Effects of Temperature and Pressure on The Density of Carbon-Carbon Nanocomposite Fabricated by Chemical Vapor Deposition

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In this study, the pyrocarbon deposition process from the methane/hydrogen gases mixture into the graphite- and coal tar-based nanocomposite in the low pressure condition was investigated. When adjusting vacuum of isotherm process and maintaining the gasses flow, the best deposition efficiency was observed at the pressure ranging from 15 - 30 kPa with enhanced nanocomposite density from 4.23 to 6.36 %. At this condition, the crystals were formed and grown from inside of the pores. At the same pressure condition and gasses ratio, the deposition temperature was of great effect on the density and porous property of nanocompsite as the density increased 4.26 % at the deposition tempearture of approximately 1,100 °C. Study on the structure of nanocomposite samples before and after chemical vapor deposition indicated that at the deposition temperature of 1,100 °C and pressure of 15 - 30 kPa, the gaps between fibers framework were filled with pyrocarbon with the crystals sizes of 3 - 5 μm.

1. Introduction

Nanocomposite materials are increasingly being used in many fields thanks to its superior properties such as corrosion, heat resistance and chemical resistance (Siti et al., 2019).Carbon-carbon nanocomposites were first fabricated in the 1960s, since then they have been extensively studied and employed in wide range of applications, especially in aerospace and rockets industries (Sunil Kumar et al., 2018). Carbon crystals in carbon-carbon compsites were formed by two main techniques including liquid-phase impregnation, gas-phase deposition and their combination into the gaps of carbon fibers framework (Fitzer and Manocha, 2008). Among these techniques, the chemical vapor deposition approach to filling the pyrocarbon in the composite demonstrated to be suitable method to fabricate carbon-carbon nanocomposite (Reznik and Hüttinger, 2002). Depend on the purpose of applications, the raw materials and reaction conditions, the various densities of pyrocarbon could be achieved. For examples, the high density of pyrocarbon could be obtained from CH_4 and C_2H_2 mixture at the temperature of 1,100 – 1,200 °C (Ford et al., 1972) and oppositely low density could be fabricated from C_2H_2 at high temperature of 1,500 °C (zhang et al., 2002) or low temperature of 950 – 1,050 °C (Dolgodvorov, 2014). Like many other decomposition processes, the CVD process is divided into two main stages (Diyar et al., 2019). In the first stage, the formation of intermediate products takes place (usually in the low temperature zone 550 – 650 °C). The second stage is the decomposition leaving only a carbon frame (in the high temperature zone of 900 – 1050 °C). The carbon deposition from gas phase resulted in three common crystal structures of pyrocarbon including: isotropic structure, smooth laminar and rough laminar (Reznik and Hüttinger, 2002). It had been evidenced that pyrocarbon deposition from carbon fibers fabricated from polyacrylonitrile fibers is of crystal structure arranged in better order than that of carbon fibers obtained cellulose hydrate (Kurbakov, 2008).

Filling method for the substrate of carbon-carbon composite (CCC) using pyrocarbon deposition from gas phase had many advantages such as increasing mechanical properties of composite, could be employed to fabricate complex parts, maintain the properties of carbon fibers matrix. There also exist several

disadvantages including time-consuming process (this process can take several weeks to complete), susceptible to block the pores on the surface of composite leading to hinder the filling process of pyrocarbon into gaps of the fibers matrix. Even though many works were carried out to fabricate carbon-carbon composite using chemical vapor deposition (CVD), no study has been taken to optimize the deposition conditions, especially the effects of temperature and pressure on the composite density during the pyrocarbon deposition using CH_4/H_2 gasses mixture.

Marinkovic and his colleagues studied the kinetics of chemical vapor deposition from a gas mixture C_3H_6 and He (Marinkovic and Dimitruevic, 1985). The authors point out that the rate of deposition of gases is proportional to the open porosity of material and the infiltration is controlled by the reactions taking place in pore volume instead of on their surface. The rate of deposition increases with increasing temperature. The sample mass increases rapidly with increasing total pressure. The authors did not give any explanation for these conclusions and optimal temperature and total pressure for CVD process with C_3H_6/He mixture.

Studying the CVD process from C_3H_8 of carbon open-cell foams, Georges and his collaborators explained that increasing of sample mass during CVD process is due to the change in gas phase composition, mainly due to the formation of polycyclic aromatic hydrocarbons at the beginning of the process (Georges et al., 2014). This explanation only explains the effect of residence time on the mass increasing of the material but cannot assess the effects of other important factors such as temperature and total pressure of gas mixture.

