Thermodynamics of the formation of CH_4 by the reaction of carbon materials by a stream of NH_3

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Abstract

To gain some insight into the thermodynamic aspects of CH_4 formation by the reaction between elementary carbon and hydrogen-bearing species, the reactions, (1) non-graphitic carbon + a stream of NH_3, (2) non-graphitic carbon + a stream of H_2 and (3) graphite + a stream of NH_3 were carried out at 900°C. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the major problems in the use of carbon in plasma machines may be erosion of wall materials under particle bombardment at elevated temperatures. A strong increase in the sputtering yield at about 800 K has been reported as a result of the chemical reaction between carbon and hydrogen ions producing CH_4 [1]. However from the thermodynamic viewpoint, the formation of CH_4 in the reaction of carbon with hydrogen gas becomes unfavorable with increasing temperature, so that a high hydrogen pressure or a hydriding agent with a high hydrogen activity, a_H, is required to convert the carbon materials into CH_4 at such high temperatures. In order to understand CH_4 formation causing the erosion, it would be necessary to discuss the hydriding ability of hydrogen-bearing chemical species in terms of their thermodynamic activity.

Ammonia may function either as a nitriding agent or as a hydriding agent. By flowing NH_3 through a high temperature region at sufficiently high speeds, the dissociation of NH_3 into H_2 and N_2 can be suppressed to a large extent. In other words, a state may be created where the dissociation equilibrium $NH_3 = (\frac{1}{2}) N_2 + (\frac{3}{2}) H_2$

is not reached. This situation must be regarded as being in an unstable state, which, in turn, may cause high nitrogen and high hydrogen activities of flowing NH_3. By flowing NH_3 at an appropriate flow rate, a mixture of NH_3, H_2 and N_2 with an arbitrary gas composition can be prepared.

When a stream of NH_3 acts as a hydriding agent, the equilibrium equation to be considered is

$$NH_3(\text{gas}) = \frac{1}{2}N_2(\text{gas}) + 3H(\text{in product}), \quad (1)$$
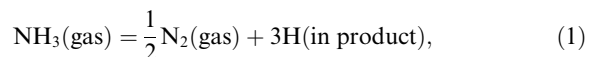
which gives the following equation for the hydrogen activity, a_H, given by the stream to the product [2]:

$$a_H = \left\{ \frac{1}{K_P} \frac{P_{NH_3}}{P_{N_2}^{1/2}} \right\}^{1/3}, \quad (2)$$

where K_P is the equilibrium constant for NH_3 formation and P_{NH_3} and P_{N_2} are the partial pressures of NH_3 and N_2 measured in bars, respectively. It is noted that the hydrogen activity is controlled by the factor of $P_{NH_3}/P_{N_2}^{1/2}$ and H_2 coexisting in the stream does not participate in this expression. Thus, a stream of NH_3 may offer an excellent device for understanding the thermodynamics of CH_4 formation by use of hydriding species with a high hydrogen activity.

There exists the so-called ''amorphous carbon'' as a metastable allotrope of elementary carbon in addition to

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graphite and diamond. The structure grades continuously from complete amorphous carbon to graphite, between which carbon with any degree of graphitization results in an increase in the thermodynamic activity of carbon, which may give rise to higher chemical reactivity. Interstitial carbon content in a non-stoichiometric carbide or in a carbonitride phase coexisting with non-graphitic carbon is higher than those coexisting with graphite when compared under the comparable reaction conditions [3–5].

Some experiments of the reaction between carbon materials and a stream of NH_3 at 900°C in this work confirmed the above theoretical analysis.

