A TDS Study of High-Temperature N₂ Adsorbed and N⁺ Ion Implanted Nuclear Carbon Materials

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Abstract – Nitrogen adsorbed on the surface of nuclear carbon materials is the main contributor to C-14 production of High Temperature Reactor – Pebble-bed Module (HTR-PM) and hence the study into the behavior of nitrogen adsorption and desorption would conducive to minimizing radioactive wastes. Experiments have been conducted on fuel element matrix graphite, IG-110 graphite and HTZ-B boron-contained carbon brick, with high-temperature N₂ adsorption at 800~1000°C for up to 3 h, 100 keV N⁺ ion implantation of 5×10¹⁶ cm⁻², 3×10¹⁷ cm⁻² and 5×10¹⁷ cm⁻² doses and temperature programmed desorption (TPD) analysis. It was shown that faster heating rate leads to a shift of desorption peaks to high-temperature direction. The adsorption amount has positive correlation with adsorption temperature and adsorption time. The mechanisms of bonding between nitrogen and carbon by high-temperature adsorption and implantation are different.

Keywords – HTR-PM, nuclear carbon materials, nitrogen, high-temperature adsorption, ion implantation, thermal desorption spectroscopy (TDS).

I. INTRODUCTION

High Temperature Reactor – Pebble-bed Module (HTR-PM) is currently under construction at Shidaowan, Shandong, China. As one type of high temperature gas-cooled reactor (HTGR), it is the first commercial Generation IV nuclear power plant built in China [1]. Besides economy and safety, the production of radioactive wastes of nuclear energy is among the most important issues that have aroused widespread concern [2]. To minimize the wastes of nuclear power plant is a common pursuit worldwide and is a mandatory requirement of Chinese government (see GB 18871-2002 and GB 6249-2011). In order to develop nuclear power and realize the energy restructuring, the minimizing of nuclear wastes should be carefully considered.

During operation of a nuclear power plant, some radionuclides can be release in gaseous chemical form to air and affect the environment and public health, including Ar, Kr, Xe, I, Sr, H-3 and C-14. Among them, C-14 has the largest amount of emission (at 10¹² Bq/a scale) [3]. Previous study indicates that C-14 contributes to over 90% of the annual effective dose [3]. With its relatively long half-life (5730 a), C-14 could accumulate in biosphere for a long period and become the potential source of internal radiation dose to human [4]. Compared with reactors using water as moderator and coolant, HTR-PM uses large amount of nuclear carbon materials with C-13 present as an isotope of C-12, O-17 as an impurity and N-14 adsorbed on the surface. Among these precursors of C-14, it is reported that the neutron activation reaction of N-14 produces more than 60% of total C-14 yield [5]:

\[ ^{14}\text{N} + n \rightarrow ^{14}\text{C} + p \]  (1)

Efforts have been made to estimate the annual yield of C-14. Early researchers [6, 7] calculated based on Eq. (1) with concentration of trace...
nitrogen impurity but didn't have considered the processes of adsorption, desorption, diffusion and penetration of nitrogen in carbon materials. Recently, X. Chen et al. [8] have taken these dynamic processes into their account, but the mechanisms haven't been clearly revealed, suggesting the inaccuracy of their calculations. It is obvious that knowing the behavior of nitrogen in nuclear carbon materials would provide important information to C-14 control.

In this research, experiments on fuel element matrix graphite, IG-110 graphite, and HTZ-B boron-contained carbon brick have been conducted with high-temperature adsorption, ion implantation and temperature programmed desorption (TPD) techniques. The behavior of nitrogen adsorption and desorption on nuclear carbon materials is studied and how they could be affected by materials, temperature, adsorption time and implantation dose is presented.

