Thin Solid Films 694 (2020) 137748

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# SiC-conversion coating from silica sol for improved oxidation resistance of carbon-fiber insulator in solar-cell ingot-growing crucibles

Su-Bin Ahn[a], Minh Dat Nguyen[a,b], Jung-Won Bang[a], Younghee Kim[a], Yoonjoo Lee[a], Dong-Geun Shin[c], Woo-Teck Kwon[a,*]

[a] Energy & Environment Division, Korea Institute of Ceramic Engineering and Technology, JinJu 52851, Republic of Korea
[b] Faculty of Mechanical Engineering, Le Quy Don Technical University, 236 Hoang Quoc Viet, Bac Tu Liem, Hanoi, Vietnam
[c] Convergence R & D Division, Korea Institute of Ceramic Engineering and Technology, JinJu 52851, Republic of Korea

ARTICLE INFO

*Keywords:*
Thermal insulators
Carbothermal reduction
SiC-conversion coating
Oxidation resistance

ABSTRACT

Carbon fibers, which have excellent mechanical and thermal properties, are used in many fields; however, they are very vulnerable to oxidation and have limited service life. Various studies have attempted to address this. In this study, a SiC–C composite material was prepared using a silica sol to coat the carbon surface and improve the oxidation resistance of a carbon-fiber insulator as a material for solar-cell ingot-growing crucibles. The SiC coating was formed on the carbon surface under various conditions by controlling the composition of the silica sol, and its characteristics were examined. Via SiC-conversion coating through a carbothermal reaction, a film of thickness 30–80 nm film was uniformly formed over the entire sample. In addition, the oxidation characteristics were enhanced by a factor of three to five, when compared with conventional carbon materials.

## 1. Introduction

Carbon fibers are lightweight and high-strength material with excellent thermal-shock resistance, and have been used in various industrial applications such as cogeneration, advanced engines, heat exchangers, heat treatment, and material-growth furnaces [1–3]. However, their limited lifetime resulting from their weak resistance against oxidation is a hindrance to wider applicability. Various methods to overcome this issue have been explored [4,5]. In particular, it is important to extend the lifetime of carbon fibers that are intended for use as a thermal-insulator material in solar-cell ingot-growing crucibles. A typical method for improving the oxidation characteristics of carbon fibers is to prevent contact with oxygen by coating the fiber surface with a layer of SiC, which has excellent oxidation resistance at high temperatures [6,7]. As defects such as pores or microcracks can affect the lifetime of a thermal insulator and subsequently the efficiency of the solar-cell ingot-growing process, it is important to suppress as much as possible the growth of defects in the carbon fibers [8]. In addition, because thermal stress due to the difference between the thermal expansion coefficients of SiC and carbon can cause cracks at the interface, a method for controlling the thermal stress must also be considered [9]. Various methods for coating SiC layers on carbon fibers, such as chemical vapor deposition (CVD), liquid-silicon infiltration (LSI), and carbothermal reduction, have been investigated [10–13]. In a study, the carbon surface was covered with a SiC layer by conversion coating via a carbothermal-reduction reaction between the silica sol and graphite fibers [14]. This process formed an SiC coating via two reactions. First, SiO, CO, and $H_2O$ gases were released by the reaction between the silica sol and carbon ($SiO_2 - 2xH_{2x} + C \rightarrow SiO + xH_2O + (1 - 2x)CO$). Next, the carbon fiber surface was coated with a polycrystalline SiC layer through a reduction reaction with SiO gas ($SiO + 2C \rightarrow SiC + CO$) [15], and the conversion coating process enabled the uniform SiC coating to strongly adhere to the carbon surface [16].

