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Abstract: In order to develop a practical process for the carbon coating on SiC fiber, high-speed and continuous pyrocarbon (PyC) coating process are under development by using a continuous CVD furnace with open-ends structure. The effects of process gas and winding speed have been investigated. It was revealed that the growth rate of PyC is in proportion to winding speed and the flow rate of process gas. PyC growth rate was reached up to 250 nm/min, which is several hundred higher than those of conventional CVI/CVD methods. This results indicates that the mass production of PyC coated SiC fiber without unexpected residual deformation (torsion and curvature) is possible. And, the mass production and practical use of SiC/SiC using PyC coated SiC fiber will be largely promoted.

Keywords: Fiber/matrix interface; Fiber coating; Pyrocarbon (PyC); SiC fiber; SiC/SiC composites

1. Introduction

SiC is very attractive ceramic material, because it has low density, good high temperature mechanical properties, chemical stability, low activation property and so on. In the late 1970s, an organosilicon polymer precursor (Polycarbosilane) and high strength SiC fiber has been developed by Prof. Yajima[1-2]. The development of these fine and flexible PCS derived SiC fibers made it possible to produce SiC fiber reinforced SiC matrix (SiC/SiC) composites with enhanced fracture resistance. SiC/SiC composites are under considering as very promising candidate material for the core components in nuclear energy system as well as aerospace system[3-5]. SiC/SiC composites are able to fabricate by several methods, such as Polymer Infiltration and Pyrolysis (PIP) method, Chemical Vapor Infiltration (CVI) method, Melt Infiltration / Reaction Sintering (MI/RS) method, Nano-Infiltration and Transient Eutectic-phase (NITE) process. Because of their very long process time, PIP and CVI method are not suitable for the mass production of SiC/SiC composites. On the contrary, NITE process requires very short process time for matrix densification compared with those of other fabrication methods. Besides, newly up-graded NITE-process, called it DEMO-NITE process, provides improved workability on the preparation of preform by the adoption of the dry type intermediate materials, such as green sheet, prepreg sheet and pre-composites ribbon. These intermediate materials are easy to handle as well as easy to restore. These advantages make it possible to fabricate SiC/SiC composites by one of the 3rd party supplier. It is expected to promote the mass production and mass consumption of SiC/SiC composites. The concept of DEMO-NITE process is shown in Fig. 1.

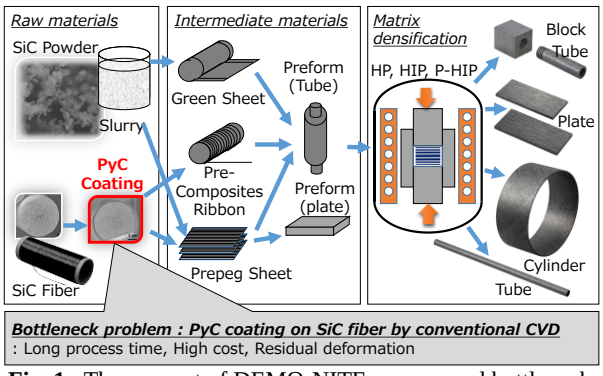

Fig. 1. The concept of DEMO-NITE process and bottleneck problem in the mass production of SiC/SiC composites

One of bottleneck problems in the mass production of NITE-SiC/SiC composites is the stable supply of SiC fiber with proper fiber coating. It was well known that fiber/matrix (F/M) interface determines the mechanical behavior of brittle-matrix composites[6,7]. Thus, the microstructure of SiC/SiC composites is usually consisted with fiber, matrix and F/M interface. In general, boron nitride (BN) and pyrocarbon (PyC) are common materials as F/M interface for SiC/SiC composites, because of their proper properties such as low friction, low shear modulus and anisotropic microstructure. SiC/SiC composites for high temperature aerospace system are usually reinforced by BN coated SiC fiber, because BN interphase provides much better oxidation resistance than PyC[8,9].

However, SiC/BN/SiC composites is difficult to apply on nuclear energy system. ^{10}B has high neutron cross section, and helium gas can be formed by its nuclear transformation under thermal neutron irradiation environment. In the case of fusion and gas fast reactor, SiC/PyC/SiC composites can be an effective solution,

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because carbon is a representative low-activation material and it has excellent high temperature properties under non-oxidative environment.

