

Surface modification of carbon nanofibers with SiC by heating different SiO vapor sources in argon atmosphere

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In order to improve interfacial bonding strength between carbon nanofibers (CNFs) and SiC matrix in CNFs/SiC composites and to disperse CNFs uniformly in the matrix, SiC coating on surface of CNFs was performed in argon atmosphere in the temperature range of 1400 to 1800°C using SiO₂, SiO, and mixture of Si and SiO₂ powders (Si/SiO₂ powder) as silicon sources, and the modification and dispersibility of the treated CNFs were investigated. β -SiC particles were deposited on the surface of the CNFs in all the specimens at 1600–1800°C. So more SiC was formed by heating CNFs with SiO powder at 1600°C. However, the formed SiC was oxidized at higher temperature, practically, at 1800°C. This oxidation was advanced more by using SiO₂ and Si/SiO₂ powders as silicon sources and very fine carbon fibers were observed on the surface of CNFs. The dispersibilities of CNFs heated with Si/SiO₂ and SiO powders were superior to those of as-received CNFs, CNFs treated with NaClO₃ solution and CNFs heated with SiO₂ powder, which resulted from the advanced oxidation of CNFs and the silanol group (–SiOH) on surface of formed SiC.

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1. Introduction

Carbon nanotubes (CNTs) are attractive candidates for the reinforcement of various materials because they have many superior properties, such as high tensile strength, high elasticity and high aspect ratio.^{1),2)} So many works have been performed to improve fracture toughness and strength of ceramics with CNTs, such as CNTs/Al₂O₃,^{3)–8)} CNTs/ZrO₂,^{9)–12)} CNTs/Si₃N₄,^{13)–17)} and CNTs/SiC^{18)–22)} composites. However, a few papers have been reported that greatly higher performance based on CNTs has been obtained. In many papers, improvements of weak bonding between CNTs and matrix, dispersion of the CNTs in the matrix, degradation of the CNTs and densification of the composites are emphasized to enhance the mechanical properties, especially, fracture toughness.^{16),21),23)–26)}

In our previous study,²⁷⁾ 3 wt% carbon nanofibers (CNFs)/SiC composite showed 50% increase in the fracture toughness, compared with the monolithic SiC. The improved fracture toughness resulted from pullout and/or bridging of the CNFs bonded with SiC grains much more closely. However, the bending strength of the composite was a little higher than that of the monolithic SiC because CNFs and/or residual carbon agglomerates which could be fracture origin, were formed during the remarkable SiC grain growth. If the CNFs coated with SiC layer are combined with SiC, the layer may improve the interface bonding between CNFs and SiC matrix and also reduce the formation of large CNFs agglomerates in the composites by inhibiting movement of CNFs during SiC grain growth.

Morisada et al. have developed a simple process for formation of the SiC coating on the surface of fine diamond particles or CNTs by heating diamond particles or CNTs with SiO powder

in vacuum of about 0.03 Pa.^{28)–30)} And they actually fabricated SiC-coated CNTs/SiC composites and showed that fracture toughness of the composites increased by dispersion of the SiC-coated CNTs.²²⁾

On the other hand, research group of Zhao have reported that thin SiC_xO_y coating,³¹⁾ SiC coating³²⁾ and amorphous SiO₂ coating³³⁾ were prepared on the surface of CNTs by heating CNTs with polycarbosilane, Si powder and mixture of Si and SiO₂ powders, respectively, in a coke bed in air. Also, while the formation of SiC nanorods by heating CNTs with Si fragments³⁴⁾ or mixture of Si and SiO₂³⁵⁾ in argon flow has been reported, the formation of SiC coating on the surface of CNTs in argon atmosphere has not been reported. In addition, the dispersibility of such coated CNTs has not been estimated.

Then, in this study, the formation of SiC coating on surface of CNFs was performed in argon atmosphere in the temperature range of 1400 to 1800°C using SiO₂, SiO, and mixture of Si and SiO₂ powders as silicon sources, and the surface modification and dispersibility of the CNFs were investigated.