II. EXPERIMENT

II.A. Techniques

A so-called temperature programmed desorption (TPD) technique has been applied to investigate the adsorption and desorption of hydrogen and its isotopes on many materials [9, 10, 11]. Desorption process requires the energy of an adsorbate molecule to be over a certain energy (the energy barrier) to break the bonds. The relationship between desorption rate and influential factors is described by Wigner-Polanyi formula:

\[ -V_m \frac{d\theta}{dt} = \gamma \theta^n \exp \left( -\frac{E_d(\theta)}{RT} \right) \]  

(2)

Here, \( \theta \) is the proportion of adsorbed molecules; \( V_m \) is the amount of adsorbed molecules when covering a single layer, then \( \theta = 1 \); \( E_d(\theta) \) is the activated energy of desorption; \( n \) is the order of the desorption reaction; \( \gamma \) is a constant of reaction frequency; \( d\theta/dt \) is the desorption rate; \( T \) is temperature; \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \).

Eq. (2) indicates that the rate of desorption is affected both by the remaining amount of adsorbed molecules and the temperature. On the one hand, desorption rate should increase with temperature being raised; on the other hand, since the remaining molecules are continuously decreasing, the rate will always reach its maxima at certain time (if temperature was raised at a constant speed, that point would correspond to a certain temperature).

Therefore, the curve of desorption rate to time appears as a peak. If the adsorbate could form several types of chemical bonds with the adsorbent, i.e. there existed several kinds of adsorption centers, desorption rate would have local maximum values of same numbers, because the activated energy for breaking bonds would be different. The curve of desorption rate to temperature with these peaks is called thermal desorption spectrum, and the analysis is called thermal desorption spectroscopy (TDS).

There are two possible ways to immit nitrogen to nuclear carbon materials: either by high-temperature \( \text{N}_2 \) adsorption or \( \text{N}^+ \) ion implantation. High-temperature adsorption can also be referred to as gas charging technique. At elevated temperature, physisorption can be ignored because of its weak bonding and chemisorption is the main form of combination.

Low-energy implantation is a convenient way to implement a concentration of several percentages for nitrogen atoms distributing at depth less than 1000 nm [12]. Using ion implantation technique to simulate the irradiation process of nuclear graphite inside reactors has been investigated and the irradiation property has been reported [13]. The annealing of track induced by heavy ion irradiation on graphite has been revealed to be caused by irradiation under high temperature [14]. A combination of ion implantation and TPD analysis has also been used to study the association of implanted \( \text{He}^+ \) with graphite vacancies [15].

II.B. Materials

There are 3 kinds of largely used nuclear carbon materials in HTR-PM. Fuel element matrix graphite (hereinafter referred to as “FE”), developed by the Institute of Nuclear and New Energy Technology of Tsinghua University, forms the vast majority of fuel pebbles. IG-110 graphite, provided by Toyo Tanso, with low equivalent boron content and small adsorption cross section, acts as neutron reflector. HTZ-B boron-contained carbon brick, provided by Fangda Carbon New Material Technology Co., Ltd., containing 5% w.t. \( \text{B}_4\text{C} \), serves as heat insulator and neutron shielding material. All samples have been cut and ground into small cuboids of 2.0 mm×2.0 mm×1.5 mm. The basic properties of these 3 materials are listed in Table 1.

II.C. Devices and System

The experimental system has been designed to consist of the following parts: gas control module,
programmed heating module and gas analysis module. This system is with the functions of performing high-temperature adsorption and executing TDS analysis.

For the gas control module, pure He and a mixture of 10.1% N₂ with 89.9% He were provided. The flows were respectively controlled with 2 Alicat MC Series gas mass flow meters.

### Table 1: Basic properties of the 3 nuclear carbon materials studied in this research.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Impurity (ppm)</th>
<th>Ash content</th>
<th>Equivalent boron</th>
<th>Lithium</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE</td>
<td>1.70–1.77</td>
<td>≤300</td>
<td>≤1.3</td>
<td>3.992</td>
<td></td>
</tr>
<tr>
<td>IG-110</td>
<td>1.76–1.78</td>
<td>≤200</td>
<td>≤0.90</td>
<td>0.1894</td>
<td></td>
</tr>
<tr>
<td>HTZ-B</td>
<td>ca. 1.70</td>
<td>≤3000</td>
<td>No data</td>
<td>13.358</td>
<td></td>
</tr>
</tbody>
</table>

For the programmed heating module, a ChemBET Pulsar TPR/TPD Automated Chemisorption Analyzer by Quantachrome Instruments was the main apparatus. This chemisorption analyzer has a furnace which can raise temperature up to 1100°C, which is beyond the normal temperature of HTR-PM and enough for the practical research on nitrogen behavior. The temperature can be programmed and controlled to rise at a constant rate. U-shaped quartz tube was employed as sample container and reaction chamber. A thermocouple thermometer was inserted into the U-shaped tube to monitor sample temperature.

