. 9. Typical FT-IR spectra for VGCF coated with silica precursor at (a) 40°C for 5 h, (b) 40°C for 15 h, and (c) 40°C for 30 h after an acid treatment at 30°C for 48 h.

3.2 Carbothermal reduction for the coating of silicon carbide on the surface of VGCF

Since the homogeneous coating of silica precursor onto the surface of VGCF was successfully carried out by acid- and TEOS-hydrolysis treatments, the authors further examined the conditions for the carbothermal reduction of silica and/or silica precursor in order to form a SiC layer on the VGCF surface. Prior to coating with silicon carbide, the formation of a surface silica layer was confirmed by heating the VGCF with silica precursor

layer at 850°C for 5 h in air. A typical XRD pattern is shown in **Fig. 10** together with a typical TEM micrograph. According to the XRD pattern, broad X-ray reflections appeared in the 2θ range of 20 to 40°. On the other hand, the TEM micrograph showed the presence of tube-like particles with thicknesses of approximately 20 nm.

Regardless of the broad XRD pattern, the precursor layer on the VGCF surface was thought to have been changed into silica (Tabatabaei et al., 2006; Wang et al., 2009) following heating at 850°C for 5 h in air. Moreover, the TEM micrograph in Fig. 10 indicated that the VGCF had been burned out to form tube-like particles. Due to the presence of the tube-like particles with homogeneous thicknesses of approximately 20 nm, the silica precursor was concluded to have been homogeneously covered onto the VGCF surface. Therefore, since the homogeneous coating of silica precursor and silica onto the surface of VGCF had been confirmed on the basis of XRD and TEM results, the conditions required for the carbothermal reduction of silica precursor/silica layer were also examined. The carbothermal reduction of TEOS-derived VGCF was conducted at a temperature between 1300 and 1600°C for 1 h with the results being shown in **Fig. 11**. Apart from the carbon reflection which appeared at 26.4°, no other reflections were noted for the carbothermal reduction of silica precursor/silica at 1300 and 1400°C for 1 h (Fig. 11(a) and (b)). On the other hand, β -SiC (JCPDS-ICDD Card. No. 29-1129), in addition to carbon, was detected when the carbothermal reduction had been conducted at 1500°C for 1 h (Fig. 11(c)). The FE-SEM micrograph in Fig. 11 indicated that the VGCF surface had been covered with

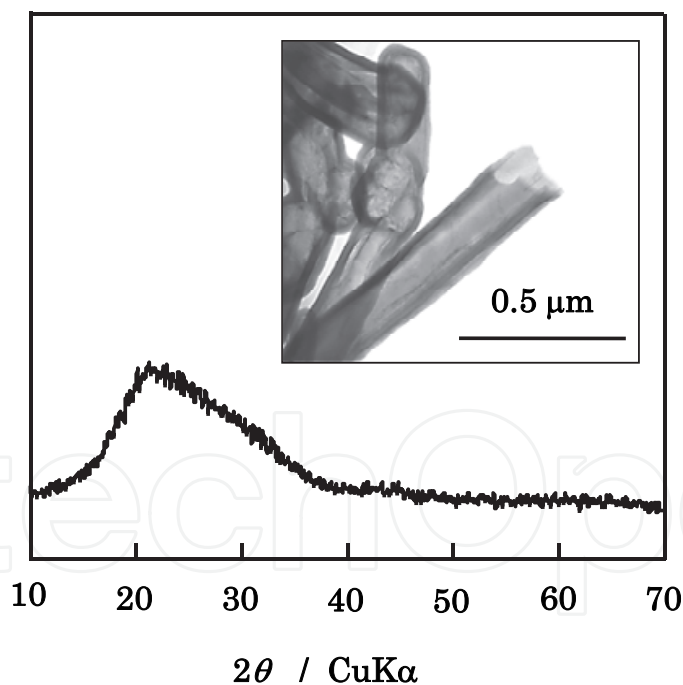


Fig. 10. Typical XRD pattern and TEM micrograph of VGCF coated with silica precursor at 40°C for 15 h and then heated at 800°C for 5 h in air.

material whilst the X-ray intensity due to β -SiC was increased as the carbothermal reduction increased from 1500 to 1600°C (Fig. 11(d)).