2. Experimental procedure

CNFs used in this study were vapor-grown carbon fibers (VGCF, Showa Denko, Japan), which are one type of multi-walled CNT. The diameter and length of the CNFs were 150 nm and 8 μ m, respectively. The CNFs were oxidized in a NaClO₃ aqueous solution at 90°C. As the silicon source, amorphous SiO₂ powder (SO-E1, purity 99.9%, Admatechs, Japan), SiO powder (SMOH-130109, purity 99.9%, OSAKA Titanium technologies, Japan), and Si (Hi-Al, purity 99.999%, Yamaishi Metal, Japan) and amorphous SiO₂ powders mixture (Si/SiO₂ powder) of which the mole ratio was 1:1, were used.

The SiO₂, Si/SiO₂ and SiO powders were placed on bottom in carbon crucibles and the CNFs powders were set onto a carbon

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felt as illustrated in **Fig. 1**. The weight ratio of silicon source to CNFs was 1:1. The carbon lids were put on the crucibles, and they were heated at 1400–1800°C for 2 h in argon atmosphere. The heating rate was 5°C/min.

The products were analyzed using X-ray diffractometry. The microstructures of the CNFs heated with SiO₂, Si/SiO₂ and SiO powders were observed using a scanning electron microscopy (SEM), a transmission electron microscopy (TEM) and a scanning TEM (STEM). The SEM images of CNFs surfaces were observed using electron beam under low accelerating voltage of 1 kV or 5 kV. The dispersibilities of as-received CNFs and the heated CNFs in aqueous solution were evaluated as follows; these CNFs were dispersed in the distilled water dissolving ammonium naphthalene sulfonate as a dispersant by ultrasonic for 1 h. The obtained suspensions were kept quietly for 0–10 days and the sediment state of the CNFs in such suspensions was observed.

3. Results and discussions

3.1 Products on surface of CNFs

X-ray diffraction (XRD) patterns of the CNFs heated with SiO₂, Si/SiO₂, and SiO powders at 1400–1800°C are shown in **Fig. 2**. The diffraction peak of CNFs was observed at 26.4° in all patterns, which was corresponding to (0 0 2) plane of the graphite, and also the diffraction peak appeared at 35.7° in all specimens heated at 1600 and 1800°C, which was attributed to the diffraction of (1 1 1) plane of β-SiC. At 1400°C, the peak appeared only a trace in the pattern of CNFs heated with Si/SiO₂

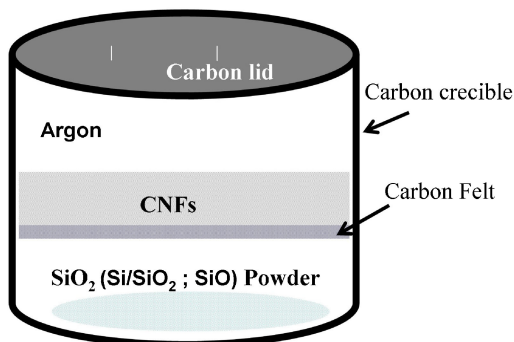
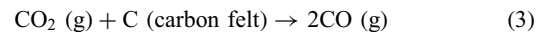
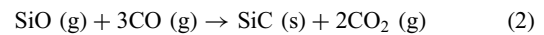
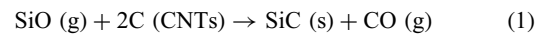


Fig. 1. Schematic illustration of setting of starting materials.

and SiO powders and was not observed in the pattern of CNFs heated with SiO₂ powder.

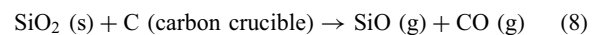
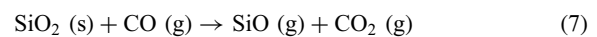
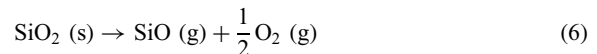
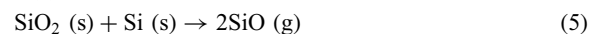
Morisada et al. reported that SiC layer was formed on the surface of CNTs through two steps at 1150–1550°C.^{22),28)} The first step is the conversion of the CNTs surface to SiC film, as shown by reaction (1), and the second step is the deposition of nanometer-sized SiC on the thin SiC film, as shown by reaction (2). The CO₂ (g) generated by reaction (2) is converted to CO (g) by reaction (3). The generation of CO (g) by reaction (3) controls reaction (2).²²⁾