For the gas analysis module, a ThermoStar™ GSD 320 type quadrupole mass spectrometer by Pfeiffer Vacuum played the role of gas composition analyzer. This mass spectrometer can measure the concentration of gaseous species with relative atomic mass between 1–100.

A schematic structural figure of the experimental system is presented in Fig. 1.

### II.D. Experimental Procedure

After referring to the previous reports of TPD application, the following procedure has been designed for this research:

1. **Preparation.** Put the samples into the U-shaped tube and connect the tube to the chemisorption analyzer. Turn on the gas mass spectrometer and begin monitoring to species including N₂, He, Ar, O₂ and CO₂.
(2) System purifying. Continuously blow pure He into the tube to wipe out impurities (O₂, CO₂, H₂O). When the amount of impurities falls to an acceptable value, shut down the pure He and switch on the 10.1% N₂. Wait until the level of impurities falls down to an adequately low degree.

(3) Raising temperature as pre-programmed. Heat up the furnace at a constant rate under the control of a computer and reach the preset adsorption temperature.

(4) High-temperature adsorption. Keep the adsorption temperature for preset adsorption time.

(5) Rapidly cooling down. The furnace has a fan to strengthen the air convection and temperature can be deduced rapidly to room temperature. Rapid cooling avoids the diffusion or desorption of adsorbed nitrogen.

(6) System purifying. At room temperature, shut down the mixture gas and switch on the pure He to clean the remaining N₂ in the tube which are not adsorbed on sample surface.

(7) Raising temperature as pre-programmed. If any adsorbed nitrogen was released, the mass spectrometer could detect and the thermal desorption spectra is recorded.

(8) Rapidly cooling down. When temperature has risen to a certain preset value and the thermal desorption spectrum is fully obtained, deduce the temperature to room temperature.

This was the procedure for samples to be treated by high-temperature adsorption. For samples implanted, the implantation treatment happened before TPD, so the procedure did not involve (2) ~ (5). The ion implantation took place at Beijing Radiation Center.

During the experiments, some conditions were controlled to remain stable. Gas flow rate was maintained at 10 sccm (standard cubic centimeters per minute). Heating rate was generally set at 10°C/min. As mentioned before, the samples had been cut and ground, limited by the caliber of the U-shape tube, therefore for the purpose of having a large surface area, 10 grains of the specimen would be put into the tube. The time for high-temperature adsorption was generally set to 3 h. As for the devices, C-SEM mode of the mass spectrometer was adopted and the voltage was set to 870 V.

III. RESULTS

III.A. Influence of Heating Rate

Fig. 2 displays the TDS spectra of experiments on implanted IG-110 graphite with almost the same conditions but different heating rates. The vertical coordinate indicates the intensity of electric current (in logarithmic) which is proportional to the concentration and the flow rate of N₂, whose relative atomic mass is 28. It should be noted that the curves have been translated along the vertical coordinate, in order to clearly compare the position of the peak.

It appears that faster heating rate can result in peaks shifting to the right (high temperature region) and slower heating rate can lead to peaks shifting to the left (low temperature region). Since heating rate has such an influence to TDS spectra, the heating rates were set identically at 10°C/min for all experiments.

III.B. High-Temperature N₂ Adsorption

The transform from intensity of electric current to flow rate of N₂ is

\[ q_{i} = q_{i_{He}} \cdot \frac{N}{N_{He}} \cdot k_{N_{2}/He} \quad (3) \]

Where \( q_{i_{He}} \) is the flow rate of He; \( i \) is the intensity of electric current of a certain gas; \( k \) is a factor that reflects the unequal possibility of stimulating electric current by different gases, whose value can be calculated by calibration.

