Temperature programmed desorption (TPD) studies on nuclear carbon materials charged with hydrogen at elevated temperatures

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Abstract – The hydrogen behavior of fuel element graphite, IG-110 graphite and carbon brick in HTR-PM has been investigated using the gas charging technique for the hydrogen adsorption and temperature programed desorption (TPD) technique for the hydrogen desorption. The curve of desorbed hydrogen amount as function of H2 concentration in inlet gas shows a linear relation, and a shift from 473°C to 464°C is observed in the TPD curve of the un-saturated adsorbed IG-110 graphite. The desorbed hydrogen amount is increasing with the adsorption increasing from 800°C to 1000°C. The desorption energy values of these three materials are calculated based on the Kissinger equation, and they are almost the same (average number is 66.0kJ/mole). A comparison of the desorbed hydrogen amount among these three materials shows that fuel element graphite has the highest desorbed amount, and carbon brick has the lowest. It corresponds to the trend of the closed porosity for these three materials.

Keywords – HTGR; Hydrogen; Adsorption; Desorption; Nuclear carbon materials; Temperature Programmed Desorption (TPD).

I. INTRODUCTION

The High Temperature Gas-cooled Reactor (HTGR) is one of the most promising advanced nuclear energy systems due to its inherent safety and economic competitiveness [1-3]. Two high temperature helium-cooled reactor - pebblebed modules (HTR-PM, 250 MW) are now under construction in China, on the basis of the successful designing and construction of the 10 MW high temperature pebblebed reactor (HTR-10) at the Institute of Nuclear and New Energy of Technology (INET), Tsinghua University [1, 4]. Carbon materials are most commonly used as the fuel element material, moderator material, reflector material and carbon brick material (high temperature resistant surrounding the active core [5]) in HTR-PM [5, 6]. During the operation lifetime, the neutron reaction of the impurities such as Li-6 and B-10 in the carbon materials will generate tritium (H-3) radioisotope, which can diffuse into the helium coolant at elevated temperature, and causes the unwanted contamination. It is highly important to investigate the H-3 behavior in the nuclear carbon materials for evaluating and minimizing the released H-3 amount in HTR-PM.

In spite of the radioactive contamination in the lab, hydrogen (H-1) is used for this study instead of tritium, considering their same chemical properties and similar physical properties. Many papers on the hydrogen behavior in graphite have been published, and ion implantation technique is the usually applied method for the hydrogen adsorption, where the atomic hydrogen is implanted into the material surface [7-16]. However, with this method additional defects are produced, and even the microstructure may be changed, which makes the experimental analysis complicated. In the present work, the gas charge technique where the specimen is exposed to the adsorption gas at high temperatures is used to avoid this complexity [17].

The Temperature Programmed Desorption (TPD) technique is a well-known technique to study the desorption behavior in many fields [16, 18-20]. By
heating the specimen at a pre-set heating rate and detecting the desorption signal continuously, the TPD curve can be plotted for analyzing the fundamental information such as the adsorption center and the desorption energy. H. Atsumi et. al. [17] have ever used gas charged technique and TPD technique to investigate the hydrogen behavior in the graphite and carbon fiber composite (CFC) applied as the plasma facing components in fusion reactor.

In this work, these two techniques are used for the hydrogen behavior study in fuel element graphite, IG-110 graphite (moderator and reflector material, produced by Toyo Tanso Co. Ltd.) and carbon brick in HTR-PM. The TPD curves as a function of adsorption temperature, adsorption time, H$_2$ concentration in inlet gas and heating rate are obtained, and the effects of the microstructural differences on the hydrogen behavior are investigated in detail.

II. EXPERIMENTAL

The materials used in this work are the un-irradiated fuel element graphite, moderator graphite, reflector graphite and carbon brick in HTR-PM in China. Among them, the moderator graphite and the reflector graphite are actually one kind of commercial nuclear graphite, called IG-110 (Isotropic Graphite, produced by the Toyo Tanso Co. Ltd.). The main properties of IG-110 nuclear graphite are shown in Table 1 [21]. All specimens used in the present experiments were machined to a cuboid shape with average outer dimensions of 2.0 mm × 2.0 mm × 1.5 mm. The graphitization degree is measured by HR800 micro-Raman Spectrometer (HORIBA JOBIN YVON). The surface microstructure is observed by Scanning Electron Microscopy (SEM, JEOL JSM-7001F).

Table 1: Main properties of IG-110 graphite.