In order to address this gap, in this study, the effects of deposition temperature and pressure on the density and properties of carbon-carbon nanocomposite are investigated in detail. The optimal temperature and pressure for the pyrocarbon deposition will be obtained. The morphologies of the resultant carbon-carbon nanocomposite will be observed.

2. Experimental

Carbon-carbon composite samples with volume of 1 cm^2 were prepared from carbon cloth, nanographite and coal tar, which were carbonized at temperature of 950 °C and underwent a heat treatment process at 2,200 °C. Carbon deposition into the substrate of carbon-carbon composite was carried out in a Nabertherm chemical vapor deposition furnace with the chamber length of 1,000 mm and diameter of 5 mm at Vietnam Academy of Science and Technology with highest vacuum of 10^{-3} Pa (Figure 1).
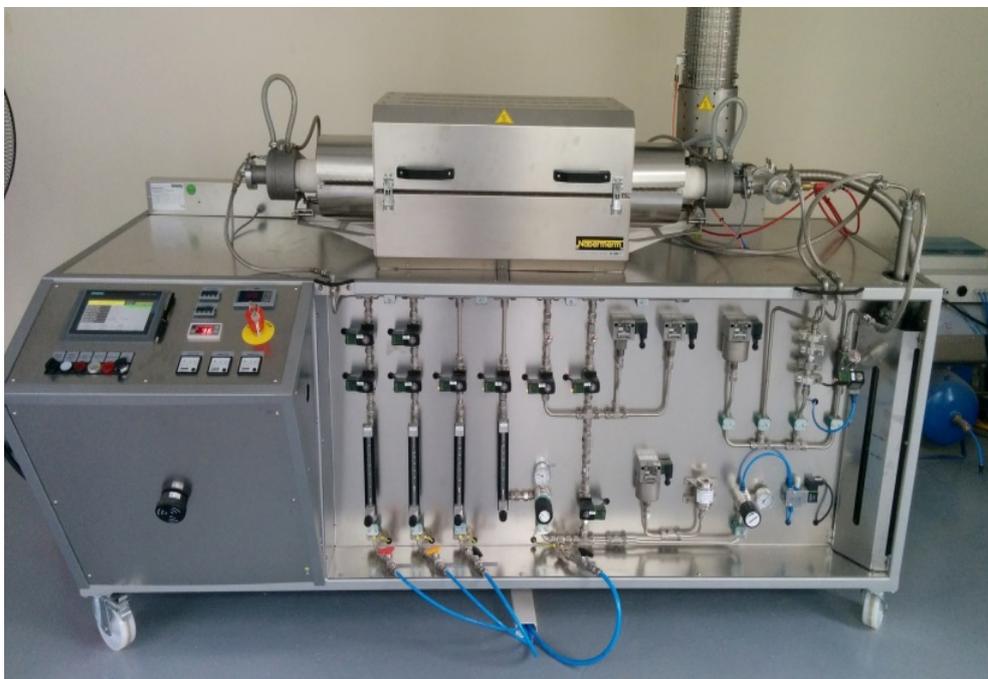
Figure 1: Nabrtherm chemical vapor deposition furnace for impregnating carbon into CCC.

Before carrying out the pyrocarbon deposition, the carbon-carbon composites were placed on the graphite plates and introduced into reaction region, increase the vacuum and risen the temperature to reaction occurred. Each reaction was carried out for 10 h at isotherm condition with $CH_4:H_2$ ratio of 1:2 (corresponding

to gasses flow of 90:180 mL/minute) (Burgio et al., 2012). The resultant nanocomposites after impregnation were cleaned and measured density, porosity and morphological observation.

Apparent density and porosity of as-fabricated samples were determined by hydrostatic balance with error of less than 10^{-4} g following the Eqs(1 - 4) (Mueller, 2008). The values were obtained after heat treatment of samples in boiling distilled water for 2 h.

$$\rho_{ad} = \frac{G_0}{G_1 - G_2} \cdot \rho_w \tag{1}$$

$$\varepsilon_{op} = \frac{G_1 - G_0}{G_1 - G_2} \cdot 100 \tag{2}$$

$$\varepsilon_s = 100 - \frac{\rho_{ad}}{\rho_{gr}} \cdot 100 \tag{3}$$

$$\varepsilon_{cp} = \varepsilon_s - \varepsilon_{op} \tag{4}$$

Where, G_0, G_1 and G_2 (g) are the weight of dried sample in air, of wet samples (immersed in water until saturation) in air and the weight of wet samples in distilled water, respectively; ρ_{ad} (g/cm^3) is the apparent density; ρ_w of 1.00 (25 °C) is the density of purified water; ρ_{gr} of 2.265 is the density of graphite [g/cm^3] (Morgan, 2005).