Fig. 3 displays the TDS spectra of different materials under same experimental condition (high-temperature adsorption happened at 1000°C and lasted for 3 hours). The vertical coordinate is \( q(28) \), which equals to the sum of \( q(16) \) multiplied by a factor and \( q(N_{2}) \); that is because the factor \( k \) in Eq. (3) for N₂/He and for CO/He could be different. All the 3 curves declined before ca. 800°C and
dramatically rose subsequently. The falling section indicates that a purification process happened when He flew through the system at low temperature, making the concentration of N₂ reduce. The rising section indicates the forming of CO by the oxidation between specimen and O₂ impurity.

Fig. 3: (a) TDS spectra of different materials under same experimental condition (1000°C, 3 h). (b) Partially enlarged view of TDS curve of HTZ-B from 800°C to 1000°C.

Beyond the baseline of CO, fuel element matrix graphite and IG-110 graphite have each shown a significant peak of N₂ desorption, while HTZ-B boron-contained carbon brick did not show any significant desorption peaks. Fuel element matrix graphite appears to have the largest adsorption capacity and IG-110 graphite has a smaller capacity, while HTZ-B has a very limited capacity to adsorb N₂ at experimented temperature range.

For the following experiments fuel element matrix graphite was chosen as the specimen in order to observe a larger amount of N₂ desorption.

Fig. 4 displays the TDS spectra of fuel element matrix graphite adsorbing N₂ at 1000°C, 950°C, 900°C and 800°C for 3 h. In Fig. 5 the background has been subtracted, then the height of the peaks stands for the maximum desorption rate and the area stands for the total desorption amount. The desorption amount and the specific desorption amount to surface area have be calculated with Eq. (4) and (5), shown in Table 2.

\[
Q = \sum_{t=1}^{T} q(t) \Delta t = \frac{t_f - t_i}{2} \cdot \left[ q(t_i) + q(t_f) \right] \tag{4}
\]

\[
Q_s = \frac{Q}{S} \tag{5}
\]

Fig. 6 displays the TDS spectra of fuel element matrix graphite adsorbing N₂ for 1, 2 or 3 hours at (a) 1000°C, (b) 950°C and (c) 800°C. In Fig. 6 (d) the peaks with background subtracted are shown. Detailed properties of the peaks are shown in Table 3. The 3 peaks of adsorbing at 1000°C were all at higher temperatures than the peaks of adsorbing at 900°C, so are peaks of 900°C to peaks of 800°C. It can be concluded that adsorption temperature has the major impact on the position of desorption peak. Meanwhile, adsorption time has a secondary influence to the central desorption temperature. Both higher temperature and longer time of
adsorption process make the position of desorption peak shift to high temperature-direction.

### III.C. N⁺ Implantation

N⁺ implantation experiments were performed as a contrast to the high-temperature N₂ adsorption experiments. 5×10¹⁶ cm⁻², 3×10¹⁷ cm⁻² and 5×10¹⁷ cm⁻² have been chosen as implantation doses. The energy of N⁺ ion was 100 keV.

<table>
<thead>
<tr>
<th>Adsorption temperature °C</th>
<th>Peak position /°C</th>
<th>Maximum desorption rate /(mL/min)</th>
<th>Maximum desorption amount /mL</th>
<th>Specific desorption amount /(L/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>946.1</td>
<td>3.42×10⁻³</td>
<td>2.94×10⁻³</td>
<td>0.147</td>
</tr>
<tr>
<td>950</td>
<td>921.0</td>
<td>2.95×10⁻³</td>
<td>3.30×10⁻³</td>
<td>0.165</td>
</tr>
<tr>
<td>900</td>
<td>891.7</td>
<td>1.35×10⁻³</td>
<td>1.70×10⁻³</td>
<td>0.0850*</td>
</tr>
<tr>
<td>800</td>
<td>869.6</td>
<td>1.49×10⁻³</td>
<td>1.70×10⁻³</td>
<td>0.0850*</td>
</tr>
</tbody>
</table>

*: Specific desorption amount of 900°C was slightly larger than that of 800°C.