<table>
<thead>
<tr>
<th>Material</th>
<th>IG-110</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/cm³)</td>
<td>1.75</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>9.6</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>70.5</td>
</tr>
<tr>
<td>Rockwell hardness (MPa)</td>
<td>74.2</td>
</tr>
<tr>
<td>Fracture toughness (MPa)</td>
<td>0.82</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>116</td>
</tr>
<tr>
<td>Impurities (ppm)</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>

The TPD experiments were performed in a temperature programmed system, which allows for the specimen-temperature increasing from room temperature to 800°C at a pre-set rate from 1°C/min to 20°C/min. The specimen was positioned in the bottom of the specimen container (a U-shape quartz tube, whose inner diameter is 4.0 mm), which was embedded into a heating furnace. The ends of the U-shape tube enable the inlet of the adsorption gas, and the outlet of the desorb gas. In the inlet end, a thermo-couple was inserted into the bottom of the tube to detect the specimen temperature correctly. In the outlet end, a quartz capillary was fixed in the bottom of the tube to detect the adsorption temperature. In the outlet gas flow to connect a quadrupole mass-spectrometer (QMS, ThermoStar by Pfeiffer Co. Ltd.) and the temperature programmed system. The specimen temperature signal was sent to the QMS operating software for outlining the TPD curve between desorbed H$_2$ concentration in outlet gas and specimen temperature.

The gas flow route of the experimental setup is shown schematically in Figure 1. A mass flow meter (MC series by ALICAT SCIENTIFIC Co. Ltd.) with a detection accuracy of 0.1 sccm (standard-state cubic centimeter per minute) was used to monitor the mass flow of the pure helium gas (He, ≥99.999%). The specimen was outgassed by feeding the pure He gas into the specimen container for 10 minutes at 5sccm. Keeping the flowing of the pure He gas through the sample chamber, the heater was opened to increase the sample temperature up to the pre-set adsorption temperature at 10°C/min. Another two same mass flow meters were used to monitor the mass flow of the helium carrier gas (≥99.999%) and the 10% H$_2$ gas (the carrier gas was He), respectively. After mixing, the H$_2$/He mixture with a concentration (≤10%) acts as the adsorption gas. Once the pre-set temperature was reached and became stable, the H$_2$/He mixture was admitted into the sample chamber, and the flowing was kept for the desired adsorption time. After finishing the adsorption process, the pure He gas was transferred into the specimen container, and a fan around the specimen container was opened to lower the sample temperature rapidly. In order to minimize the hydrogen remaining in the QMS, the pure He gas was kept flowing into the specimen container and the QMS for at least 1 hour before starting the TPD testing. During the TPD testing process, the sweeping gas (pure He) was monitored at 5 sccm, and the composition of the outlet gas (concentrations of H$_2$) was measured by the QMS.
Desorption mechanism for the commercial IG-110 nuclear graphite is investigated in detail in this section. Figure 2 shows the experimental TPD curves and the respective Gaussian fitting curves under different adsorption time (1h, 3h and 6h). The adsorption gas was 10% H$_2$ (carrier gas is He), and the adsorption temperature was 1000°C. The heating rate during the desorption process was 10°C/min. It should be noted that the variation of the mass among the specimens is minor in this work (average mass is 10.0 mg).

Here is to be some discussions over this TPD curve. We found the strength and position of peaks of different conditions can vary.

Another experiment that desorbing one adsorbed specimen for twice continuously was performed and the result showed that at the position where the peak had showed up there was no peak anymore. This phenomenon indicates that the hydrogen in this adsorption center desorbs completely. Hence, the desorbed H$_2$ amount can be calculated as the equation,

$$V_{d_{H_2}}(\text{mL/g}) = \frac{w_{\text{flow}}}{m_{\text{mass}}} \cdot \beta \cdot S_{\text{peak}}$$  \hspace{1cm} (1)

where $w_{\text{flow}}$ is the mass flow (5 sccm) of the sweeping gas He, $\beta$ is the heating rate (10°C/min) during the desorption process, $m_{\text{mass}}$ is the specimen mass, $S_{\text{peak}}$ is the integral area of the corresponding TPD peak.

H. Atsumi and his co-workers [17] have carried out the TPD experiments for ISO-880U graphite with an equilibrium pressure ranging from 83Pa to 79kPa. The plots for the desorbed amounts as function of charging gas pressure and function of the square root of charging gas pressure are compared to determine whether the molecular desorption or the atomic desorption works. Similarly, the desorbed amounts as function of H$_2$ concentration in inlet gas from 0.5% to 10.0% are studied, whose results are shown in Figure 3.

The linear relation between the desorbed H$_2$ amount and the H$_2$ concentration in inlet gas implies that the TPD peak should be ascribed to the release of hydrogen which are adsorbed in the form of molecule or confined in a molecular state. Considering molecular adsorption cannot result in a
peak at such high temperature because its weak binding, the confined molecular state should account for the adsorption center, which can be described in this way that the molecular H\textsubscript{2} are stored in the closed pores\textsuperscript{[17]}. For explaining the origin of the molecular H\textsubscript{2} in the closed pores, the adsorption gas H\textsubscript{2} dissociates into atomic hydrogen on the open pore surface of the specimen at high temperatures, and an equilibrium between the molecular hydrogen and atomic hydrogen which obeys the Sieverts’ law is established, at the same time, the atomic hydrogen can diffuse between and within the grains to establish the equilibrium beside the closed pore surface, which results in the storage of molecular hydrogen in the closed pores. For the un-saturated adsorbed specimen (1 h adsorption) in Figure 2, the ratio of the confined H\textsubscript{2} near the volume surface is higher than that of the saturated ones (3 h and 6 h adsorption). It makes the diffusion process easier which results in the shift in Figure 2.