In order to employ the SiC-coated carbon-fiber insulator in actual solar cells, it is necessary to develop an economical process for large-capacity coatings, with high efficiency, low operating cost, and processability. The most widely used CVD method has issues regarding safety, large-area coatings, and costs, while with LSI, it is difficult to uniformly coat the inside of materials [17]. In contrast, impregnation coating using carbothermal reduction is efficient, inexpensive, and safe [18]. There have been extensive studies on the preparation of SiC coatings from silicon monoxide; however, these have been difficult to apply in the production of carbon-insulator materials for solar ingots that require large-scale processing [19,20]. First, extra costs are incurred because additional reactors are required to generate $SiO_2$ gas. Second, it is almost impossible to fabricate a large heater with a SiC or

* Corresponding author.
*E-mail address:* wtkwon@kicet.re.kr (W.-T. Kwon).

https://doi.org/10.1016/j.tsf.2019.137748
Received 17 December 2018; Received in revised form 9 December 2019; Accepted 9 December 2019
Available online 10 December 2019
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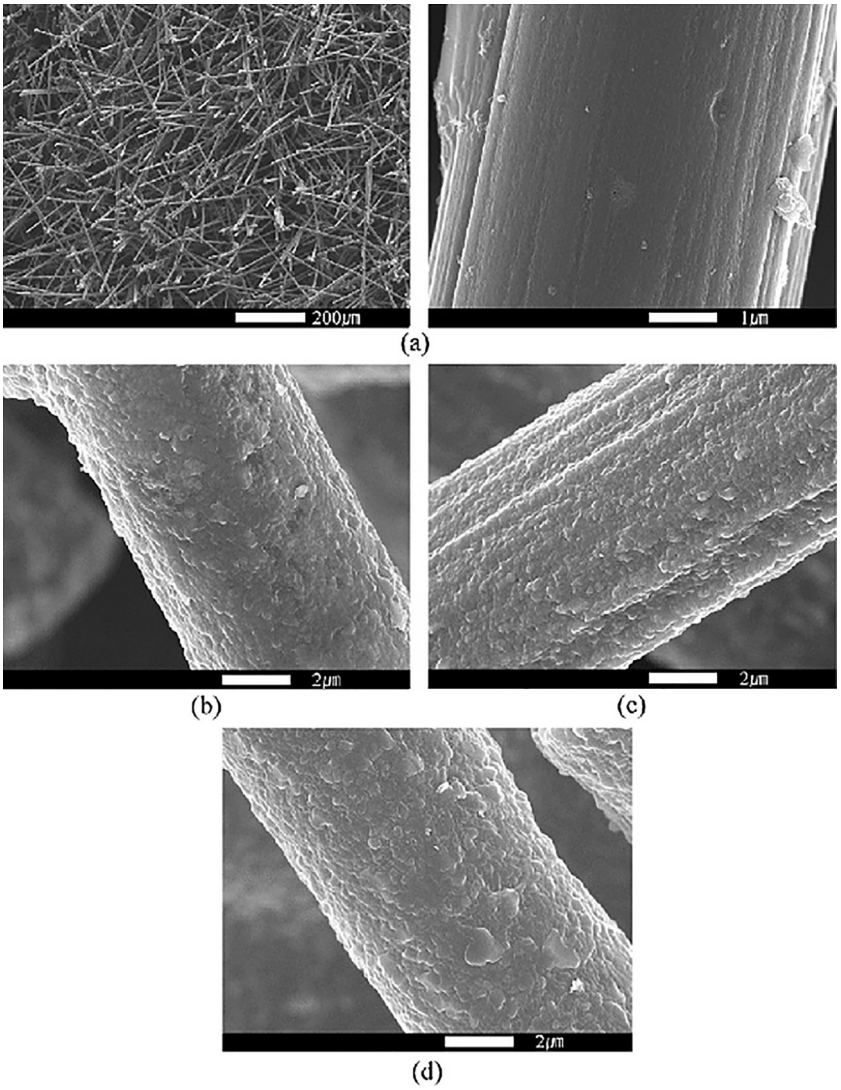


**Fig. 1.** FE-SEM image of (a) mat-type carbon thermal insulator. FE-SEM images of coated samples prepared using diluted solutions consisting of silica sol mixed with methanol at ratios of (b) 1:3, (c) 3:13, and (d)1:7.