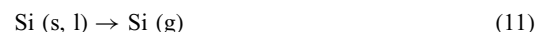
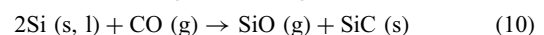
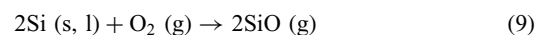
Furthermore, Morisada et al. showed that SiO (g) evaporated from SiO powder at about 1200°C in vacuum according to reaction (4).²⁹⁾



On the other hand, in Si/SiO₂ powder, SiO₂ (s) reacted with Si (s) to form SiO (g) in coke bed according to reaction (5) and the formed SiO (g) reacted with CNTs to form SiC at >1300°C in coke bed.³³⁾ In addition, SiO₂ is thermally decomposed about at 1600°C according to reaction (6) and also reacts with CO (g) and C (carbon crucible) to form SiO (g) according to reactions (7) and (8).³⁶⁾



Si powder not only reacts with CO (g) and O₂ (g) to form SiO (g) according to reactions (9) and (10) and but also can evaporate Si (g) according to reaction (11).³²⁾



When SiO₂ powder was used as silicon source in this study, SiO (g) might be formed through the reaction (6) about at 1600°C in argon atmosphere. Therefore, SiC was not formed at 1400°C and was formed above 1600°C through reactions (1)–(3). In

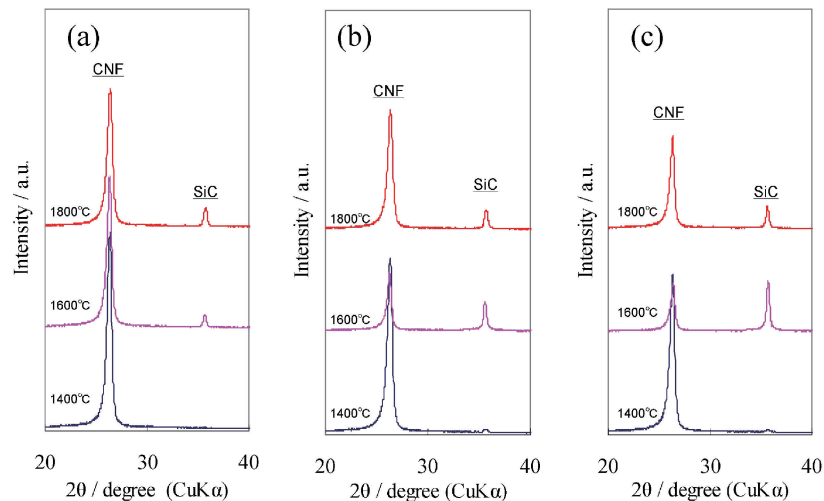


Fig. 2. XRD patterns of the CNFs heated with (a) SiO₂, (b) Si/SiO₂ and (c) SiO powders at 1400–1800°C.

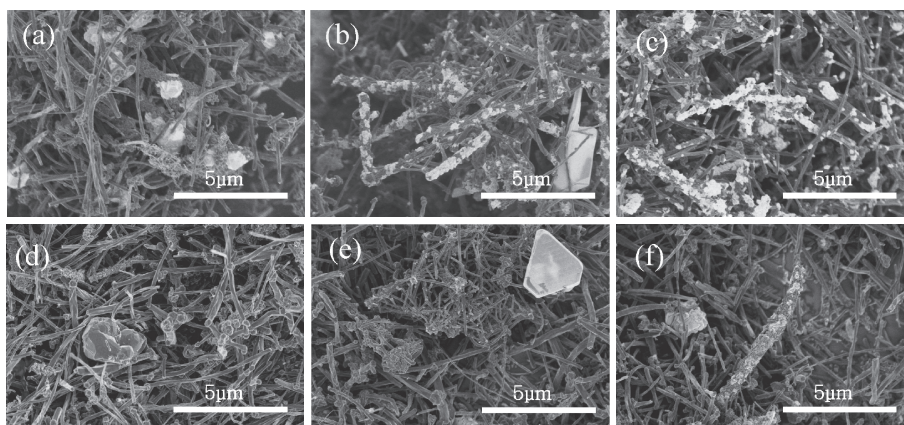


Fig. 3. SEM images of the CNFs heated with (a) SiO₂, (b) Si/SiO₂ and (c) SiO powders at 1600°C, and heated with (d) SiO₂, (e) Si/SiO₂ and (f) SiO powders at 1800°C.