It should be noted that a broad X-ray background, attributed to the presence of SiO_2 in an amorphous state (Wang et al., 2009), was present in the range of $2\theta = 20$ to 30° for the cases

of carbothermal reduction at 1300 and 1400°C (see Fig. 10). Furthermore, the reduction in intensity of the carbon reflection, simultaneously accompanied with an increased β -SiC reflection (Fig. 11(c) \rightarrow (d)), suggests that the VGCF had been consumed to form β -SiC due to the carbothermal reduction from silica precursor/silica (Wang et al., 2009). This carbothermal reduction was presumed to have occurred as follows (Lin et al., 2003):



The optimum temperature for the carbothermal reduction was considered to be 1500°C due to the presence of crystalline β -SiC at this temperature.

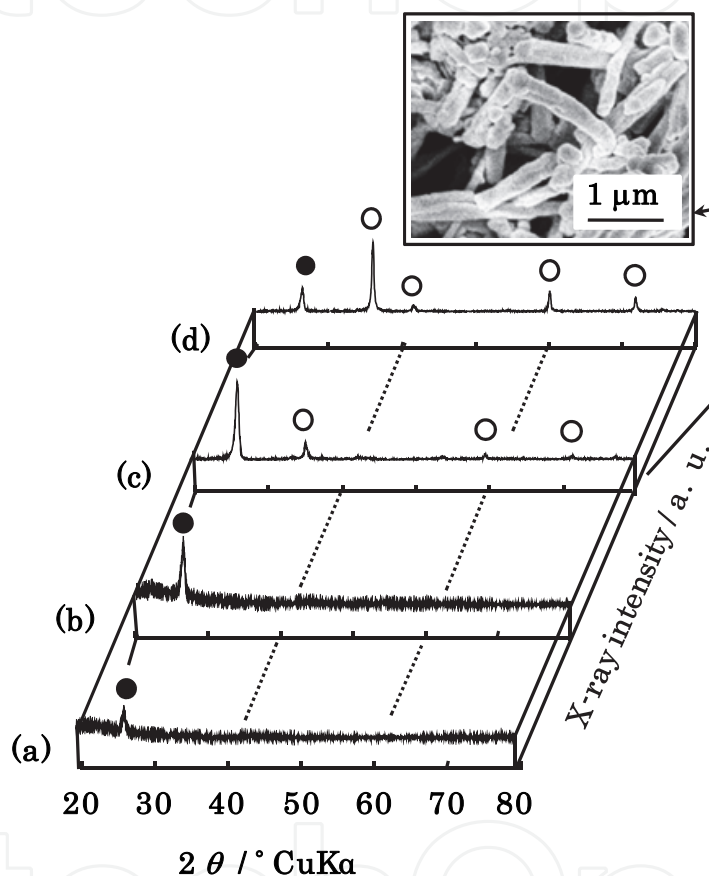


Fig. 11. Typical XRD patterns of VGCF coated with silica precursor carbothermally-reduced at (a) 1300°C, (b) 1400°C, (c) 1500°C, and (d) 1600°C for 1 h in Ar atmosphere. Note that the VGCF coated with silica precursor was prepared by heating the TEOS at 40°C for 15 h.

●: Carbon ○: β -SiC

FE-SEM, FE-STEM and TEM micrographs of SiC-coated VGCF are shown in **Fig. 12**. Whereas FE-SEM indicated the VGCF surface to have been homogeneously coated with material (Fig. 12(a)), the FE-STEM micrographs indicated the presence of spherical particles with diameters of 1 μm or less, in addition to the coating layer, as being present on the VGCF surface (Fig. 12(b)). Likewise, appearance of VGCF observed by TEM was similar to that observed by FE-STEM. Therefore, it was concluded that spherical particles appear to have stuck to the VGCF surface, in addition to the homogeneous layer. Such spherical particles, as well as the layer, were attributed to carbothermal reduction of an excess amount

of silica precursor/silica over the amount required for the homogeneous coating of the VGCF surface.