The morphology of the carbon-carbon nanocomposites before and after pyrocarbon impregnation was observed by using scanning electron microscopy (SEM) (Jeol 6610A, Japan).

3. Results and discussion

3.1 Effect of deposition pressure on CVD process

The reaction was carried out at isotherm condition at temperature of 1,100 °C for 10 h with various total pressures of CH$_4$/H$_2$ gases mixture including 6.6, 16.0, 30.0, 60.0 and 93.3 kPa (Li et al., 2008) and retention time of gasses mixture during pyrocarbon deposition was calculated with Eq(5) (Burgio et al., 2012). The results were shown in Table 1.

$$\tau = \frac{V_r}{Q_t \times \left(\frac{T}{T_0}\right) \times \left(\frac{P_0}{P}\right)} \tag{5}$$

Where, τ (s) is retention time; V_r (m^3) is the volume of furnace chamber; T (K) and P (Pa) are the temperature and pressure of reaction chamber; Q_t (m^3/s) is total flow at standard conditions of 272 K and 1 atm.

While the total pressure was too low, deposition rate was slow and could form anisotropic, the high total pressure could lead to formation of big and dense crystals on the surface of nanocomposites, which block capillaries, as a result, hindering the pyrocarbon crystals enter further into inside of nanocomposite (Kurbakov, 2008). The effect of pressures on the density and porosity of carbon-carbon nanocomposite before and after pyrocarbon deposition was shown in Table 1.

Table 1: Dependence of porosity properties and density of carbon-carbon nanocomposite before and after pyrocarbon deposition on the total pressures.

Sample	Pressure (kPa)	Before CVD			After CVD		
		Density (g/cm^3)	Open porosity (vol%)	Close porosity (vol%)	Density (g/cm^3)	Open porosity (vol%)	Close porosity (vol%)
C1	6.6	1.604	15.10	14.09	1.642	13.37	14.14
C2	15.0	1.606	15.39	13.71	1.674	11.88	14.22
C3	30.0	1.605	15.08	14.05	1.707	8.55	16.08
C4	60.0	1.612	14.71	14.12	1.715	8.21	16.07
C5	93.3	1.612	14.83	14.00	1.715	8.32	16.97

It can be clearly seen from these tables that at the low pressure region, the weight and density of the nanocomposite increased negligibly due to the short retention time (approximately 5 s) of gasses mixture for deposition. Porosity properties of materials obtained by hydrostatic balance at this low pressure indicate that

open porosity insignificantly decreased and closed porosity negligibly increased, which facilitated the pyrocarbon deposition. The completion of the pyrocarbon deposition process was time-consuming and expensive. When total pressures increased (vacuum decreased), rate of pyrocarbon deposition significantly increased, as a result, the densities of the composites quickly increase at the same deposition time. At total pressure of 6.6 kPa, the density of impregnated carbon-carbon composite increased 2.37 % after 10 h of deposition time. The density increased to 4.23 % at pressure of 16 kPa (corresponding to retention time of 10 seconds) and reached to 6.36 % at 30 kPa (retention time of 20 s). Further increase of total pressures witnessed the insignificant increase of the densities. It is of note that with the total pressures of higher 30 kPa, open porosity of composites were quickly declined along with remarkably increase of closed porosity, which demonstrate that with retention time of higher than 20 s decomposion of CH_4 occurred quickly on the composite surface and outside of capillaries hindering the further impregnation of pyrocarbon into inside of carbon fibers matrix, as a results, the mechanical properties of the resultant composites decreased. In this case, the pyrocarbon could be further deposited inside of the carbon matrix by using mechanical method to clean the surface. Repeat of these processes will raise the cost for fabrication of carbon-carbon composite. These results are consistent with previous work reported by (Glikin et al., 2000) about the kinetics Eq(6) obtained from experimental data for methane decomposition in presence of mineral substrate

$$w = 0.4 \cdot \exp\left(\frac{52200}{RT}\right) \cdot P_{CH4} \tag{6}$$

Where, w is the decomposition rate of methane, P_{CH4} is the partial pressure of methane.

3.2 Effect of temperature on the CVD process

Experiments were carried out at total pressure of 16 kPa for 10 h at various deposition temperatures of 1,000; 1,050; 1,100 and 1,150 °C. The results are shown in Table 2.

