Denitrogen and Graphitization Kinetics Analyze and Mechanism of Density Change for Polyacrynitrile-Based Carbon Fibers Heat Treated up to 2400°C

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Abstract—Polyacrynitrile-based carbon fibers were continuously heat treated up to 2400°C under N_2 atmosphere for different time. Element analyse, X-ray diffract spectrum and gradient column were used to determine the nitrogen content, crystal size and density of the resulted carbon fibers respectively. The density steadily decreased with increasing of temperature up to around 1700°C, then increased quickly with further increasing of temperature. A mechanism of density change was proposed with respect to denitrogen reaction and graphite crystal growth during heat treatment. The kinetics parameters of the denitrogen reaction and the graphite crystal growth were calculated separately. By applying these kinetics parameters, bulk density of the carbon fibers treated at different temperature was predicted, which is in good accordance to the experimental data.

Index Terms—Carbon fiber; Denitrogen; graphitization. Kinetics;

I. INTRODUCTION

Polyacrynitrile（PAN）-based carbon fibers offer numerous advantages, such as lightweight and excellent mechanical properties at room and elevated temperature[1-4]. The production of carbon fibers is usually undergoes high temperature treatment below 1500°C, which gives the tensile modulus of carbon fibers below 300GPa. To expand application of carbon fibers in the field of aerospace, higher modulus is required for the purpose of dimensional stability. Thus higher treatment temperature is essential in preparation of carbon fibers with high tensile strength and high modulus[3,5-12].

Efforts have been made to study the evolution of the compositions, graphite structures and mechanical properties of carbon fibers during high temperature treatment[5,13-18]. Gao et al[13] studied correlation between graphite crystallite and mechanical properties of PAN-based carbon fibers at 1500-2400°C, and found that dangling bonds play a key role in the growth mechanism of graphite crystallites, which leading to rapidly decrease of the tensile strength with increasing treatment temperature for fibers with dispersed crystallite structure. Using in situ X-ray scattering at temperatures up to 1700°C, Rennhofer et al[15] discovered that the main part of the structural change occurs in the short time period of heating the fibers, followed by an additional but smaller amount of structural change with time which is due to dislocation movement, dislocation annealing and gliding of graphene planes. By investigating the densification mechanism of carbon fibers during high temperature treatment, Gao et al[6] found that the density of carbon fibers decreased initially with treatment temperature up to about 1700°C, and then increased rapidly with further increasing of temperature. No mechanism related to the denitrogen reaction and the graphite crystal growth of carbon materials during heat treatment has even been proposed.

In this paper, PAN-based carbon fibers were continuously treated up to 2400°C under high purity nitrogen gas. The evolution of the composition and the graphite structures were studied. By analyzing the kinetics of the denitrogen reaction and the graphite crystal growth, A mechanism for density change was proposed for carbon fiber during high temperature treatment.

II. EXPERIMENTAL

A. Materials

PAN-based carbon fibers of T300 grade contained 3000 strands of monofilament from Research Institute of Jilin Petrochemical Company, China were used. The properties and composition of the as received carbon fibers were listed in the Table 1. Prior to high temperature treatment, the carbon fibers was pre-treated according to the procedure as described in the previous paper[6] to remove sizing. The desized carbon fibers were then continuously fed to a furnace under high-purity nitrogen flow. The fibers length was kept constant throughout the heat treatment, and the treatment time was adjusted by controlling the speed of the drive rollers set at the two ends of the furnace.

Table 1 The composition and properties of the carbon fibers

Carbon fiber	T300-3K
Density/g/cm³	1.7485
Tensile strength/GPa	3.43
Tensile modulus/GPa	212
Elongation/%	1.62
C content/wt%	93.53
N content/wt%	6.02
H content/wt%	0.13

B. Characterizations

An Elementar Vario MICRO CUBE (Germany) system was used to characterize the carbon, hydrogen and nitrogen content of the desized and heat treated carbon fibers.

Changes in crystal structure that occurred during heat treatment were determined using a Philips X0Pert PROMDP diffractometer (operated at 40kV and 40mA) with Ni-filtered CuKa radiation. The multifilament yarns were bundled and fixed on an X-ray fiber specimen holder that was10mm wide and 20mm long. Data were collected over the 2θ range 10–90º at 1 º min⁻¹ scan rate. The apparent crystallite size was calculated from the fully corrected and resolved peak profiles of the X-ray diffract (XRD) spectra. By accurate determination of diffraction peak positions and the fullwidths at halfmaximum (FWHM), the crystallite size was calculated from the Scherrer equation: L(nkl)=Kλ/Bcosθ

where θ is the diffraction peak position of the(nlk) plane, λ=0.15406 nm is the wavelength of the X-rays, B is the FWHM in radians of the peak and K=0.9 is the Scherrer geometricor shape factor.