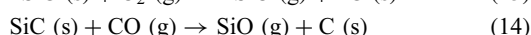
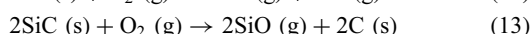
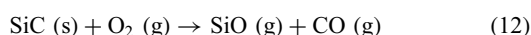
addition, SiO₂ powder might react with CO (g) generated by reactions (1) and (3) and carbon to form SiO (g) through reactions (7) and (8), respectively.

When Si/SiO₂ was used as silicon source in this study, SiO (g) might be formed through the reaction (5) at >1300°C in argon atmosphere. Therefore, SiC was formed above 1400°C through reactions (1)–(3). In addition, SiO (g) might be formed through reactions (6)–(8). Also Si (g) evaporated from Si powder according to reaction (11) might react directly with CNFs to form SiC.

When SiO powder was used as silicon source in this study, SiO (g) must be formed at >1200°C according to reaction (4) in argon atmosphere. So SiC was formed above 1400°C. Because more SiO (g) must be evaporated from SiO powder, the diffraction peak intensity of SiC in XRD pattern of CNFs heated with SiO powder at 1600°C was stronger than that of SiC in XRD pattern of CNFs heated with SiO₂ and Si/SiO₂ powders at 1600°C (Fig. 2), that is, the formation of SiC was promoted by using SiO as silicon source.

In such ways, the formation process of SiC depended strongly on the heating temperature and the raw materials of silicon source in argon atmosphere.

The diffraction peak intensity of SiC at 1800°C became just a little stronger than that of SiC at 1600°C [Fig. 2(a)], or became weaker than that of SiC at 1600°C [Figs. 2(b) and 2(c)], which resulted from the oxidation of the formed SiC. It is known that SiC is oxidized actively even under a low O₂ and/or CO partial pressure according to reactions (12),^{28),29),36)} (13)³⁶⁾ and/or (14).^{37),38)}



In this study, the reactant O₂ (g) must be supplied from the residual O₂ (g) in furnace, trace O₂ (g) containing in the argon gas and O₂ (g) formed through the reaction (6), and the reactant CO (g) might be supplied from formed CO (g) through the reactions (1), (3), (8) and (12).

3.2 Surface modification of CNFs

SEM images of the CNFs heated with SiO₂, Si/SiO₂ and SiO powders at 1600 and 1800°C are shown in Fig. 3. In these images, carbon and SiC appeared as dark image and whitish image, respectively. So a large amount of SiC particles were

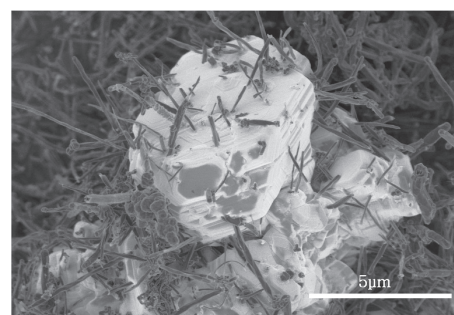


Fig. 4. SEM image of the CNFs heated with SiO₂ powder at 1800°C.

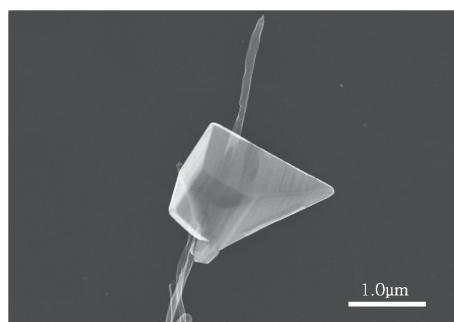


Fig. 5. STEM image of the CNFs heated with Si/SiO₂ powder at 1600°C.

deposited particularly on the surface of CNFs heated with SiO powder at 1600°C. They did not always coat uniformly on the surface but some CNFs were covered wholly with SiC. An amount of SiC particles on the surface of CNFs heated with Si/SiO₂ and SiO powders at 1800°C obviously decreased than that of SiC particles on the surface of CNFs heated at 1600°C, but there was no change in the amount of SiC particles on the surface of CNFs heated with SiO₂ powder at 1600 and 1800°C. In addition, some large SiC grains could be also observed in all specimens. Some CNFs were embedded in such SiC grains. For example, many CNFs were buried in large spherical SiC agglomerate (Fig. 4), and a CNF was stuck into a shaped SiC grain (Fig. 5). Some SiC particles were formed on the surface of CNFs clearly (Fig. 6). The size of the SiC particles was about 100 nm. The (1 1 1) plane of β-SiC should be formed on the