Kanthal® Super ($MoSi_2$, SiC, or metallic) heating element that is resistant to oxidation by SiO. Finally, to minimize contamination of the product, graphite must be used as a thermal insulator in the process furnace. To simplify the process and minimize the generation of SiO gas, which damages the inside of the graphite furnace, heat treatment by dip coating in a low-concentration silica sol has been attempted. To increase the oxidation resistance of carbon fibers in our study, a SiC film was formed by drying and heat treatment of a carbon insulator impregnated with a silica sol. The optimum coating conditions were investigated by comparing the characteristics of the coating and oxidation resistance according to the concentration of the silica sol. The heat treatment was carried out in a vacuum atmosphere at 1600 ˚C. The oxidation characteristics were also evaluated in terms of the weight loss caused by heating the sample under oxidizing conditions. In addition, the thermal conductivity was calculated to determine the effect of the SiC coating on the heat-insulating properties of the carbon material.

## 2. Material and methods

### 2.1. SiC coating

A manufactured silica sol (particle size of silica: 40 nm; concentration of silica: 40%) based on an organic solvent (isopropanol, propylene glycol, and monomethyl ether) was used to prepare the coating material. Using methanol (high-performance liquid chromatography (HPLC)-grade, Honeywell, USA) as a diluting solution, coating solutions containing different concentrations of the silica sol were obtained. A mat-type carbon-fiber insulator was acquired from Cocarb Inc., Korea, and cut into small pieces measuring 2 × 2 × 2 cm for the coating test. Each piece was dip-coated in a silica-sol coating solution, removed, left to be impregnated with the solution for 5 min, and then dried for approximately 12 h at 70 ˚C, air. The dried samples were then heated at a rate of 5 ˚C $min^{-1}$ and annealed in a vacuum atmosphere at 1600 ˚C for 1 h. The heat treatment was performed with equipment comprising a graphite heater and graphite crucible.

### 2.2. Preparation of SiC–C insulator

When the carbon insulator was impregnated with the original silica sol, the oxidation reaction due to oxygen contained in the silica sol was excessive, and the carbon-fiber insulator was broken. To resolve this, the viscosity of the silica sol could be lowered, or blowing could be performed after immersion. Instead, in this study, the silica concentration was decreased by diluting the solution, as it enabled cost reduction and process simplification.

SiC–C insulator samples were prepared by impregnating bare

carbon-fiber cubes with diluted solutions containing silica sol mixed with methanol at ratios of 1:3, 3:13, and 1:7; the concentrations of the diluted silica sols were 10, 7.5, and 5 wt%, respectively.

### 2.3. Characterization

High-resolution X-ray diffraction (HRXRD; Smartlab, Rigaku, Japan), with 9 kW Bragg–Brentano focusing optics alignment, and field-emission scanning electron microscopy (FE-SEM; JSM-7610F, JEOL, Japan) were used to determine the surface properties and crystal structure of the coated samples. The operating voltage of the FE-SEM was 10 kV.

To confirm that the oxidation resistance of the carbon insulator was improved by SiC, SiC coatings prepared using coating solutions with various concentrations of silica sol were heat-treated for 100 h at 400 °C in an air atmosphere. This was carried out in accordance with ASTM C1179, an international standard for evaluating the oxidation resistance of carbon insulators. The antioxidation properties were evaluated by analyzing the weight loss caused by oxidation via heat treatment in a box furnace, in accordance with the international standard ASTM C1179 (400 °C, air atmosphere, 100 h). In order to determine the thickness of the coating, a specimen was removed by heat treatment (800 °C, air atmosphere, 24 h) from a coated carbon sample and then examined by FE-SEM. In addition, the cross section of a fiber was processed with a focused ion beam (FIB; Helios NanolabTM 600, FEI, USA) using gallium as the ion source. The FIB system was operated at an accelerating voltage of 30 kV with beam current of 50 pA. The sample was then observed by transmission electron microscopy (TEM; Talos F200X, FEI, USA) with an electron accelerating voltage of 200 kV. Inductively coupled plasma mass spectrometry (ICP-MS; 7900 ICP-MS, Agilent, USA) was used to measure the amount of SiC coating the carbon surface and the amount of impurities in the coating. The surface state of the SiC coating after the antioxidation test was confirmed by X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe, ULVAC-PHI, Japan). The thermal conductivity of the carbon-fiber insulator and coated samples was measured using specimens sized 20 × 20 × 4 cm, in accordance with the Korean standard KS L ISO 679.