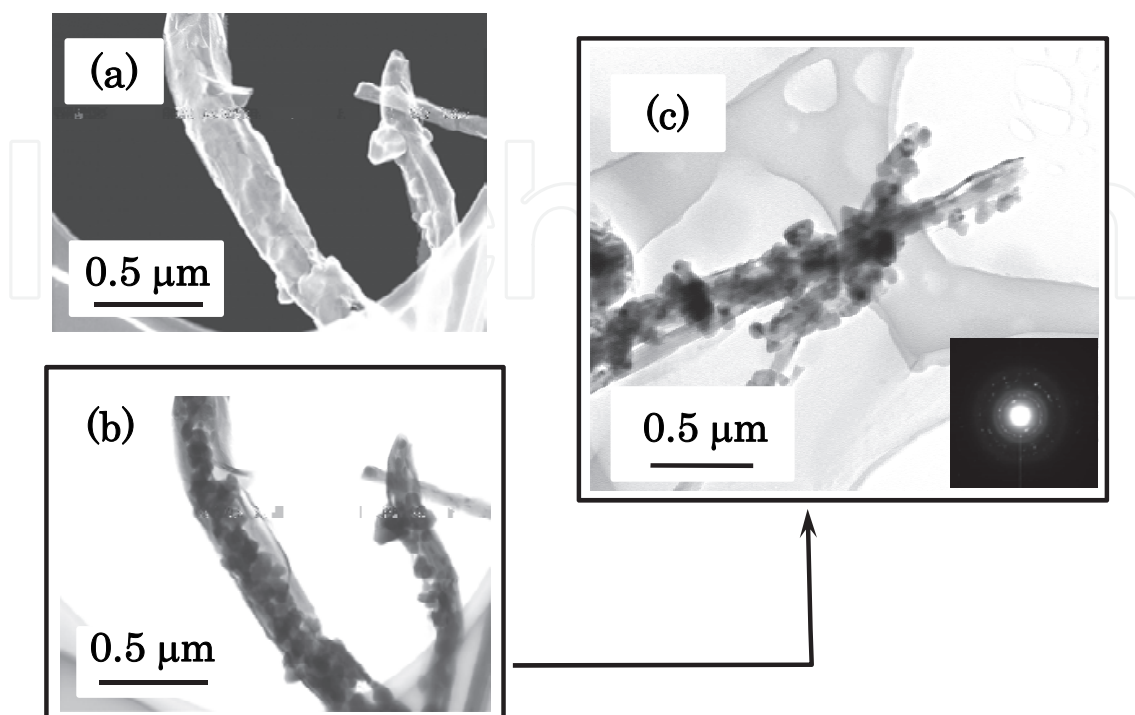


Fig. 12. Typical (a) FE-SEM, (b) FE-STEM, and (c) TEM micrographs of VGCF coated with silicon carbide obtained by carbothermally reduction of the silica precursor at 1500°C for 1 h in Ar atmosphere. Note that the VGCF coated with silica precursor was prepared by heating TEOS at 40°C for 15 h.

From the results presented above it was concluded that VGCF coated with silicon carbide could be prepared by making use of the acid-treated VGCF. A schematic diagram for the formation of the silicon carbide layer on the surface of VGCF *via* the formation of silica precursor/silica is shown in Fig. 13. The preparation process of the VGCF coated with silicon carbide could be divided into three parts, *i.e.*, (a) interaction of acid-treated VGCF with TEOS, (b) formation of silica precursor on the surface of acid-treated VGCF, and (c) formation of silica layer on the surface of acid-treated VGCF. In addition to this, excess spherical SiC particles were also included in the layer formed on the VGCF surface.

As a final step, VGCF with a SiC layer was heated in air in order to examine the oxidation resistance with the TG results being shown in Fig. 14. The mass loss of as-received VGCF started to occur at approximately 700°C and increased with a further increase in temperature (Fig. 14(a)). In contrast to this, the temperature at which the mass loss of acid-treated VGCF started was reduced to approximately 100°C (Fig. 14(b)), whereas mass loss of SiC-coated VGCF initiated at approximately 650°C and increased with a further increase in temperature (Fig. 14(c)). The mass losses of these VGCFs at 1000°C were arranged as follows: acid-treated VGCF (67.9%) > as-received VGCF (50.1%) > SiC-coated VGCF (45.7%). The significant mass loss in the case of acid-treated VGCF may be attributed to the formation of cracks or lattice defects on the surface of VGCF. The lower mass loss in the case of SiC-coated VGCF, compared to the case of as-received VGCF, demonstrates that the SiC had coated the VGCF surface.

