Carbon nanostructure coating on carbon/carbon composite by Plasma Assisted Chemical Vapor Deposition

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Abstract: In order to eliminate the infirmity of carbon/carbon composite such as low temperature oxidation and optimize the interfaces in carbon fiber reinforced ceramic composites, a thin layer of carbon nanostructure has been developed by a Plasma Assisted Chemical Vapor Deposition (PACVD) process operating at reduced temperature on C/C composite. C/C composite with grade of T300-3K (Torayca Company) was chosen as substrate, argon and methane gas was considered as career and reactant gas, respectively. After cleaning the surface of sample with argon Plasma, the process of coating by flow of Methane (15 sccm flow rate) and Argon (45 sccm flow rate) was done in 30 minutes and 2 amperes pulse direct current in 170°C. XRD test for detecting the structure of layer and FE-SEM analysis for characterizing of coating morphology were done. FE-SEM studies showed that the thickness of layer was about 70 to 90nm and XRD revealed the structure of thin film was nano-crystalline carbon. Raman spectroscopy was conducted to determine types of deposited carbon bonds, it was calculated that the sp^3 contents in carbon nanostructure coating were 32.8%, It means that this nanostructure of carbon is Diamond Like Carbon (DLC).

Keywords: Carbon nanostructure; Carbon/Carbon composite; plasma; coating;

Introduction

Carbon/carbon (C/C) composites are composed of carbon fibers in a carbon matrix. C/C components and carbon fibers have been produced in all over the world, in The United States for over 20 years in response to sustained aerospace and military needs specially [1,2]. They are lightweight materials that can perform structurally at extreme stresses. Carbon fibers have been used as reinforcement in ceramic and polymer composites in recent years due to its high specific strength, high specific modulus, and attractive mechanical, thermal and chemical properties. C/C is used widely to synthesis C/C-SiC composite i.e. [3,4]. However, oxidation resistance of C/C composite is poor (as low as 400 °C). These problems limit the application of carbon fibers as reinforcement in metal or ceramic matrix composite, and it could be overcome by applying a protective coating on the surface of the carbon fibers i.e. [5]. Carbon nanostructure coating is one of the best materials for depositing on C/C composite to eliminate its infirmity and modify the interfaces in carbon fiber reinforced silicon carbide composite (C/C-SiC) [6,7]. This thin and nanostructure film of carbon can be deposited by Plasma Assisted Chemical Vapor Deposition (PACVD) method.

PACVD is a technique for the deposition of a wide variety of films by breaking down gaseous precursors into radicals which deposit onto a substrate. The technique has many advantages, including large area uniformity, accurate control over the composition of alloy films and high film purity [8]. However, advances have been made in the other competing deposition techniques, the introduction of the ion-assisted deposition (IAD) process to physical vapor deposition (PVD) has enabled control to be gained over the density and stress levels in the films, properties which are important in obtaining high film quality. These advantages are important in many applications to which PACVD would otherwise be the method of choice, so that it would be useful to extend the advantages of IAD to PACVD i.e. [9].

In this paper we have prepared carbon nanostructure coating on carbon/carbon composite by PACVD method. The structure and thickness of coating can be controlled by adjusting the direct pulse current, time, duty cycle, temperature, frequency, and flow rate of career and reactant gases.

Materials and method

Carbon/carbon composite with grade of T300-3K (Torayca Company) was used as substrate. For coating operation, pulsed 5 kilo watt PACVD instrument (made by Plasma fanavar Amin Company) was considered. It consists of vacuum pump, plasma chamber, flow rate controllers and connection of gas cylinders. Argon (with 99.995% purity) and methane gas (with 99.999% purity) were utilized as career and reactant gases, respectively. A sample of 2-dimensional C/C composite in the form of 5×5 cm^2 in area was put on the stage of chamber which plays a role as a cathode during plasma Ionization. The temperature of chamber was adjusted to 170°C. For cleaning and activating the surface of sample, plasma was conducted by flow of argon in 15 minutes before coating process. The coating process was done by combination argon and methane gases in 30 minutes. Flow rates of argon and methane were 45 and 15 sccm (standard cubic centimeter per minute), respectively. Conditions of process are observed in Table1.