Fig. 6: TDS spectra of FE adsorbing N₂ for 1, 2 or 3 hours at (a) 1000°C, (b) 900°C and (c) 800°C. (d) TDS peaks with background subtracted of FE adsorbing N₂ at 1000°C and 900°C for 1, 2 or 3 hours.
Table 3: Properties of desorption for FE adsorbed at different temperatures for different times.

<table>
<thead>
<tr>
<th>Adsorption temperature /°C</th>
<th>Adsorption time /h</th>
<th>Peak position /°C</th>
<th>Maximum desorption rate /(mL/min)</th>
<th>Desorption amount /mL</th>
<th>Specific desorption amount /(L/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>3</td>
<td>946.1</td>
<td>3.42×10⁻³</td>
<td>2.94×10⁻³</td>
<td>0.147</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>946.0</td>
<td>1.35×10⁻³</td>
<td>1.53×10⁻³</td>
<td>0.0765</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>935.8</td>
<td>1.46×10⁻³</td>
<td>1.30×10⁻³</td>
<td>0.0650</td>
</tr>
<tr>
<td>900</td>
<td>3</td>
<td>891.7</td>
<td>1.35×10⁻³</td>
<td>1.70×10⁻³</td>
<td>0.0850</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>885.0</td>
<td>1.31×10⁻³</td>
<td>1.81×10⁻³</td>
<td>0.0905</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>882.5</td>
<td>1.23×10⁻³</td>
<td>1.24×10⁻³</td>
<td>0.0620</td>
</tr>
<tr>
<td>800</td>
<td>3</td>
<td>869.6</td>
<td>1.49×10⁻³</td>
<td>1.70×10⁻³</td>
<td>0.0850</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&lt;869.6</td>
<td>&lt;1.49×10⁻³</td>
<td>&lt;1.70×10⁻³</td>
<td>&lt;0.0850</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>Lower</td>
<td>Smaller</td>
<td>Smaller</td>
<td>Smaller</td>
</tr>
</tbody>
</table>

Table 4: Properties of N₂ release from IG-110 implanted with 100 keV N⁺ of different doses.

<table>
<thead>
<tr>
<th>Implantation dose /cm⁻²</th>
<th>Peak position /°C</th>
<th>Maximum release rate /(mL/min)</th>
<th>Amount /mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>5×10¹⁷</td>
<td>680.6</td>
<td>1.42×10⁻³</td>
<td>1.684×10²</td>
</tr>
<tr>
<td>3×10¹⁷</td>
<td>681.7</td>
<td>1.43×10⁻³</td>
<td>1.672×10²</td>
</tr>
<tr>
<td>5×10¹⁶</td>
<td>687.5</td>
<td>1.11×10⁻³</td>
<td>1.303×10²</td>
</tr>
</tbody>
</table>

Fig. 7 displays the TDS spectra of implanted samples (vertical coordinate in logarithmic) and Table 4 shows some properties of N₂ release. It is noticeable that at ca. 700°C all of 3 implanted curves had a release peak, while the un-implanted curve didn’t contain such a peak.

It seems the properties of N₂ release of 3×10¹⁷ cm⁻² and 5×10¹⁵ cm⁻² have few disparities. That might be explained by the fact that these 2 doses were close to each other. By contrast, the 5×10¹⁶ cm⁻² experiments were quite different. It can be concluded for certain that higher dose of N⁺ implantation results in larger release amount of N₂, larger maximum release rate and lower central temperature of the release peak.

As can be seen, the positions of the desorption peaks in the high-temperature adsorption experiments and the release peaks in the ion implantation experiments were different; the former were generally over 800°C and the latter were slightly below 700°C. It can also be seen that the release amounts of implantation experiments were one magnitude order larger than the desorption amounts of adsorption experiments. It implied that the mechanisms of infusing nitrogen by gas charging and ion implantation have large
differences. It is inferred that during implantation process the microstructure of carbon materials was damaged and nitrogen atoms stayed at non-equilibrium positons, which was conducive to nitrogen diffusion and release; but for high-temperature adsorption the nitrogen atoms tended to diffuse into deeper zone of specimen and form stable chemical bonds with Carbon atoms. According to literature, the 700°C release peaks of ion implantation experiments stands for the -C= N- bonding [16].