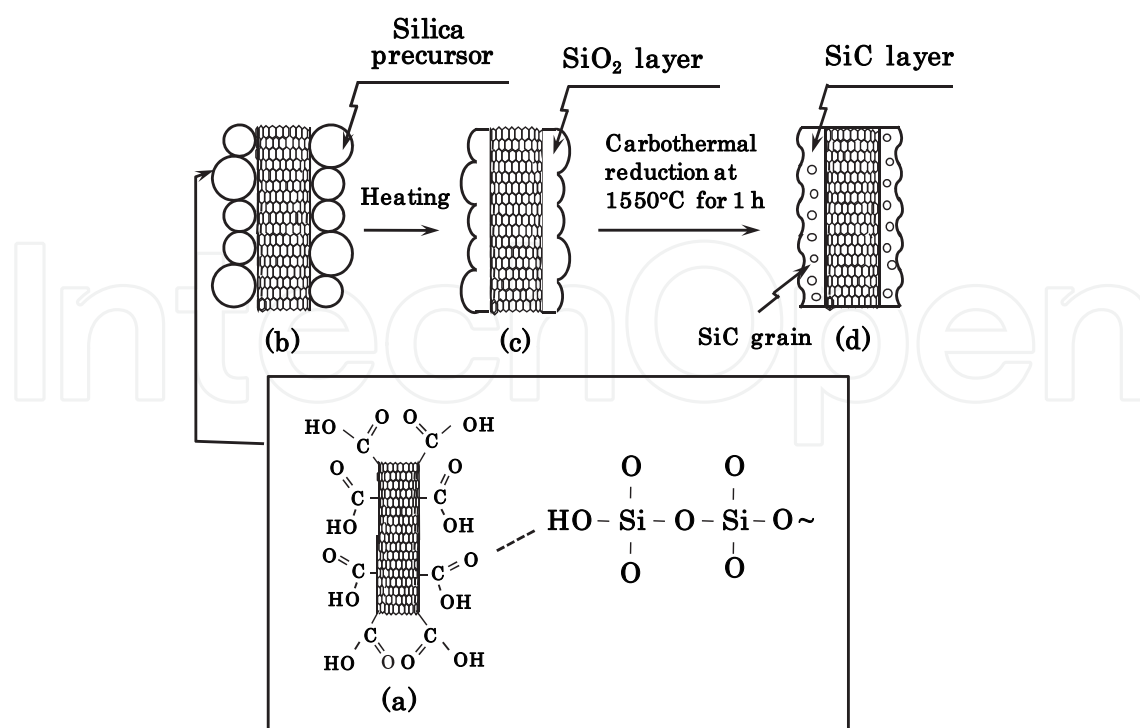


Fig. 13. Schematic diagram of the formation of a silicon carbide layer on the surface of VGCF via the formation of silica precursor/silica.

- a. Interaction of acid-treated VGCF with TEOS
- b. Formation of silica precursor on the surface of acid-treated VGCF
- c. Formation of silica layer on the surface of acid-treated VGCF
- d. Formation of silicon carbide layer on the surface of carbothermally-reduced VGCF, together with silicon carbide grains.

4. Conclusions

The conditions for the formation of a SiC layer on the surface of vapor grown carbon nanofiber (VGCF®) were examined by the sol-gel method and subsequent carbothermal reduction at a temperature between 1400 and 1600°C for 1 h in argon atmosphere. The results obtained were summarized as follows:

- i. Two types of techniques to coat silica precursor onto the surface of VGCF by a sol-gel technique, using TEOS, were examined, *i.e.*, (i) the coating of silica precursor at 40°C for 30 h after the modification of surface properties from hydrophobic to hydrophilic, using PVP as a surfactant, and (ii) the coating of silica precursor at 40°C for 15 h after acid treatment (concentrated sulfuric and 70% nitric acids) to form hydrophilic carboxyl groups at 30°C for 48 h. Relating to the technique of (i), VGCF and spherical silica precursors were independently present in the powder with no significant coating of silica precursor noted on the VGCF surface. Relating to the technique of (ii), the coating of silica precursor was successfully conducted due to the formation of hydrophilic carboxyl groups.
- ii. The carbothermal reduction of VGCF coated with silica precursor was further investigated at a temperature between 1300 to 1600°C for 1 h in Ar atmosphere. When the VGCF coated with silica precursor was carbothermally reduced at 1500°C for 1 h, a

notably crystalline SiC layer could be formed on the VGCF surface with this surface layer being found to enhance the heat resistance of VGCF in air.