From all above, it is concluded that the TPD peak from 150° C to 750°C is ascribed to the release of the confined molecular hydrogen in the closed pores of the specimen, and the desorption process is diffusion-controlled.

II.A. Desorption for different carbon materials

The Kissinger equation (2) is used to calculate the desorption energy ($E_d$) of the three kinds of nuclear carbon materials from HTR-PM\textsuperscript{[12]},

$$\frac{\partial}{\partial \beta} \left( \ln \left( \frac{\beta}{T_{\text{max}}} \right) \right) = \frac{E_d}{R} \left( \frac{1}{T_{\text{max}}} \right)$$

(2)

where $\beta$ is the heating rate, $T_{\text{max}}$ is the peak center temperature in the TPD curve, $R$ is the universal gas constant, $E_d$ is the desorption energy for the corresponding peak.

Changing the heating rate from 3°C/min to 15°C/min, the Kissinger plots are shown in Figure 5. The values of desorption energy $E_d$ of fuel element graphite, IG-110 graphite, and carbon brick are to be calculated respectively. Right now, it is reasonable to make the conclusion that the desorption mechanisms for these three carbon materials are the same.

Figure 6 shows the desorbed H\textsubscript{2} amounts for these three carbon materials after 1000°C and 6 h adsorption with 10.0% H\textsubscript{2} concentrations in inlet gas.

From the conclusion in section I, the equilibrium between the H\textsubscript{2} pressure in the closed pore and the atomic hydrogen concentration beside the closed pore is established during the adsorption process. The amount of H\textsubscript{2} in the closed pores is proportional to the closed pore volume and the atomic hydrogen concentration beside the pore surface\textsuperscript{[22]}. It has been reported that the total
adsorbed hydrogen amounts vary much among the specimens with different graphitization degrees, and the lower graphitized ones tend to have higher amounts, especially at high temperatures such as 1000°C \cite{17, 23}. The hydrogen trapping site can exist on dangling bonds (at the edge surface grains or within the crystallites), and the closed porosity \cite{22, 24, 25}. The specimen of lower graphitization degree tends to have more dangling sites, which is the dominant adsorption center at high temperatures.

![Graph showing desorbed H2 amounts for the three nuclear carbon materials in HTR-PM](image)

**Fig. 6:** Desorbed H2 amounts for the three nuclear carbon materials in HTR-PM (adsorption temperature: 1000°C, adsorption time: 6h).

Figure 7 shows the Raman spectra (measured for graphitization degrees) of the materials used in this study. The ratio between G peak intensity and D peak intensity ($I_G/I_D$) represents the graphitization degree. Among these three materials, it appears that the graphitization degree of fuel element graphite is the highest, and carbon brick is the lowest. However, the carbon brick has the lowest desorbed hydrogen amount in this work. Since the adsorption center in this work is related to the closed pore, it can be assumed that carbon brick has the lowest closed porosity and fuel element graphite has the highest closed porosity.

**Fig. 7:** Raman spectra for the three nuclear carbon materials in HTR-PM.

In order to verify this assumption, the closed porosity is investigated by the following equation,

$$P_{\text{closed}}(\%) = 1 - \frac{\rho_{\text{apparent}}}{2.25} - P_{\text{open}}$$

where $P_{\text{closed}}$ and $P_{\text{open}}$ are the closed porosity and open porosity, respectively. $\rho_{\text{apparent}}$ is the apparent density of the specimen, and 2.25 g/cm$^3$ is the theoretical density of single crystal graphite. The apparent density of these three materials is between 1.70 and 1.77 g/cm$^3$. The surface micrographs shown in Figure 8 reveal the pore structure distribution of these three materials, and it denotes that carbon brick has the highest open porosity and fuel element graphite has the lowest. Based on Equation (2), it can be calculated that carbon brick has the lowest closed porosity, which verifies our previous assumption.

**Fig. 8:** SEM micrographs for (a) fuel element graphite, (b) IG-110 graphite, and (c) carbon brick.
IV. CONCLUSIONS

The hydrogen behavior on fuel element graphite, IG-110 graphite and carbon brick in HTR-PM has been investigated using the gas charging technique and temperature programeed desorption (TPD) technique. A series of experiments have been performed and the major findings are as follows:

1. The TPD peak from 200°C to 750°C is ascribed to the hydrogen diffusion to the closed pore.
2. The desorbed hydrogen amount is increasing with the adsorption increasing from 800°C to 1000°C.
3. The values of desorption energy of these three materials are almost the same.
4. Among the three materials studied in this work, fuel element graphite has the highest desorbed amount, and carbon brick has the lowest. It corresponds to the trend of the closed porosity for these three materials.

REFERENCES