(0 0 2) plane of CNFs and grow.²⁸⁾

TEM images of the CNFs heated at 1600°C with SiO₂, Si/SiO₂ and SiO powders and X-ray maps of C, Si and O elements are shown in Fig. 7. The X-ray maps showed existence of Si element on the CNFs. Compared the CNFs heated with SiO₂ powder with the CNFs heated with Si/SiO₂ and SiO powders, Si element on the former CNFs was less than that on the latter CNFs.

On the other hand, very fine fibers were observed on the surface of some CNFs heated with SiO₂ and Si/SiO₂ powders at 1800°C as shown in the Figs. 8(a) and 8(b), and also some branch-like tubes on the surface of the CNFs heated at 1600°C were observed as shown in the Fig. 9. Morisada et al. reported that β -SiC nano whiskers were formed on the surface of SiC-coated diamond by vapor growth.²⁹⁾ Also, Tang reported that SiC

nanorods were formed by heating CNTs with Si/SiO₂ powder in argon flow at 1400°C³⁵⁾ and Wu reported that SiC nanorods were formed by heating CNTs with Si fragment in argon flow at 1450°C.³⁴⁾ The other side, there are some reports that CNTs and graphene were formed epitaxially on SiC at >1250°C by thermal decomposition of silicon carbide.³⁷⁾⁻⁴³⁾ The mechanisms of CNTs and graphene formation on SiC substrate were explained by the research group of Kusunoki.³⁷⁾⁻⁴⁰⁾ The fine fibers and branch-like tubes formed in this study might not be SiC but carbon because an amount of the formed SiC decreased in the specimen heated with Si/SiO₂ powder at 1800°C, that is, the formed SiC was

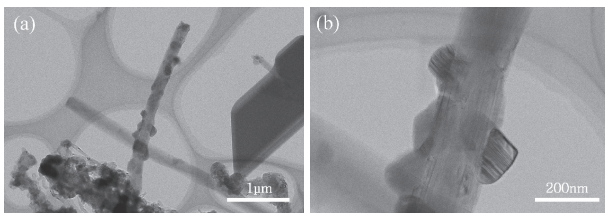


Fig. 6. TEM images of the CNFs heated with Si/SiO₂ powder at 1600°C.

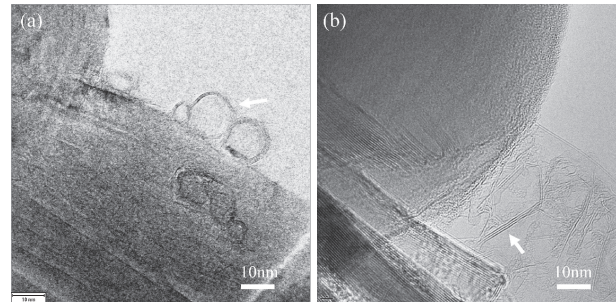


Fig. 9. TEM images of the CNFs heated with (a) SiO₂ and (b) Si/SiO₂ powders at 1600°C.