Density was measured at 25ºC in a density gradient column (LLOYD, UK), prepared with a mixture of 1,2-dibromoethaneand carbon tetrachloride, which gave a density gradient from about 1.66 to1.88g/cm³ from top to bottom.

III. RESULTS AND DISCUSSION

A. Density change with temperature

Carbon fibers of T300 grade with density of 1.7485g/cm³ was heat treated at 1400 to 2400 ºC. Change of density with treatment temperature is shown in Fig. 1. The density steadily decreased with increasing of temperature up to around 1700 ºC, then increased quickly with further increasing of temperature. Carbon fibers showed lowest density at about 1700 ºC. Similar trend was reported, though steadily increase

of density of carbon fibers with temperature had been reported in many literature [5,6,9,12,19,20] at graphitization process at treatment temperature above 2000 ºC. The steadily increase of density was often referred as result of perfection of graphite crystal and increase of graphite degree in the fibers, as the density of graphite crystal is 2.266 g/cm³, which is higher than carbon fibers. Gao et al[6] explained the initial decrease of density as the result of enlargement of micropore in the fibers due to expel of nitrogen in the form of nitrogen gas. For deeply understanding of the mechanism of density changes in relation of denitrogen and grahpitization, kinetics of denitrogen and graphitization is to be studied.
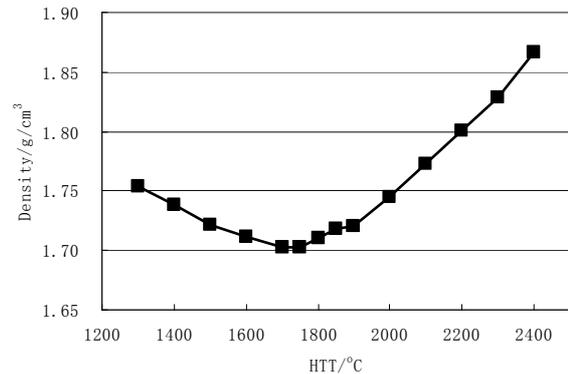

Fig. 1 Density change of carbon fiber during heat treatment

B. Kinetics of denitrogen reaction

T300 carbon fibers were treated at 1500 and 1900 ºC for 18 to 144s, and the change of composition was listed in Table 2. It can be seen from Table 2 that the C content increases with increasing of treatment time, while the N content decreases. This implies denitrogen reaction took place during treatment, resulting increase of relative content of C in the fibers.

Table 2 Change of composition of carbon fibres at 1500 and 1900℃

Temperature/℃	Treatment time/s	18	24	36	72	144
1500	C content/%	97.59	97.74	98.31	98.58	98.98
	N content/%	1.83	1.14	1.57	0.75	0.44
1900	C content/%	99.55	99.61	99.77	99.84	99.93
	N content/%	0.12	0.11	0.08	0.04	0.02

As there is no other reagents added to the furnace, the reaction of denitrogen takes place within the solid of the fibers, so it is feasible to assume the rate of the reaction is only related to the relative content of N and temperature, and it is reasonable using the following formula to calculate the apparent activation energy and the pre-exponential factor.

$$\frac{1}{N_t} - \frac{1}{N_0} = k_T^{(N)} t \qquad (1)$$

$$\ln k_T^{(N)} = -\frac{Ea^{(N)}}{RT} + \ln A_0^{(N)} \qquad (2)$$

Where t is the treatment time in seconds, N_t and N_0 is the content of N with and without treatment in percentage, $k_T^{(N)}$ is the reaction rate at temperature T, $Ea^{(N)}$ and $A_0^{(N)}$ is the apparent activation energy and the pre-exponential factor respectively for denitrogen reaction.