Table1: PACVD conditions

Time (min)	Current (A)	Frequency (KHz)	Duty cycle (%)
30	2	12	33

After 30 minutes the sample was cooled in vacuum. XRD (XPert MPD) Co Kα X-Ray (1.78897 A°) test for detecting the structure of layer and FE-SEM (ZEISS 15kV) analysis for characterizing of coating morphology were done. Raman Spectroscopy was conducted to determine types of deposited carbon bonds, too.

Results and Discussion

Obtained coating apparently has a smooth surface in black color. FE-SEM images of carbon fibers without coating and any surface processing are shown in “Fig. 1”. In images the fiber diameter is about 5 µm clearly.

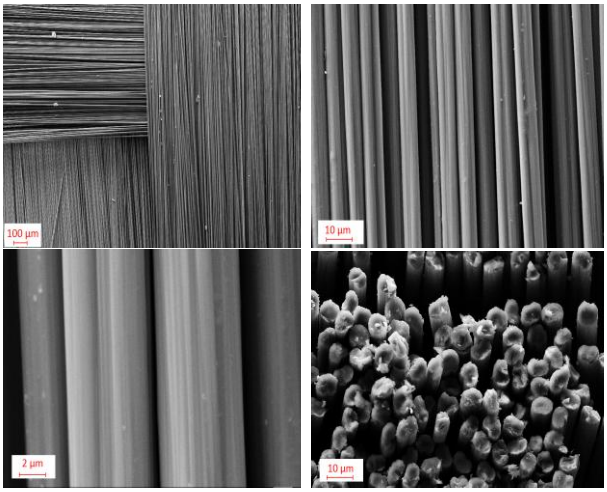

Fig.1: FE-SEM images of carbon fibers without coating

Carbon nanostructure coating images on carbon/carbon composite are shown in “Fig. 2”. Images are related to surface and cross section of coated fibers.

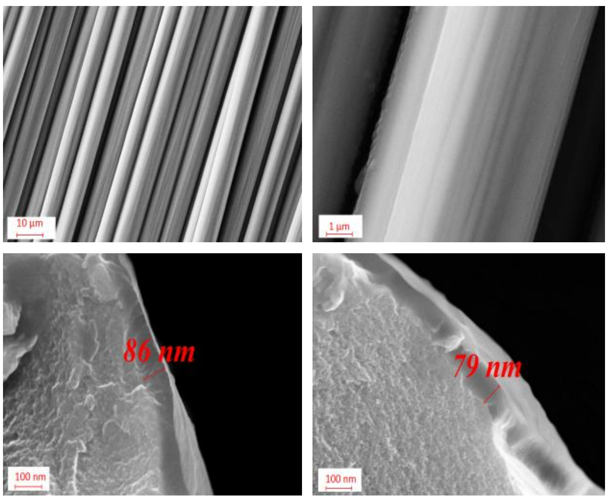

Fig.2: FE-SEM images of carbon nanostructure coating on carbon/carbon composite

The carbon nanostructure is deposited uniformly on fibers by PACVD method and it covers whole surfaces of fibers. Modified and uniform surface of fibers are observed in images related to surface of fibers. Furthermore, from cross sectional images, the thickness of coating on different fibers is determined. By 30 minutes PACVD operating with flow of methane and argon and 2 pulse direct current, the obtained coating has a thickness about 70-90 nm. The results of Raman spectroscopy for substrate without coating and Carbon nanostructure coating are shown in “Fig. 3”. In both results, there are two significantly important peaks of carbon, first D band (almost 1350 cm^{-1}) and second G band (almost 1600 cm^{-1}). D band shows simple C-C bonds vibration and G band shows vibration of hexagon structure of carbon [10].