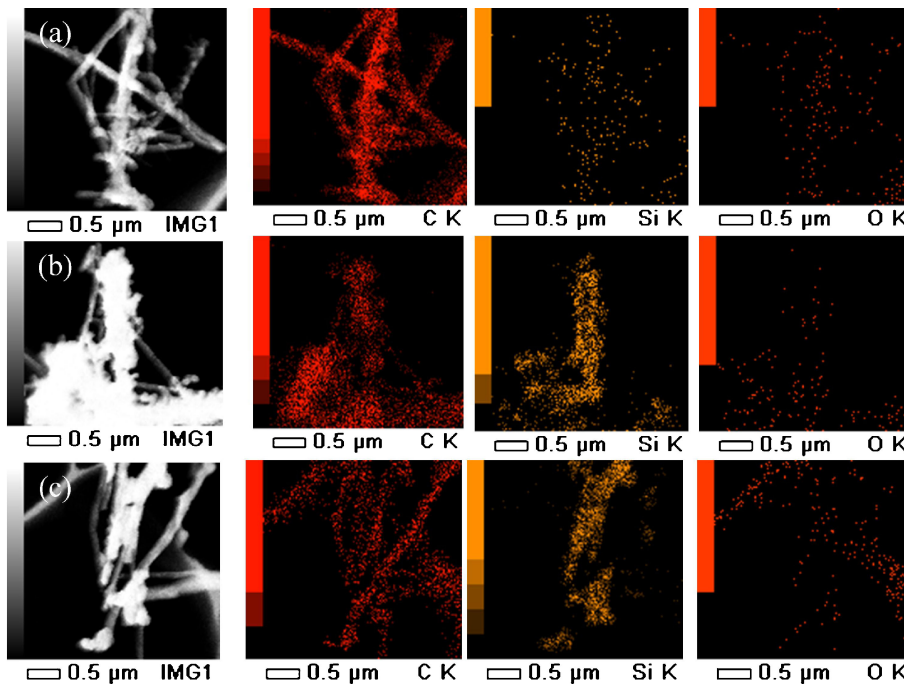


Fig. 7. TEM images of the CNFs heated with (a) SiO₂, (b) Si/SiO₂ and (c) SiO powder at 1600°C and X-ray maps of C, Si and O elements.

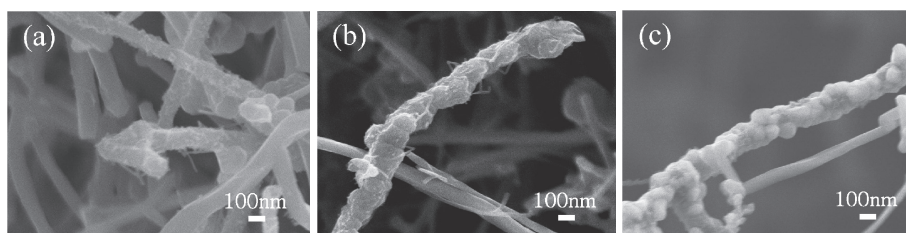


Fig. 8. SEM images of the CNFs heated with (a) SiO₂, (b) Si/SiO₂ and (c) SiO powders at 1800°C.

reacted with O_2 (g) and CO (g) to form carbon through the reactions (13) and (14). When CNFs were heated with SiO_2 and Si/SiO_2 powders at 1600 and 1800°C in this study, SiC particles were formed on the surface of CNFs. At the same time, O_2 (g) and CO (g) should be released through the reactions (1), (3) and (6), which caused the reactions (12)–(14) and then resulted in the generation of SiO (g) and carbon. The carbon must be formed as the very fine carbon fibers on the based CNFs. However, the very fine carbon fibers were not observed on the surface of CNFs heated with SiO powder. When CNFs were heated with SiO powder, SiC was formed through reactions (1)–(3) and CO (g) was released, which caused the reaction (14) and decreased the SiC at 1800°C. The other side, more SiO (g) must evaporate from SiO powder, especially at higher temperatures, that is, partial pressure of SiO increased and so the reaction (14) was difficult to occur. In addition, O_2 (g) was not released during the formation of SiC. Therefore, the significant oxidation of SiC did not occur even at 1800°C. Consequently, more SiC remained even at 1800°C as shown in Fig. 2, and the very fine carbon fibers could not be observed.

In vacuum, the SiC particles with size of about 50 nm were formed on the surface of CNTs heated with SiO powder at 1150°C.^{28),30)} In this case, though SiC was oxidized actively to generate SiO (g) and CO (g),²⁸⁾ the formation of carbon such as very fine carbon fibers were not reported.^{28),30)} In the coke bed in air, a thin amorphous SiO_2 coating was formed on the surface of CNTs heated with Si/SiO_2 powder at temperature at 1300°C,³³⁾ very thin SiC coating was formed on the surface of CNTs heated with Si powder at 1300–1400°C,³²⁾ and then these CNTs transformed into SiC nanowires and/or nanorods with an increase in heating temperature.^{32),33)} In such coke bed atmosphere, the oxidation of the formed SiC and the formation of carbon such as very fine carbon fibers were not reported.^{32),33)} In argon flow, Tang³⁵⁾ and Wu³⁴⁾ synthesized SiC nanorods instead of SiC coating, mentioned above. In argon atmosphere in this study, SiC particles were certainly formed by heating CNFs with SiO_2 , Si/SiO_2 , and SiO powders at higher temperature of above 1400°C, however, the formed SiC was oxidized at further higher temperature, practically, at 1800°C and very fine carbon fibers were formed on the surface of particularly CNFs heated with SiO_2 and Si/SiO_2 , which is the special feature in argon atmosphere.