By linear fitting of $(1/N_t - 1/N_0)$ to treatment time t as shown in Fig. 2, the denitrogen rates K_T were obtained for 1500 and 1900ºC, which is 1.355 and 40.636 respectively, and the apparent activation energy and preexponential factor of denitrogen reaction of carbon fibers during heat treatment is calculated, which is 272kJ/mol and 6.99*10⁻⁹respectively. By applying these two kinetic parameters, the N contents of the fibers heat treated from 1400 to 2400 ºC for 36s were predicted as shown in Fig. 3. The predicted N content in the fibers treated at different temperature is in good accordance with the experimental data, which confirms the accuracy of the calculated kinetic parameters of the denitrogen reaction.
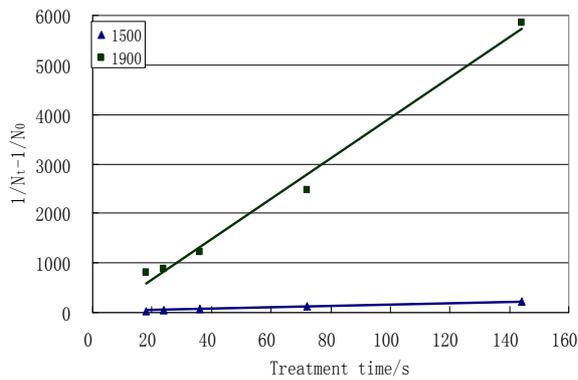
Fig. 2 Correlation between （1/N_t-1/N_0）and treatment time at 1500 and 1900℃
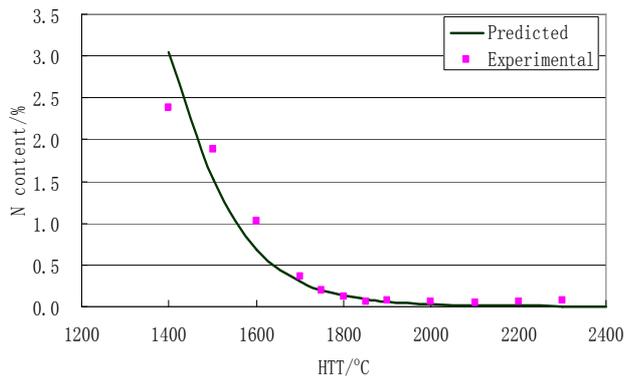

Fig. 3 Comparison of the predicted and experimental results for N content of carbon fibres treatment at different temperature for 36s

C. Kinetics of graphite crystal growth

The structures of graphite crystal of the heat treated carbon fibers were characterized using XRD. Fig. 4 shows growth of the graphite crystal size Lc for carbon fibers treated at 1500 and 1900 ^{o}C for different time. With prolong of treatment time, the graphite size Lc growth steadily, which is more pronounce at higher temperature.
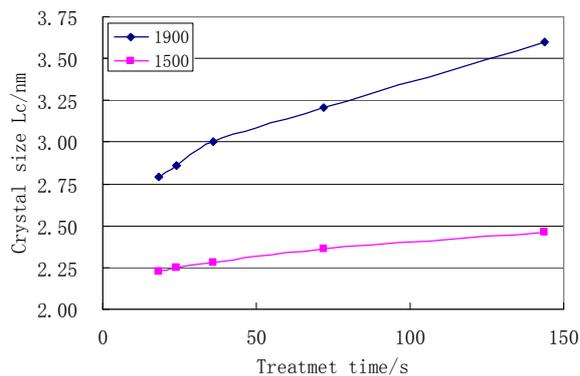

Fig. 4 The growth of graphite crystal Lc at 1500 and 1900℃ with time

For PAN based carbon fibers, carbon atoms will rearrange and make graphite crystal growth at temperatures higher than 1500 ^{o}C. As a result, the graphite degree and the crystal size in the carbon fibers increase with increasing of treatment time. The rate of graphite crystal growth is depended on the treatment temperature. As temperature is the only driving force for crystal growth in the carbon fibers, it is reasonable

using the following formula to calculate kinetic parameters of crystal growth.

$$\frac{Lct}{Lc0} - 1 = k_T^{(C)} t \qquad （3）$$

$$\ln k_T^{(C)} = -\frac{Ea^{(C)}}{RT} + \ln A_0^{(C)} \qquad （4）$$

Where t is the treatment time in seconds, Lct and Lc0 is the graphite crystal size of carbon fibers with and without treatment, $k_T^{(C)}$ is the crystal growth rate at temperature T, $Ea^{(C)}$ and $A_0^{(C)}$ is the apparent activation energy and the pre-exponential factor respectively for crystal growth.

By linear fitting of (Lcr/Lc0-1) to treatment time t as shown in Fig. 5, the crystal growth rates $k_T^{(C)}$ were obtained for 1500 and 1900 ^{o}C, which is 0.00106 and 0.00357 respectively, and the apparent activation energy and preexponential factor of crystal growth of carbon fibers during heat treatment is calculated, which is 97.2kJ/mol and 1.45 respectively. By applying these two kinetic parameters, the crystal size of the fibers heat treated from 1400 to 2400 ^{o}C for 36s were predicted as shown in Fig. 6. The predicted Lc of the fibers treated at different temperature is in good accordance with the experimental data, which confirms the rightness of the calculated kinetic parameters of the crystal growth.
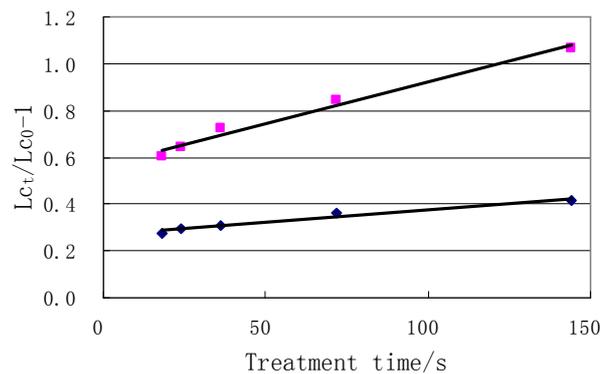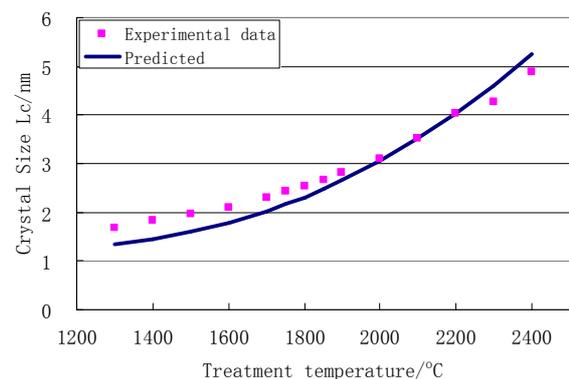