IV. DISCUSSIONS

At the beginning of section III, it is displayed that the positon of a peak has positive correlation to heating rate. This phenomenon matches the prediction of Wigner-Polanyi formula. Assuming the temperature is raised at $B$ (°C/min) constantly,

$$T = A + Bt$$
$$\frac{dt}{dT} = (1/B) \cdot \frac{dT}{T}$$

Replace $dt$ with $dT$, Wigner-Polanyi formula will point out the relationship of desorption rate to heating rate as

$$\frac{d\theta}{dT} = -\frac{\gamma E_0}{V_e B} \exp\left[-\frac{E}{RT}\right]$$

Consider the simplest case with $E_0(\theta) = E_0$, the second derivative of $\theta$ to $T$ would be

$$\frac{d^2\theta}{dT^2} = \left(\frac{\gamma E_0}{V_e B}\right) \exp\left[-\frac{E}{RT}\right] \theta^{-1} \left[\frac{d\theta}{dt} + \theta \frac{E}{RT}\right] = -\frac{\gamma E_0}{V_e B} \exp\left[-\frac{E}{RT}\right] \theta^{-1} \left[-\frac{E}{RT} \theta^{-1} \exp\left[-\frac{E}{RT}\right] + \frac{E}{RT}\right]$$

On the top of a peak, there should have $d^2\theta/dT^2 = 0$. Simply the model one more step with $n=1$, the position of the peak is expressed as

$$T^* = \frac{V_eB E_0}{\gamma R} \exp\left(\frac{E}{RT}\right)$$

Although for $T$, Eq. (10) is a transcendentual equation, it can be easily proved that with larger $B$, $T$ as the root increases.

The experiments on different nuclear carbon materials showed a difference in adsorption capacity. Tests on the specific surface areas, porosities and degrees of crystallinity have been done, whose results are not presented here, but it seems there would not be clear links between adsorption amounts with these factors.

With the effects of adsorption temperature and time to adsorption amount, a model of adsorption and desorption process is built like this. N$_2$ molecules collide with the surface of carbon materials and they have a possibility to remain on the surface. Most of the retention molecules desorb from the surface, while some remain long enough for the diffusion into the materials or the reaction with surface atoms. Higher temperature leads to higher diffusivity, together with a long period of adsorption a larger number of nitrogen accumulate in the materials. During the desorption process, nitrogen at deep positon would take a long time to diffuse and release, resulting in the shift of desorption peaks to high-temperature direction.

V. CONCLUSIONS

In this work, high-temperature adsorption, ion implantation and temperature programmed desorption techniques were adopted to study the behavior of adsorption and desorption of nitrogen on nuclear carbon materials used in HTR-PM. Nitrogen is the main precursor of C-14 in HTR-PM, thus this research conclude to radionuclides management and the minimizing of nuclear wastes.

The dominant adsorption form of nitrogen on nuclear carbon materials is chemisorption. Capacity of chemisorption varies with carbon materials. Among the 3 materials, fuel element matrix graphite has the largest capacity, IG-110 graphite less, and HTZ-B boron-contained carbon brick has little capacity of adsorbing nitrogen.

The adsorption amount has positive correlation with adsorption temperature and adsorption time. Higher temperature as well as longer time of desorption can also lead the desorption peak to shifting to high-temperature direction; the influence of adsorption temperature is more significant.

Higher dose of implantation results in a shift of release peak to low-temperature direction. The mechanisms of bonding between nitrogen and carbon with these 2 techniques are different. N$^+$ ion implantation forms -C=N- bonds. High-temperature adsorption is inferred to cause less microstructure damage.

Ongoing work is to reveal the relationships between adsorption amount and the properties of nuclear carbon materials, including specific surface area, surface chemical state, impurity and degree of crystallinity. The saturation time of nitrogen adsorption, the form of bonding between adsorbed
nitrögen ve karbon ve nitrögenin derinlik dağılımı ve nitrögenin derinlik dağılımı gelecekte incelenmesi planlanmaktadır.

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