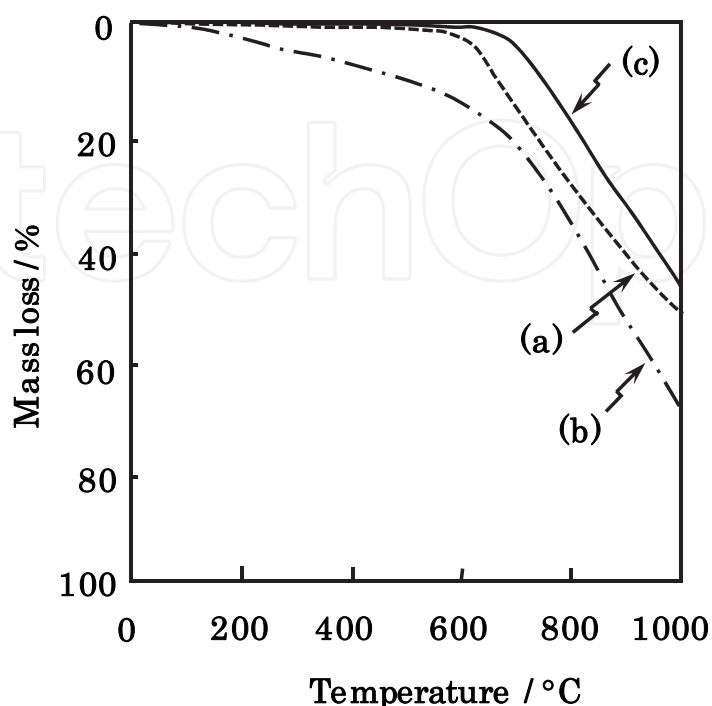


Fig. 14. TG curves of (a) as-received VGCF, (b) acid-treated VGCF, and (c) VGCF coated with silicon carbide obtained by carbothermally reducing the silica precursor at 1500°C for 1 h in Ar atmosphere. Note that the VGCF coated with silicon carbide was prepared by heating TEOS at 40°C for 15 h. Heating rate: 10°C·min⁻¹

5. References

- Asai, M., Fujita, N., Sano, M. & Shinkai, S., (2003). Silica Gel Fabrication of [60]Fullerene Aggregates and Carbon Nanotubes Utilizing the Amphiphilic Nature of Poly(*N*-vinylpyrrolidone) As a 'Glue', *Journal of Materials Chemistry*, Vol. 13, pp. 2145-2149, ISSN 1364-5501
- Jacobsen, R. L., Tritt, T. M., Ehrlich J. R. & Gillespie, D. J. (1995), Mechanical Properties of Vapor-Grown Carbon-Fiber, *Carbon*, Vol. 33, pp. 1217-1221, ISSN 0008-6223
- Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD), Card. No.29-1129, Swarthmore, PA, USA.
- Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD) Card. No.41-1487, Swarthmore, PA, USA.
- Duque, J. G., Cognet, L., Parra-Vasquez, A. N. G., Nicholas, N., Schmidt, H. K. & Pasquali, M. (2008). Stable Luminescence from Individual Carbon Nanotubes in Acidic, Basic, and Biological Environments, *Journal of the American Chemical Society*, Vol. 130, pp. 2626-2633, ISSN 0002-7863
- Kita, J., Suemasu, H., Davies, I. J., Koda S. & Itatani, K. (2010). Fabrication of Silicon Carbide Composites with Carbon Nanofiber Addition and Their Fracture Toughness, *Journal of Materials Science*, Vol. 45, Number 22, pp. 6052-6058, ISSN 0022-2461