2. Experimental details

The carbons used in this work are powdered non-graphitic active carbon (Aktivkohl from E. MERK AG Darmstadt, Germany) and powdered nuclear grade graphite. The X-ray diffraction (XRD) patterns of these two types of carbon materials are shown in Fig. 1. NH_3 (99.998%) and H_2 (99.9999%) were supplied from commercial gas cylinders and were fed into the system by
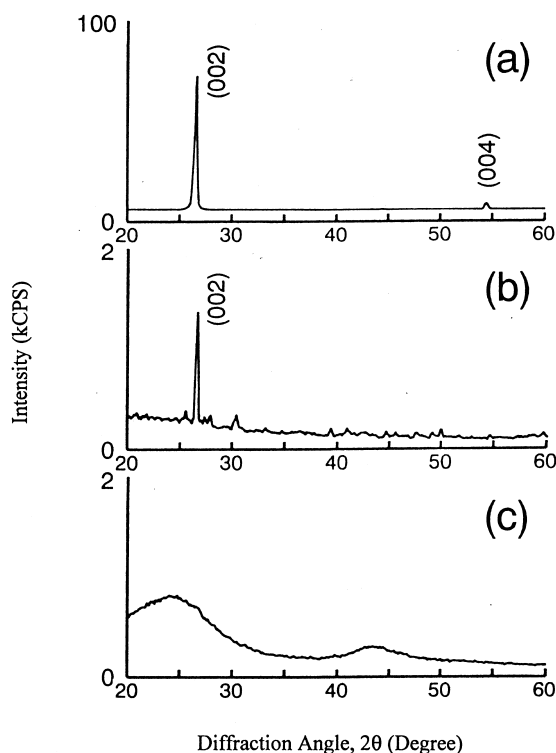

Fig. 1. X-ray diffraction patterns of: (a) nuclear grade graphite; (b) the solid remained after the reaction between non-graphitic carbon and NH_3; (c) non-graphitic carbon (E. MERCK AG Darmstadt, Germany).

stainless steel tubes without further purification. The apparatus consisted of a vacuum system, a gas supply system, a resistance furnace and a gas chromatograph system. The vacuum system comprised two rotary pumps and a turbo-molecular pump, by which the whole system could be evacuated up to the order of 10^{-6} Pa. The gas chromatograph system consisted of a gas chromatograph (type GC-8APT, Shimadzu, Japan), an integrator (type C-R6A, Shimadzu, Japan) and a gas sampler with two sampling loops, and helium gas with 99.999% purity was used as a carrier gas. A quartz reaction tube (30 mm in diameter and 750 mm in length) was fitted into the cylindrical resistance furnace. This furnace comprised upper and lower halves, which were connected with each other by hinges in such a way that the upper half could be opened for occasional visual observation of the specimen. Two types of non-graphitic carbon samples were used, one being received as non-graphitic carbon powder and the other a thin disk (about 10 mm in diameter). The disk was prepared by compacting 0.05 g of non-graphitic carbon under 1 ton/cm^2 of pressure using a press.

After placing a quartz boat containing a carbon sample in the center of the reaction tube, the system was evacuated to the order of 10^{-5} Pa at room temperature. The temperature was raised to 900°C while maintaining the system below 10^{-4} Pa and then kept at 900°C for 8–14 h for degassing. Then ammonia gas or hydrogen gas was supplied constantly as a stream. All experiments were carried out at 900°C. When NH_3 was used, the partial pressures of NH_3 and N_2 (P_{NH_3} and P_{N_2}) in the outlet gas were determined by the gas chromatograph measurement and those of H_2 (P_{H_2}) was calculated by the relation $P_{total} = P_{NH_3} + P_{N_2} + P_{H_2}$. Here P_{total} is the total pressure. In some cases, a rough estimation of the partial pressure of CH_4 (P_{CH_4}) in the outlet gas was also made, but the above relation was used for determining P_{H_2} since P_{CH_4} was less than 133 Pa (1 Torr). A visual observation was performed to check whether the removal of carbon samples was accomplished.

3. Results and discussion

Table 1 summarizes the experimental results of these reactions between non-graphitic carbon powder and NH_3 or H_2 and those of graphite between NH_3. Runs 1 and 2 were carried out under the same experimental conditions except for the reaction time. In these runs, no quantitative estimation of P_{CH_4} was made and only the presence of CH_4 in the outlet gas was checked by the gas chromatograph. As given in Table 1, during runs 4 and 5 the gas chromatogram did not reveal the presence of CH_4, whereas, in runs 1–3, the amount of CH_4 continued to decrease with time until it fell well below the detection limit. The visual observation of the carbon

Table 1
Experimental results of reaction of carbon with a stream of NH_3 or H_2 at 900°C