Table 2: Dependence of porosity properties and density of carbon-carbon nanocomposite before and after pyrocarbon deposition on temperature.

Sample	Temperature (°C)	Before CVD			After CVD		
		Density (g/cm^3)	Open porosity (vol%)	Closed porosity (vol%)	Density (g/cm^3)	Open porosity (vol%)	Closed porosity (vol%)
C6	1,000	1.615	14.64	14.06	1.629	13.31	14.75
C7	1,050	1.612	15.09	13.74	1.629	13.32	14.76
C8	1,100	1.606	15.39	13.71	1.674	11.88	14.22
C9	1,150	1.616	14.76	13.89	1.696	8.78	16.34

In the experimental condition, the efficiency of pyrocarbon deposition into pore of carbon-carbon nanocomposites depends on the 2 main factors: diffusion process of gasses into porous structure and the decomposition of methane. It is obvious from Table 2 that the densities of composites insignificantly increased with 0.89 % and 1.05 % at temperatures of 1,000 and 1,050 °C. The open porosity and closed porosity also varried insignificantly due to diffusion rate is much higher than deomposition rate of methane leading to the shift of reaction kinetics to diffusion region. Thus, pyrocarbon deposition at this temperature region is of low depositing efficiency and expensive. When temperature increases, reaction kinetics gradually shift to reacting region, which is evidenced by increase of density at the same reaction time with enhanced percentage of densities were 4.26 and 4.29 % at temperature of 1,100 and 1,150 °C. The observation of porosity properties at temperature of 1,150 °C indicates that the open porosity significantly declined along with remarkable increase of closed porosity. This phenomenon demonstrates the reaction process is dominant in comparison with diffusion process or the decomposition rate of methane is much higher than diffusion rate of reacting gasses. This leads to deposition of pyrocarbon on the surface and outside of pores, as a result, hinder the increase of composite density. From these results, the optimized temperature for pyrocarbon deposition into carbon-carbon nanocomposite selected is around 1,100 °C.

3.3 Morphologies of carbon-carbon nanocomposite

The morphology of CCC before CVD process was observed by SEM as shown in Figure 2a. It can be clearly seen that the carbon-carbon composite obtained after carbonization and heat treatment is of porous structure due to the evolution of gasses from inside of samples during carbonization process, the remaining carbon from coal tar links with fibers of carbon cloth to form stable matrix with porosity. The size of porosity depends on the temperature of heat treatment process. Therefore, optimizing the heat treating temperature is one

decisive factor to control the open pores in the composite, which is important for the carbon impregnation. The morphology of the CCC after pyrocarbon deposition at temperature of 1,100 °C was also observed by SEM as shown in Figure 2b. It can be recognized that pyrocarbon crystals were successfully and densely deposited on the composite and uniformly filled into open pores of the composite.

In order to clearly observe the distribution of pyrocarbon crystals on the carbon-carbon nanocomposite, SEM images of the carbon-carbon composite before and after pyrocarbon deposition were obtained (Figure 3a - b). Before CVD process, the carbon resulted from carbonization of coal tar filled between carbon fibers, however, there still remained many gaps between fibers (Figure 3a). After pyrocarbon deposition, carbon was not only deposited on the fibers surface, but also filling into the gaps between fibers, as a result, the density of the composite increased and open porosity decreased due to the dense arrangement of carbon crystals.