## 3. Results and discussion

The carbon-fiber insulator used in this study is shown in Fig. 1(a). It can be seen that the insulator was processed in a non-directional manner using short fibers. FE-SEM images of the coated samples are shown in Fig. 1(b–d). A uniform polycrystalline coating of small grains was formed on the fiber surface by the carbothermal reaction, and no cracks or defects were observed on the fiber surface after coating under all conditions..

HRXRD analysis was performed to confirm the crystallinity and type of the coatings; a typical XRD pattern is shown in Fig. 2. In the XRD patterns of all samples, a large peak appears at 26°, which is the main peak of graphite. Sharp and distinct peaks appear at 35.7°, 60°, and 71.8°, which are all assigned to β-phase SiC. In addition, a relatively weak peak appears at 33.3°, indicating that some α-phase SiC was present in the β-phase SiC. These results confirm that the coating observed by FE-SEM was a SiC crystal.

SiC coating was expected to produce a surface layer with superb antioxidation capability. In this connection, the antioxidation characteristics of the specimens are shown in Fig. 3. The bare carbon-insulator specimen used in this study showed a weight loss of 6.02% when exposed to the air atmosphere, while those with the SiC-conversion coating showed a weight change of approximately 2% regardless of the heat-treatment conditions. In particular, the mass loss by oxidation of the coating prepared from the solution with a silica-sol concentration of 7.5 wt% was the highest at 1.69%. For the carbon-insulator specimens protected by a coating with silica sol, carbon fibers were lost owing to the excessive carbothermal reduction reaction, which

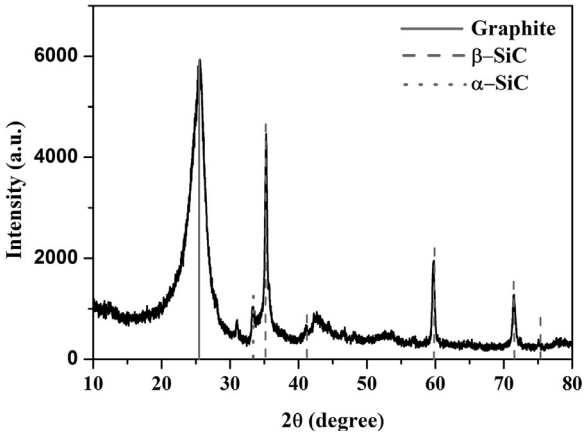


**Fig. 2.** X-ray diffraction patterns of SiC-coated samples prepared from a solution of 7.5 wt% silica sol.

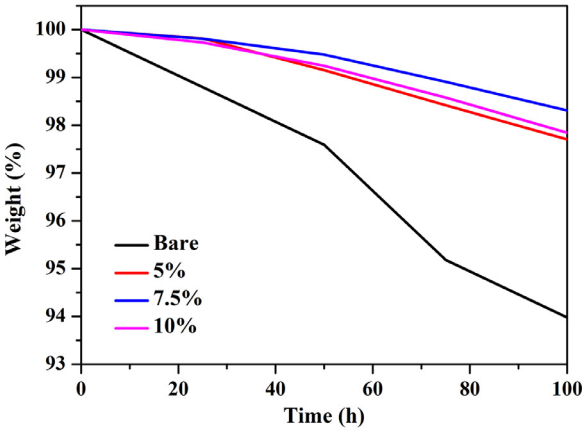


**Fig. 3.** Mass changes of thermal-insulator blocks prepared using solutions with different concentrations of silica sol and subjected to oxidation in air at 400 °C.

depended on the silica-sol concentration; this may indicate a weak point of oxidation. When a coating solution with a silica-sol concentration of 7.5 wt% was used, the SiC covering on the fiber surface was sufficient and minimized the loss of carbon fibers.