The argon atmosphere was easier to oxidize the formed SiC than vacuum, coke bed and argon flow atmospheres since the argon atmosphere did not exhaust the formed O_2 (g) and CO (g), which was different from vacuum and argon flow atmospheres, and the argon atmosphere was not reducing atmosphere, which was different from coke bed atmosphere.

3.3 Dispersibility of the CNFs

Hydrophobic CNTs cannot readily disperse in polar liquids such as water. So CNFs are oxidized in a liquid medium⁴⁴⁾ and are modified with the oxygenated functional groups, such as hydroxyl or carboxyl groups.^{44)–46)} In this study, CNFs were oxidized in a $NaClO_3$ solution at 90°C. Raman spectra of as-received CNFs, CNFs treated with $NaClO_3$ solution at 90°C, CNFs heated with SiO_2 powder at 1400–1800°C, and CNFs heated with Si/SiO_2 and SiO powders at 1600°C are shown in Fig. 10. D-band (defect-mode) and G-band (E_{2g2} mode) are observed at 1314 and 1576 cm^{-1} , respectively. The intensity ratio of D-band to G-band (D/G ratio) of CNFs treated with $NaClO_3$ solution at 90°C and CNFs heated with SiO_2 at 1400°C was a little higher than D/G ratio of as-received CNFs, which suggests that a few defects were formed by treating with $NaClO_3$ solution at 90°C and heating with SiO_2 at 1400°C. The D/G ratio of CNFs treated with SiO_2 became higher with an increase in heating temperature. The other side, the D/G ratios of CNFs heated with Si/SiO_2 and SiO powders at 1600°C were higher than that of CNFs heated with SiO_2 powder [Fig. 10(b)]. These results indicate that the defect increased in the CNFs as an amount of the formed SiC increased.

In order to compare the dispersibilities of the CNFs heated with SiO_2 , Si/SiO_2 and SiO powders at 1600°C with that of the as-received CNFs and the CNFs treated with $NaClO_3$ solution at 90°C, they were dispersed in water of which pH was 10 with tetra methyl ammonium hydroxide and were kept quietly for 0–10 days as shown in Fig. 11. The CNFs in all suspensions were dispersed just after sonication. The as-received CNFs were sedimented at bottom in less than 4 h. Most of the CNFs treated with $NaClO_3$ solution were dispersed for 1 day but were sedimented at bottom after 3 days. Most of the CNFs heated with SiO_2 powder were dispersed for 3 days but were sedimented at bottom after 10 days. Most of the CNFs heated with Si/SiO_2 and

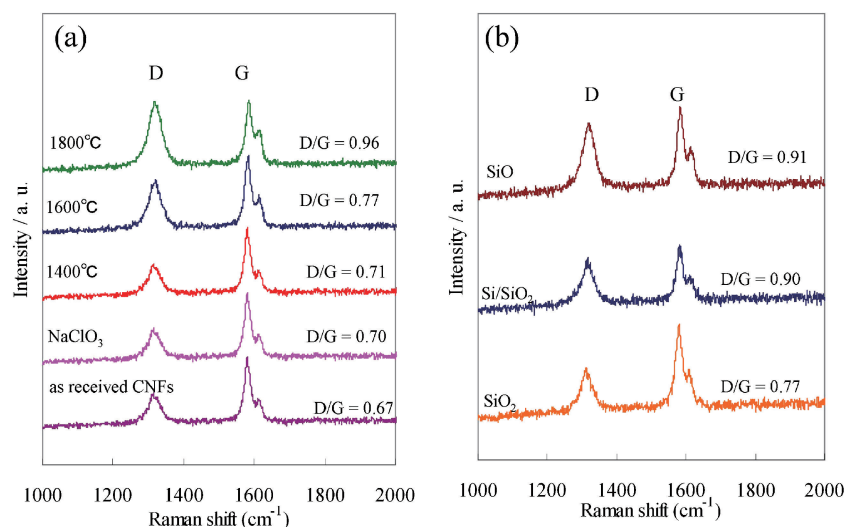


Fig. 10. Raman spectra of (a) as-received CNFs, CNFs treated with $NaClO_3$ at 90°C and CNTs heated with SiO_2 at 1400–1800°C, (b) CNTs heated with SiO_2 , Si/SiO_2 and SiO at 1600°C.