CVI or Chemical Vapor Deposition (CVD) methods are well-established and classic fabrication methods for SiC/SiC composites with high purity and crystalline SiC matrix. They can be also applied to the formation of C matrix in C/C composites and PyC coating on SiC fiber[9,10].

Most drawback of conventional CVI/CVD methods is their extremely long process time. Moreover, conventional CVI/CVD was performed by batch process using a closed type chamber. Thus, the shape and size of products were limited by their chamber size. In general, continuous and long fiber was installed in the shape of fiber ball for the fiber coating process. It makes some troubles like the unexpected residual deformation (twist or curvature) and the cross-bonding between adjacent fiber bundles.

In order to solve these technical issues and to promote the mass-production and practical use of SiC/SiC composites in the field of nuclear application, very unique CVD furnace has been designed and constructed. And, the effects of fabrication conditions including the flow rate of process gas and winding speed on PyC growth rate have been investigated as a preliminary study concerned on the continuous CVD method.

2. Experimental procedures

Continuous CVD furnace was consisted with feeder, main furnace and winder, as shown in Fig. 2. Main furnace is the horizontal type furnace with open ends. Because of its open structure, fiber can be continuously moved from feeder to winder. Passing time through CVD furnace was controlled by winder. In this research, the condition of winding speed is ranged from 80 mm/min to 320 mm/min.

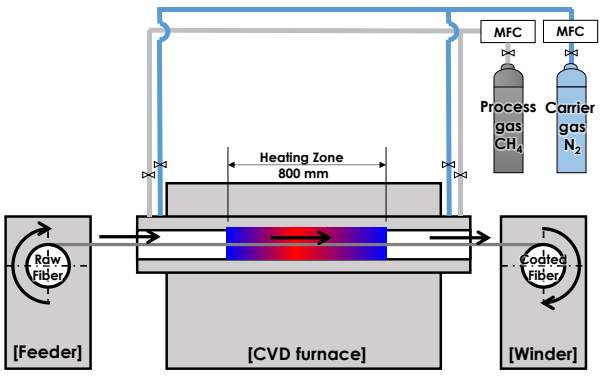

Fig. 2. Conceptual diagram of horizontal continuous CVD furnace with open ends

Fiber is passed through graphite heater tube installed in CVD furnace. The inner diameter of graphite tube is φ 40 mm and the length of heating zone was 800 mm. N_2 and CH_4 gas are selected as carrier gas and process gas, respectively. Flow rate of CH_4 gas is ranged from 1.0 to 3.0 ℓ/min. Flow rate of N_2 was fixed a constant value. In order to avoid the infiltration of harmful gas (oxygen) from the outside of furnace, the inner pressure of continuous CVD furnace was maintained slightly higher (approx. 100 kPa) than atmospheric pressure. The temperature of heating zone in continuous CVD furnace was also fixed to 1600 ℃.

Highly crystallized stoichiometric SiC fiber, Cef-NITE™ (GUNZE Limited, Japan), was used as substrate material. Fiber diameter and the number of fiber filaments per one bundle are about 10 μm and 800, respectively. After coating, fibers were cut by scissors for the measurement of PyC thickness using FE-SEM (JSM-6700F, JEOL Ltd., Japan),

3. Experimental results

It was success to fabricate PyC coated SiC fiber by using horizontal type continuous CVD furnace. Fig. 3 shows the appearance comparison of SiC fibers coated by conventional CVD (batch process) and continuous CVD method. It could be observed the residual deformation (torsion, curvature) from the SiC fiber bundle coated by conventional method.

On the other hand, straight SiC fiber bundle could be obtained by continuous CVD method. Torsion and curvature of SiC fiber bundle couldn't be observed.