The sample coated with the 7.5 wt% silica-sol solution was heat treated at 800 °C for 24 h to leave only the SiC layer. Fig. 4 shows the FE-SEM images of a specimen obtained after carbon was removed by heat treatment. The SiC layer is composed of crystals that are smaller than those seen in Fig. 1. Depending on the crystal size, the thickness of the SiC layer varied from 60 to 90 nm. To more accurately determine the thickness, fiber sections of the same specimen were milled using a FIB. Fig. 5(a) illustrates the preparation of the carbon fiber specimen with a FIB. The interface between the fiber and coating was observed by TEM, and a typical image is shown in Fig. 5(b). The darkest side of the image corresponds to the carbon fiber, and the gray layer on top of the fiber corresponds to the SiC coating. Both TEM and FE-SEM measurements confirmed that the SiC coating had a thickness of approximately 30–80 nm. The difference between the thermal expansion coefficients of SiC and carbon could cause thermal stress at the interface of these two dissimilar materials, which may deteriorate the bonding force between the coating and the base material, resulting in peeling; therefore, ways to minimize the thermal stress must be considered. In particular, the thermal stress generated between the coating interfaces is known to be inversely proportional to the thickness of the coating. The SiC coatings formed in this study were expected to remain stable despite defects resulting from thermal expansion below 100 nm. In fact, the SiC coatings remained intact even after heat treatment to remove the carbon layer.

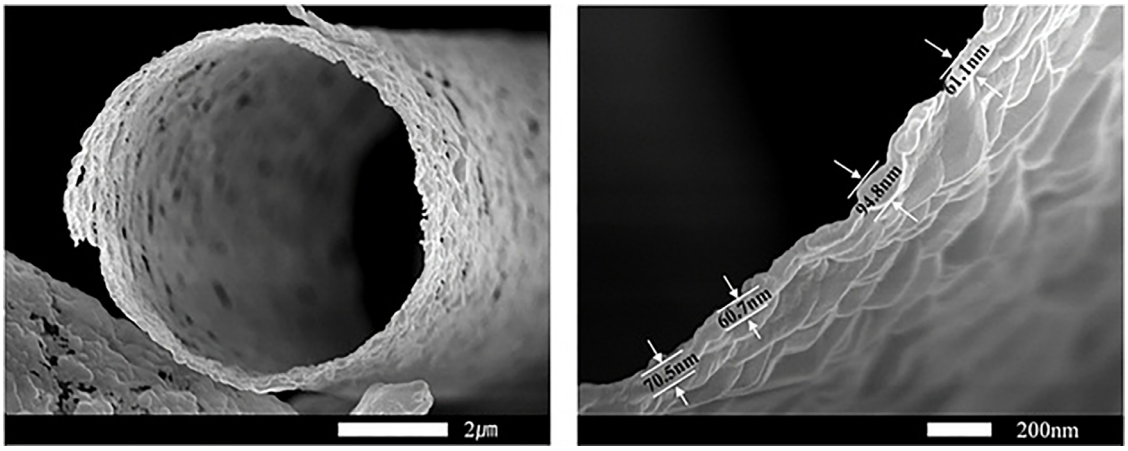


**Fig. 4.** FE-SEM images of SiC coating prepared from a solution of 7.5 wt% silica solafter carbon was removed by heat treatment at 800 °C in air.