Run	Reaction	Time (h)	a_H	Detection of CH_4	Removal of carbon
1	Non-graphitic carbon (0.048 g) + NH_3 (200 ml/min)	19	19	Detected	Removed
2	Non-graphitic carbon (0.048 g) + NH_3 (200 ml/min)	9	21	Detected	Removed
3	Non-graphitic carbon (0.50 g) + NH_3 (200 ml/min)	23	17	Detected	Removed
4	Graphitic (0.048 g) + NH_3 (200 ml/min)	20	18	Not detected	Not removed
5	Non-graphitic carbon (0.048 g) + H_2 (200 ml/min)	21	1	Not detected	Not removed

sample made at intervals clearly showed that the amount of the sample continued to decrease and eventually almost all the carbon sample was removed from the boat. However, after run 3 (the initial carbon: 0.50 g), a small amount of solid remained in the boat, which was identified to be graphite by XRD analysis (see Fig. 1). Although a solid material remained in the boat after runs 1 and 2 (the initial amount of carbon: 0.048 g), the amount was too little to give an XRD pattern. In other words, the non-graphitic carbon includes a small amount of graphite. These results show that only the combination of the non-graphitic carbon and a stream of NH_3 may lead to the formation of CH_4, no other combination of graphite or non-graphitic carbon and NH_3 or H_2 can produce CH_4 at 900°C. These experimental facts may suggest that both high hydrogen activity a_H, exhibited by a stream of NH_3 and high carbon activity, a_C, of the non-graphitic carbon play key roles in the formation of CH_4. The hydrogen activity, a_H, in the final stage of each run calculated from P_{NH_3} and P_{N_2} values using Eq. (2) is evaluated to be 17–21. These values of a_H may correspond to 290–440 bars of H_2 if the relation $a_H = P_{H_2}^{1/2}$ is applied. The fact that the combination of the non-graphitic carbon and H_2 did not produce CH_4 must be ascribed to much lower hydrogen activity of H_2 than that of NH_3. The fact that CH_4 was not produced even when NH_3 passed over a graphite sample is clearly consistent with the fact that graphite as impurity in the non-graphitic carbon remained after reaction with NH_3. A lower a_C value of graphite than that of the non-graphitic carbon may have to do with this consistence.

A compacted non-graphitic carbon sample in the form of a thin disk (0.05 g) was reacted with a stream of NH_3 at flow rates of 100, 200 and 300 ml/min at 900°C. Figs. 2 and 3 show the time variations of $P_{total}, P_{NH_3}, P_{N_2}$ and P_{H_2} at flow rates of 100 and 300 ml/min, respectively. These pressure variation curves are divided into two regions. Namely, region I, where P_{NH_3} decreased and P_{N_2} and P_{H_2} increased with time and, region II, where eventually a steady state was attained. The time variations of P_{CH_4} roughly estimated by chromatograms are shown in Fig. 4. It seems that the conversion of the carbon sample into CH_4 was completed by the end of
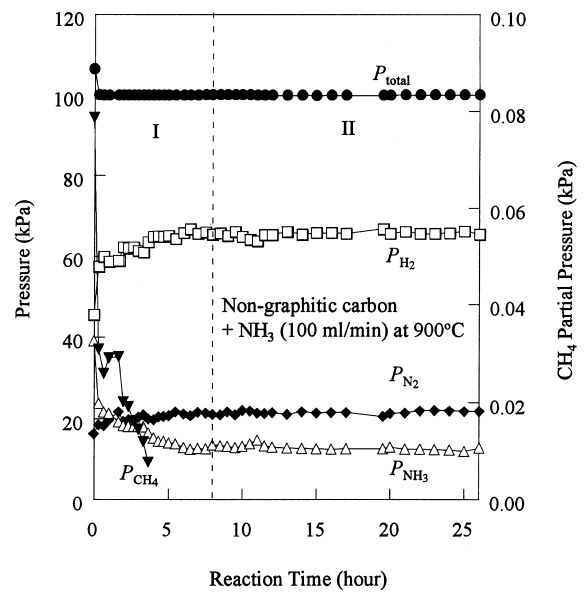

Fig. 2. Changes in $P_{total}, P_{H_2}, P_{N_2}, P_{NH_3}$ and P_{CH_4} with time during the reaction of non-graphitic carbon with NH_3 (100 ml/min) at 900°C.