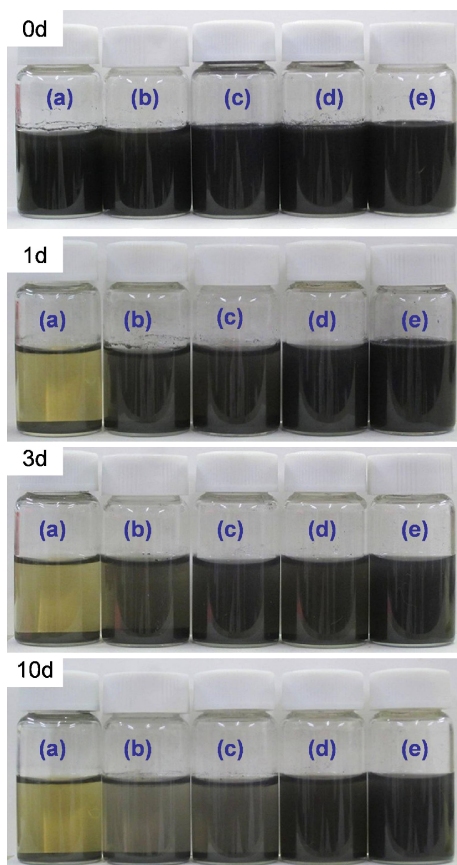


Fig. 11. Dispersibilities of (a) as-received CNFs, (b) CNFs treated with NaClO_3 at 90°C , and CNFs heated with (c) SiO_2 , (d) Si/SiO_2 and (e) SiO powders at 1600°C .

SiO powders kept their dispersibilities for 10 days. These results indicate that the dispersibilities of CNFs heated with Si/SiO_2 and SiO powders were superior to those of as-received CNFs, CNFs treated with NaClO_3 solution and CNFs heated with SiO_2 powder. The improved dispersibility of CNFs was caused mainly by two effects. The first is the increased defects of CNFs, that is, the oxidation of CNFs. So the oxygenated functional groups enhanced the dispersibility of CNFs in water. The second is the improvement of the wettability between CNFs and water. The SiC particles formed on the surface of the CNFs should be modified by silanol group ($-\text{SiOH}$) in water, which turned hydrophobicity of CNFs into hydrophilicity. In addition, pH of this solution (pH 10) was above the isoelectric point (IEP) for SiC (IEP: pH 2.5–3.0)^{47–49} and CNTs (IEP: pH 7.5),⁵⁰ and so the surface of SiC -coated CNFs had negative charge. The electrostatic effect made the dispersibility of CNFs improve.

4. Conclusions

In this study, the formation of SiC coating on surface of CNFs was performed in argon atmosphere in the temperature range of 1400 to 1800°C using SiO_2 , SiO , and mixture of Si and SiO_2 powders as silicon sources, and the surface modification and dispersibility of the treated CNFs were investigated. The obtained results could be summarized as follows.

- (1) SiC particles were formed on the surface of the CNFs by heating CNFs with SiO_2 , Si/SiO_2 and SiO powders at 1600 – 1800°C in argon atmosphere. More SiC was formed by heating CNFs with SiO powder at 1600°C . As an amount of the formed SiC increased, the defect increased

in the CNFs.

- (2) The formed SiC was oxidized by O_2 (g) and CO (g) at higher temperature, practically, at 1800°C . So this oxidation was advanced more by using SiO_2 and Si/SiO_2 powders as silicon sources and very fine carbon fibers were observed on the surface of CNFs, which is special feature in argon atmosphere.
- (3) The dispersibilities of CNFs heated with Si/SiO_2 and SiO powders were superior to those of as-received CNFs, CNFs treated with NaClO_3 solution and CNFs heated with SiO_2 powder.

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