The particle sizes of pyrocarbon crystals obtained after CVD process at temperature of 1,100 °C are from 3-5 μm, which is relatively small in comparison with crystal sizes obtained at 1,050 °C (Figure 3c). The activation energy of forming nucleation from methane is 317.2 kJ/mol, which is significantly higher than the activation energy of crystals growth. Thus, the average size of crystals remarkably declines in response to increase of temperatures during CVD. The process CVD of CCC is most effective for eliminating pores up to 10 μm while filling pores of a larger size with PU is extremely problematic. The morphology of pyrocarbon deposited inside a large pore is very unusual. Threadlike formations of a cylindrical shape are located along the direction of fiber reinforcement (Tolbin et al., 2012). Consequently, the formation of small spherical crystals is a favorable condition for increasing the density of CCC materials.
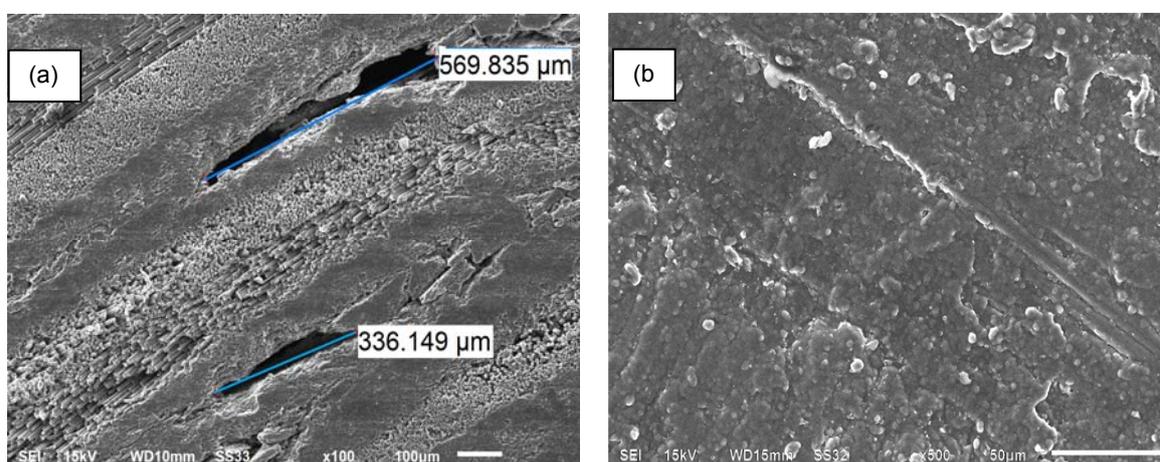

Figure 2: Low resolution SEM images of carbon-carbon nanocomposite (a) before and (b) after CVD process
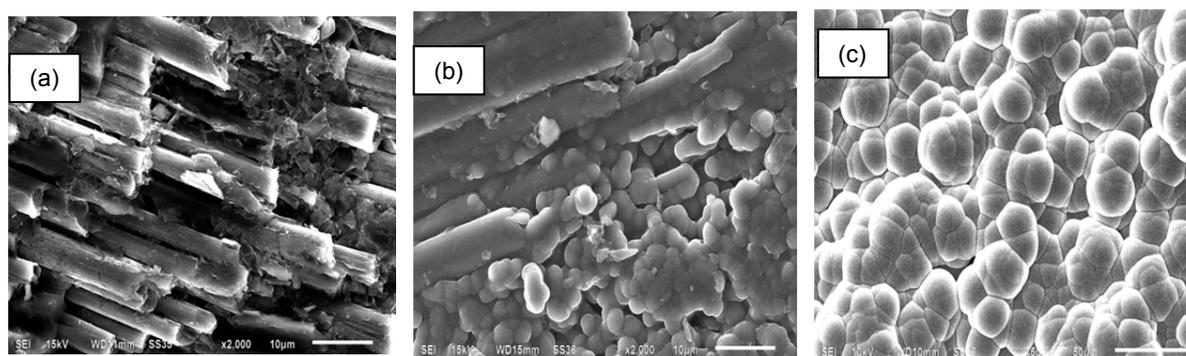

Figure 3: SEM images of carbon-carbon nanocomposite before and after CVD process with magnification of 2000X: a) Before CVD, b) After CVD and c) Pyrocarbon crystals obtained at temperature of 1050 °C.

4. Conclusions

In short, the carbon-carbon nanocomposite was successfully fabricated by using chemical vapor deposition method. The effects of CVD temperature and pressure on the efficiency of pyrocarbon deposition was studied in detailed. While the pressure of lower than 16.0 kPa, the efficiency of the pyrocarbon deposition is low and

long impregnation period, the pressure of higher than 30.0 kPa leads to hinder the deposition of pyrocarbon into penetrate into inside of the pores, as a result, decrease the mechanical property of the resultant composite. Thus, the optimized vacuum for CVD process is from 16 to 30 kPa. When increasing the temperature from 1,000 to 1,100 °C, reaction kinetics shifted from diffusion region to reacting region. If the diffusion rate was too quick (at temperature of lower than 1,050 °C), the deposition efficiency was low. In constrast, if the reaction rate was high (≥ 1,150 °C), the crystals formed on the surface of the composite, which hinder deposition of pyrocarbon inside of the pores leading to decrease mechanical property of the composite. The optimized temperature for CVD process is approximately 1,100 °C. The SEM ressults indicate that the pyrocarbon crystals were densely and uniformly depostion on the surface of carbon fibers with small particles sizes ranging from 3 to 5 μm at temperature of 1,100 °C. Future studies will focus on optimizing the temperature and pressure of CVD process using various gases mixtures as well as investigating mechanical properties and mophologies of the carbon-carbon nanocomposite.

Acknowledgments

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