Table 1 shows the results of ICP–MS analysis to determine the amount of SiC in the prepared specimens. Chemical composition analysis and calculation revealed that the concentrations of C and SiC were 99.4 mass% and 0.36 mass%, respectively; together they accounted for 99.76 mass% of each specimen. In addition, trace amounts of metal oxides were detected. It can be concluded that a high-purity SiC–C insulator is suitable for use in research for solar-ingot growth.

Fig. 6 shows the results of XPS analysis to confirm the chemical characteristics of the surface after the oxidation-resistance test in air at 400 °C for 100 h. In Fig. 6(a), the Si 2p peak is composed of Si–C bonding peaks and Si–O bonding peaks [21,22], indicating that the SiC surface was contaminated by oxygen. The depth profile shown in Fig. 6(b) indicates that silicon retained approximately 43 at% of the total content, and the carbon concentration tended to increase as the coating thickness increased. The ratio of oxygen decreased from 27.4 at % at the surface to 3 at% at a depth of 100 nm. The results clearly show that the SiC layer effectively blocked any contact between oxygen and the graphite fibers.

The SiC coating with silica sol was expected to improve the oxidation resistance of carbon and extend the service lifetime of the carbon insulator. However, as the thermal conductivity of SiC differs from that of carbon, it was measured to check the effect of the coating on the thermal properties of the carbon insulator. The analytical specimens were 20 × 20 × 4 cm in size; the uncoated specimens were compared with the specimens heat-treated at 1600 °C. The thermal conductivities of the uncoated and heat-treated specimens were measured to be 0.20 and 0.21 $W(m\ K)^{-1}$, respectively. Even though the thermal conductivity of SiC is relatively high, the SiC coating was thin and did not seem to have a significant effect on the heat-insulating properties of carbon.

**Table 1**
ICP-MS analysis data of SiC-coated carbon-fiber insulator.

| | |
|---|---|
| C (mass%) | 99.4 |
| SiC (mass%) | 0.36 |
| Na (mg/kg) | 436 |
| Al (mg/kg) | 115 |
| Cr (mg/kg) | 364 |
| Ca (mg/kg) | 131 |
| Fe (mg/kg) | 435 |
| As (mg/kg) | 190 |

## 4. Conclusion

In order to improve the lifetime of mat-type carbon insulators made of fibrous materials, silica sol was used to form a SiC coating and improve the oxidation resistance. The impregnation method was selected because it is considered the most suitable for large-capacity coatings, owing to its advantages in cost reduction, and for the simplicity of the process; these are important factors for application in many industrial sectors. A dense and uniform coating of SiC crystals was formed by a carbothermal reaction between the silica sol and graphite. The best antioxidation property was obtained when 7.5 wt% silica sol was used. It was confirmed that granular SiC crystals were formed in a coating with a thickness of 30–80 nm under optimum conditions, which