region I. This is in full accord with the visual observation of the carbon sample, in which the carbon was continuously removed from the boat. The variations of a_H with time are given in Fig. 5. In an equilibrium state at 900°C, more than 99.9% of NH_3 should dissociate into N_2 and H_2. Figs. 4 and 5 suggest that as the flow rate of NH_3 decreases, the extent of dissociation of NH_3 becomes lesser. The extent of dissociation was found to be well below the equilibrium value by flowing NH_3. It is interesting to note that the presence of non-graphitic carbon suppresses the dissociation of NH_3, in region I in Figs. 2 and 3, more effectively than in region II where non-graphitic carbon no longer exists. This suppression might be caused not by the presence of non-graphitic carbon but the progress of the reaction $C + \left(\frac{4}{3}\right)NH_3 = CH_4 + \left(\frac{2}{3}\right)N_2$. Although this suppression is indeed an experimental fact, why this is the case remains unsolved for us.
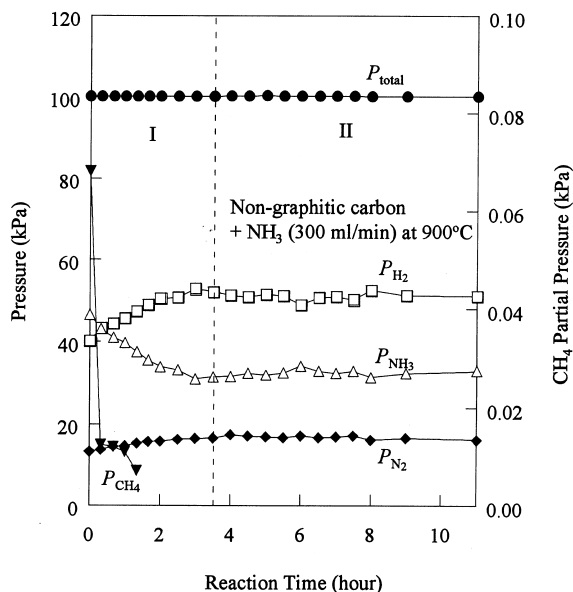
Fig. 3. Changes in $P_{total}, P_{H_2}, P_{N_2}, P_{NH_3}$ and P_{CH_4} with time during the reaction of non-graphitic carbon with NH_3 (300 ml/min) at 900°C.
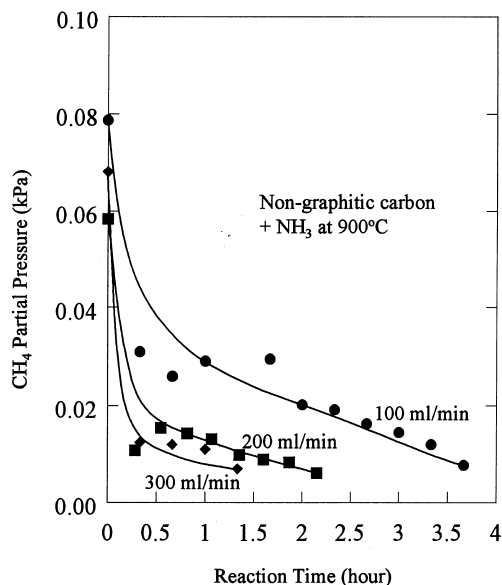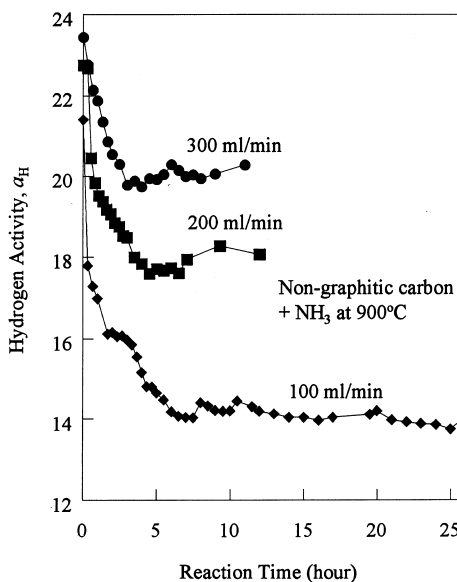

Fig. 5. Change in hydrogen activity with time during the reactions at 900°C with NH_3 flow rates of 100, 200 and 300 ml/min.

Fig. 4. Change in P_{CH_4} with time during the reactions at 900°C with NH_3 flow rates of 100, 200 and 300 ml/min.

4. Concluding remarks

(1) The reaction of non-graphitic (active) carbon or graphite with a stream of NH_3 or H_2 was carried out at 900°C. Only the combination of non-graphitic carbon and NH_3 can form CH_4. This may be ascribed to high hydrogen activity exhibited by a stream of NH_3 and high carbon activity of the non-graphitic carbon.

(2) The presence of non-graphitic carbon or the progress of the reaction $C + \left(\frac{4}{3}\right)NH_3 = CH_4 + \left(\frac{2}{3}\right)N_2$ suppresses the dissociation of NH_3 more effectively than in the case where non-graphitic carbon is absent in the system.

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