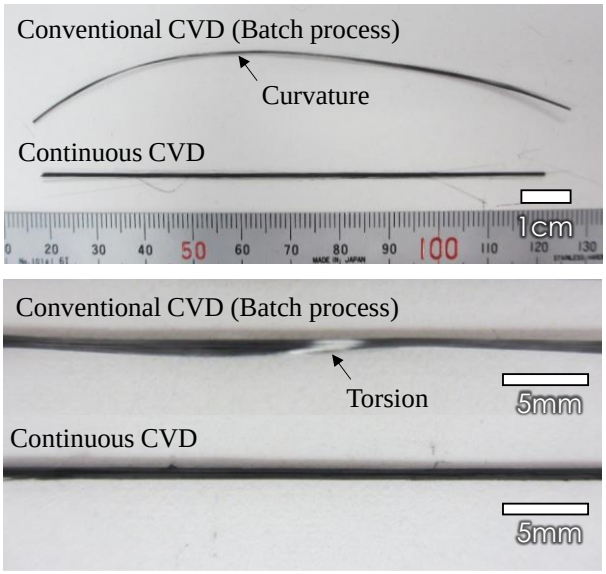

Fig. 3. Appearance comparison of SiC fibers coated by batch CVD and continuous CVD method

Macroscopic and microscopic FE-SEM images of SiC fiber bundle coated at the condition of 240 mm/min winding speed and 2.0 ℓ/min flow rate of process gas were shown in Fig. 4. as an example. It was observed the gap between PyC coat and SiC fiber surface, which seems a cutting damage during the sample preparation for FE-SEM observation. From the macroscopic view of fiber bundle, it was confirmed that all of fiber are coated by PyC homogeneously. According to the microscopic view of randomly selected SiC fibers, it was also observed that PyC coat has laminar structure.

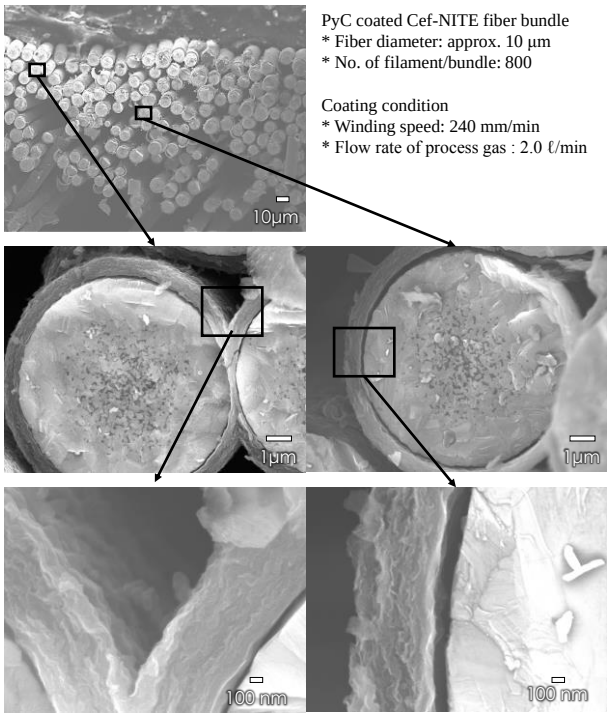

Fig. 4. Example of PyC coated SiC fiber bundle

Fig. 5 shows the cross section of SiC fibers coated by continuous CVD furnace under various coating conditions. Fig. 5 also shows the effects of the flow rate of process gas and winding speed on the thickness of PyC. In case of lower winding speed (80~160 mm/min), PyC thickness increased with increasing of the flow rate of process gas. However, in case of higher winding speed (240~320 mm/min), PyC thickness didn't increased with increasing of the flow rate of process gas. In conventional CVI/CVD process, coating thickness is proportional to their process time. But, in this research, the effect of process time (= inverse function of winding speed) on the coating thickness was limited.

4. Discussions

In the view point of mass production, PyC growth rate is important experimental factor must be considered, because high speed growth of PyC make it possible to reduce the process time as well as the construction/maintain/ operation cost of coating facility.

Fig. 6 and 7 show the effects of flow rate of process gas and winding speed on PyC growth rate.