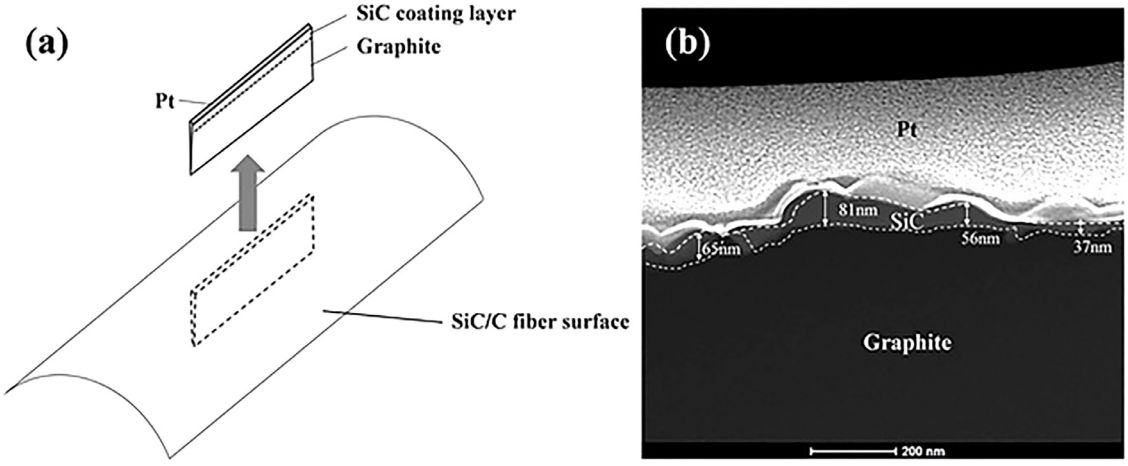


**Fig. 5.** (a) Sample preparation using FIB. (b) High-resolution TEM image of cross section of a carbon fiber coated with a solution of 7.5 wt% silica sol.

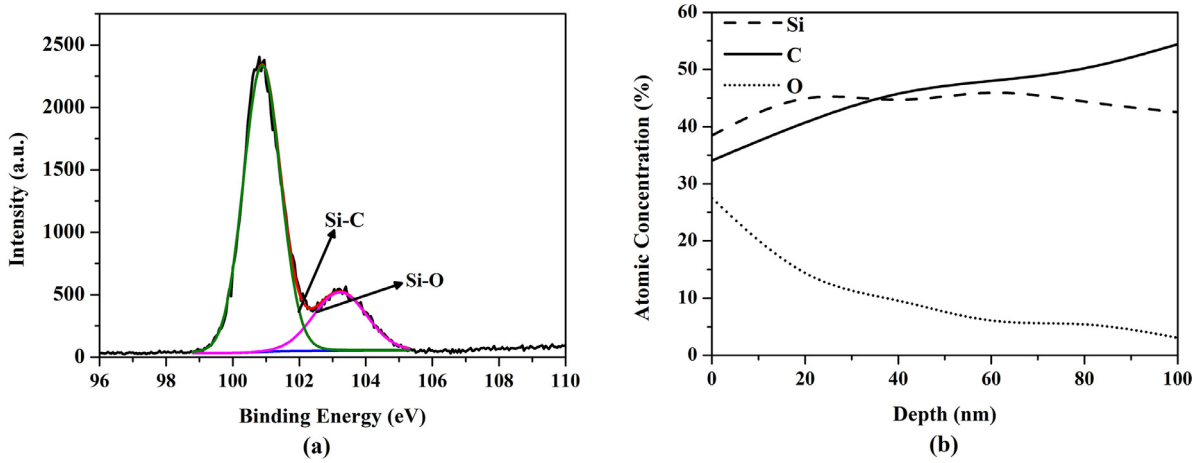


**Fig. 6.** (a) XP Si 2p spectra and (b) depth profile of carbon-fiber insulator coated with a solution of 7.5 wt% silica sol after oxidation for 100 h in air at 400 °C.

exhibited a dense distribution on the surface of the carbon fibers. In addition, it was confirmed that a tough film resistant to thermal stress was formed. As a result, the SiC coating not only improved the oxidation resistance, but also maintained the thermal conductivity of carbon. The SiC coating was not expected to have a significant effect on the adiabatic characteristics because of its low thickness.

## CRediT authorship contribution statement

**Su-Bin Ahn:** Conceptualization, Methodology, Writing - original draft, Software. **Minh Dat Nguyen:** Data curation, Methodology, Writing - review & editing, Formal analysis, Software. **Jung-Won Bang:** Investigation, Software. **Younghee Kim:** Supervision, Project administration. **Yoonjoo Lee:** Supervision, Project administration. **Dong-Geun Shin:** Supervision, Project administration. **Woo-Teck Kwon:** Supervision, Project administration, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This research was supported by the New Renewable Energy R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (grant number 20163030013440) and the Material Component Technology R&D Program of the Korea Evaluation Institute of Industrial Technology (grant number 20000765), funded by the Korean government.

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