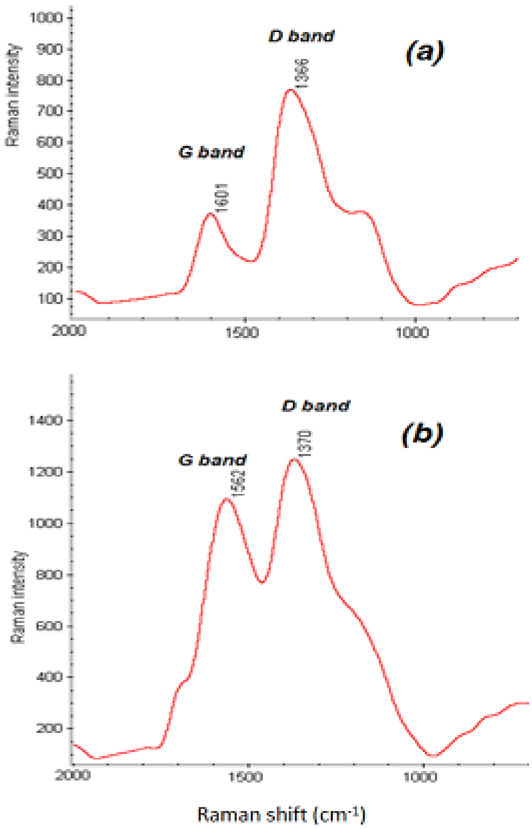

Fig.3: Raman Spectroscopy
(a)Substrate, (b)Carbon nanostructure coating on carbon/carbon composite

The position (ω) and intensity (*I*) of D and G bands are illustrated in Table2.

Table2: ω and *I* extracted from Raman results

Sample	I_D	I_G	$\omega_D(cm^{-1})$	$\omega_G(cm^{-1})$
Substrate	780	375	1366	1601
Carbon nanostructure coating	1255	1100	1370	1562

The sp^3 contents (shows percentage of diamond bonds in carbon nanostructures materials), can be calculated by using "Eq. (1)" [11].

$$sp^3 contents = 0.24\text{-}48.9(\omega_G\text{-}1580)\times 10^{-4} \qquad (1)$$

By considering ω_G and "Eq. (1)" the sp^3 contents in carbon/carbon composite as substrate, was 13.7%, but the sp^3 content in carbon nanostructure coating was 32.8%. With this sp^3 contents in deposited film, this carbon nanostructure is called Diamond Like Carbon (DLC) [12].

In "Fig. 4" X-Ray diffraction pattern is showing the structure of thin film.

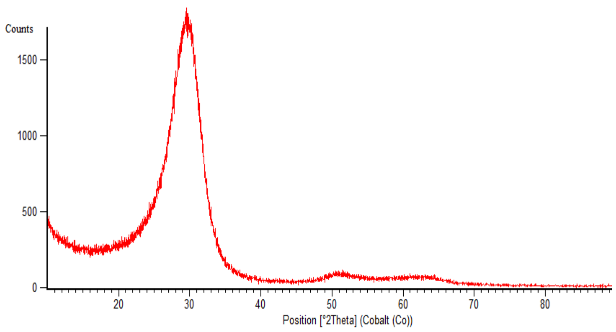

Fig.4: X-Ray diffraction pattern (Co Kα) of Carbon nanostructure film

The broaden peak was observed. This is expected since DLC films are always found to be nano-crystalline carbon [12].

Conclusions

By PACVD method thin layer of carbon nanostructure can be deposited on C/C composite in low temperature in contrast to other high temperature methods such as thermal CVD. The carbon nanostructure film was coated uniformly on C/C composite. Polarity of the substrate was negative in plasma media of gas mixture of methane and argon in 30 minutes. The thickness of obtained layer was 70-90 nm. Raman spectroscopy explains the ratio of the bonding sp^2 and sp^3. The sp^3 contents were achieved 32.8% in coating. Plasma ionization caused to appear more diamond bonds in coating comparison with substrate. According to XRD result, the thin layer structure was nano-crystalline carbon. This carbon nanostructure coating with diamond bonds is Diamond Like Carbon.

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