Fig. 5 Relationship between (Lct/Lc0-1) with time

Fig. 6 Comparison predicted and experimental results for Lc of carbon fibre treatment at different temperature for 36s

D. Mechanism of density change

The change of density of PAN-based carbon fibers during heat treatment is closely related to the denitrogen reaction and the growth of graphite crystal. Due to removal of nitrogen atoms in the fibers in the denitrogen reaction, micro-voids are produced, which lead to decrease of the density of the fibers.

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If only considering the denitrogen reaction after heat treatment, the density of the resulted carbon fibers can be expressed as eq 5. The density of the fibers will increase in the result of graphite crystal growth during graphization, which can be expressed as eq 6 with respect to the crystal size Lc. The bulk density of the fibers is the combination result of the denitrogen and crystal growth, which is expressed as eq 7.

$$_\nabla\rho_{TN} = \rho_0 \times (\frac{N_0 - N_T}{100}) \qquad (5)$$

$$_\nabla\rho_{TC} = \rho_0 \times (\frac{L_{ct}/L_{c0}}{4})^3 \qquad (6)$$

$$\rho_T = \rho_0 + _\nabla\rho_{TN} + _\nabla\rho_{TC} \qquad (7)$$

Where $_\nabla\rho_{TN}$ is the change of the density of the fibers induced by denitrogen at temperature T, $_\nabla\rho_{TC}$ is change of the density of the fibers induced by graphite crystal growth, ρ_T is the bulk density of the treated fibers, ρ_0 is the density of the fibers as received, N_T and N_0 are the content of nitrogen in percent of the treated fibers and the fibers as received respectively, L_{ct} and L_{c0} are the size of graphite crystal of the treated fibers and the fibers as received respectively.

As the nitrogen content and crystal size is well predicted for carbon fibers treated at different temperature in the previous sections, changes of density induced by denitrogen and crystal growth during high temperature treatment can be calculated using eq 5 and eq 6 respectively. The bulk density of the fibers at different treatment temperature is predicted using eq 7, and is shown as curve d in Fig. 7. The predicted results are compared with experimental data (data points a in Fig. 7), which is in good accordance. This confirms the proposed density change mechanism for carbon fibers heat treated up to 2400 °C.
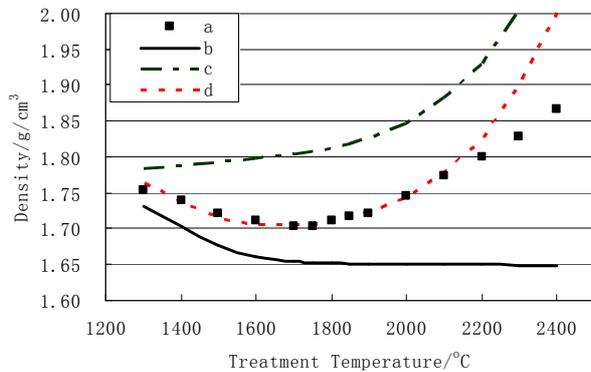

Fig. 7 Comparison of the density predicted with experimental data (a: experimental data, b: change of density due to denitrogen, c: change of density due to crystal growth, d: predicted density)

IV. CONCLUSION

The density of PAN-based carbon fibers steadily decreased with increasing of temperature up to around 1700 °C, then increased quickly with further increasing of temperature. By dynamic analyze, the kinetics parameters were calculated. The apparent activation energy and preexponential factor of denitrogen reaction of carbon fibers during heat treatment is 272kJ/mol and $6.99*10^{-9}$ respectively. The apparent activation energy and preexponential factor of crystal growth is 97.2kJ/mol and 1.45 respectively. There is two independent process of denitrogen and crystal growth for carbon fibers during high temperature treatment, which is closely related to the change of density of the carbon fibers. By applying these parameters, bulk density of carbon fibers treated at different temperature was predicted, which is in good accordance to the experimental data.

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