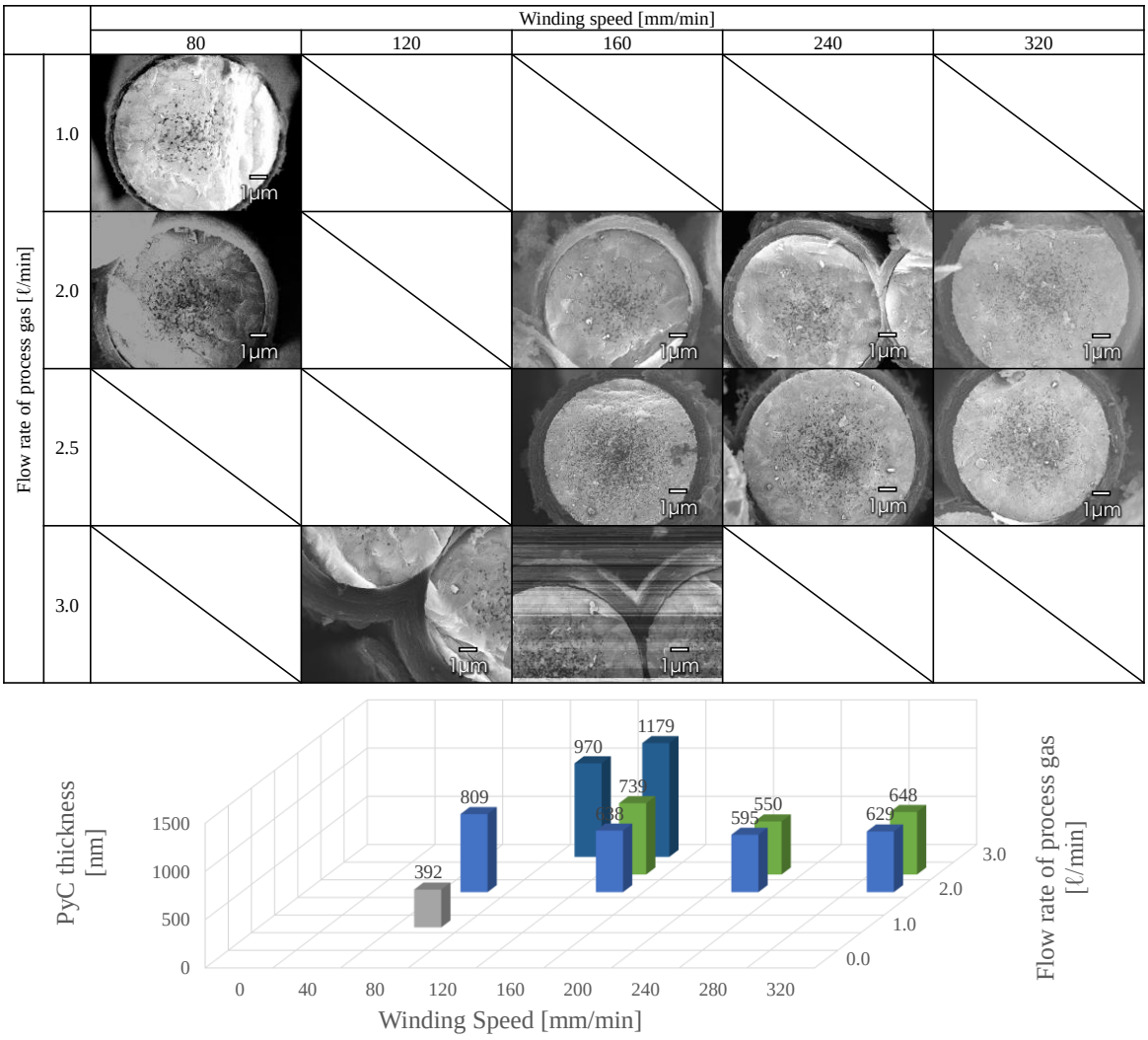

Fig. 5. Cross section and PyC thickness distribution of SiC fibers coated at various conditions

In the case of low winding speed (≤160 mm/min), PyC growth rate is proportional to the flow rate of process gas. On the contrary, in the case of high winding speed (240 and 320 mm/min), the effect of the flow rate of process gas was decreased.