- Kubota, S., Nishikiori, H., Tanaka, N., Endo, M. & Fujii, T. (2005). Dispersion of Acid-Treated Carbon Nanofibers into Gel Matrices Prepared by the Sol-Gel Method. *Journal of Physical Chemistry B*, Vol. 109, pp. 23170-23174, ISSN 1520-6106
- Lin Y.-J. & Tsang, C.-P., (2003), The Effects of Starting Precursors on the Carbothermal Synthesis of SiC Powders, *Ceramics International*, Vol. 29, Issue 1, pp. 69-75, ISSN 0272-8842
- Maensiri, S., Laokul, P., Kinkaewnarong, J. & Amornkitbamrung, V. (2007). Carbon Nanofiber-Reinforced Alumina Nanocomposites: Fabrication and Mechanical Properties, *Materials Science and Engineering A*, Vol. 447, pp. 44-50, ISSN 0921-5093
- Navamathavan, R., Kim C. Y. & Jung, A. S. (2008). Deposition and Characterization of Porous Low-Dielectric-Constant SiOC(-H) Thin Films Deposited from TES/O₂ precursors by Using Plasma-Enhanced Chemical Vapor Deposition. *Journal of the Korean Physical Society*, Vol. 53, pp. 351-356, ISSN 0374-4884
- O'Connell, M. J., Boul, P., Ericson, L. M., Huffman, C., Wang, Y., Haroz, E., Kuper, C., Huffman, J., Ausman K. D. & Smalley, R. E. (2001). Reversible Water-Solubilization of Single-Walled Carbon Nanotubes by Polymer Wrapping, *Chemical Physics Letters*, Vol. 342, pp. 265-271, ISSN 0009-2614
- Raj, R. (1993). Fundamental Research in Structural Ceramics for Service Near 2000°C, *Journal of American Ceramic Society*, Vol. 76, Issue 9, pp. 2147-2174, ISSN 0002-7820
- Sun J. & Gao L. (2003). Development of a Dispersion Process for Carbon Nanotubes in Ceramic Matrix by Heterocoagulation, *Carbon*, Vol. 41, Issue 5, pp. 1063-1068, ISSN 0008-6223
- Tabatabaei, S., Shukohfar, A., Aghababazadeh, R. & Mirhabibi, A. (2006). Experimental Study of the Synthesis and Characterisation of Silica Nanoparticles via the Sol-Gel Method, *Journal of Physics: Conference Series*, Vol. 26, pp. 371-374, ISSN 1742-6588
- Wang, K., Cheng Y.-B. & Wang, H. (2009). Growth of SiC Whiskers by Carbothermal Reduction of Mesoporous Silica-Carbon Composites Infiltrated With SiC Nuclei, *Journal of the Australian Ceramic Society*, Vol. 45, No. 1, pp. 10-12, ISSN 0004-881X
- Wang, F., Liu, J., Yang, H., Luo, Z., Lv, W., Li, C. & Qing, S. (2008). Spherical Particles from Tetraorthosilicate (TEOS) Sol-gel Process with Dimethyldiethoxysilane (DDS) and Diphenyldiethoxysilane (DPDS) Addition, *Journal of Non-Crystalline Solids*, Vol. 354, Issues 45-46, 5047-5052, ISSN 0022-3093
- Woo, H.-Y., Jung, W.-G., Ihm, D.-W. & Kim, J.-Y. (2010). Synthesis and Dispersion of Polypyrrole Nanoparticles in Polyvinylpyrrolidone Emulsion. *Synthetic Metals*, Vol. 160, pp. 588-591, ISSN 0379-6779
- Zhang, J., Zou, H., Qing Q., Yang, Y., Li, Q., Liu, Z., Guo, X. & Du, Z. (2003). Effect of Chemical Oxidation on the Structure of Single-Walled Carbon Nanotubes. *Journal of Physical Chemistry B*, Vol. 107, pp. 3712-3718, ISSN 1089-5647



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Since their discovery in 1991, carbon nanotubes have been considered as one of the most promising materials for a wide range of applications, in virtue of their outstanding properties. During the last two decades, both single-walled and multi-walled CNTs probably represented the hottest research topic concerning materials science, equally from a fundamental and from an applicative point of view. There is a prevailing opinion among the research community that CNTs are now ready for application in everyday world. This book provides an (obviously not exhaustive) overview on some of the amazing possible applications of CNT-based materials in the near future.

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