During continuous CVD process, SiC fiber was continuously passed from inlet to outlet with joggling, and these dynamic motion (horizontal moving with joggling) changed the contact status between fiber surface and process gas significantly. These active exchange of source species could be contribute to improve PyC growth rate. Moreover, SiC fiber was drastically heated up from room temperature to 1600 ℃ by graphite tube heater when it entered the inside of furnace and it makes large thermal gradient. High winding speed makes more significant thermal gradient, and it can be also a reason of faster growth of PyC in high winding speed.

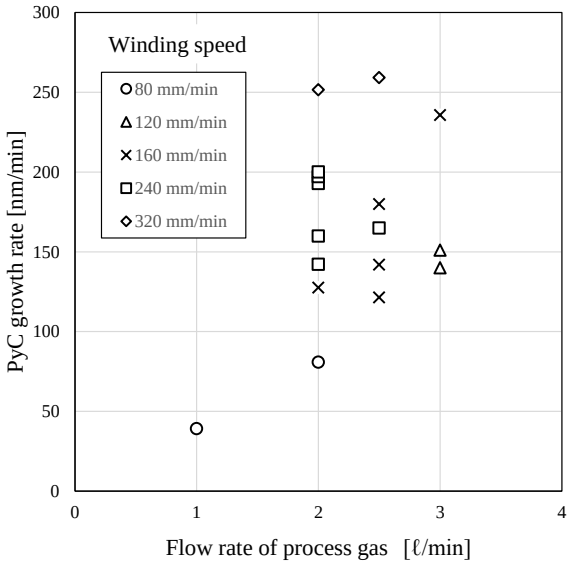

Fig. 6. Effects of process gas on PyC growth rate

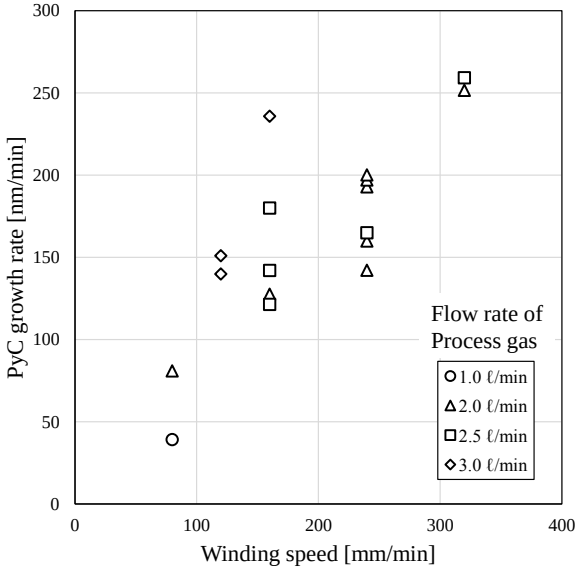

Fig. 7. Effects of winding speed on PyC growth rate

It must be addressed that extremely high speed of PyC growth (up to 250 nm/min) was recorded at the condition of winding speed (320 mm/min). In conventional isothermal CVI method, the growth rate of C was only 0.1~0.2 μm/hour. In case of thermal gradient or more advanced CVI methods, C growth rate was recorded 50 μm/h[9,10]. Growth rate achieved in this research was several ~ several hundred times higher than that of conventional methods. In general, F/M interphase thickness of SiC/SiC composites is ranged from 100 to 500 nm[11-13]. It means PyC coated fiber for the fabrication of SiC/SiC composites can be produced within 1~2 min by using continuous CVD method.

5. Summary

In order to develop a practical process for the carbon coating on SiC fiber, high-speed and continuous PyC coating process are under development by using a continuous CVD furnace with open-ends structure. The effects of process gas and winding speed have been investigated.

PyC growth rate depends on the flow rate of process gas at the condition of winding speed lower than 160 mm/min. PyC growth rate is significantly affected by winding speed and it is increased with increasing of winding speed. In this research, PyC growth rate was recorded up to 250 nm/min, which is several hundred higher value than those of conventional CVI/CVD methods. This results indicates that the mass production of PyC coated SiC fiber without unexpected residual deformation (torsion and curvature) is possible. And, the mass production and practical use of SiC/SiC using PyC coated SiC fiber will be largely promoted.

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